

# Quantum Mechanics for Chemistry

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This interactive electronic textbook is designed to provide a comprehensive introduction to quantum mechanics in a context of chemistry. This book comprises three extensive chapters, treating model systems, atoms and molecules in turn, applying symbolic calculations with computer program *Maple*. The contents have been generated or collected and adapted from various sources; I am grateful to G. J. Fee, F. M. Fernandez, M. Horbatsch, H. Huber and J. B. Pedersen, among others, for contributions that are acknowledged at the specific locations. 2021 July 9

## chapter 1 Model systems

### 1.0 overview

Derived from latin quantum that means *how much*, in English the term *quantum* signifies a small discrete unit rather than part of a continuous quantity. We distinguish first between quantum physics, implying experimental measurements on atomic systems and their analysis, quantum mechanics, implying a collection of computational methods or algorithms applicable to systems on an atomic scale, as listed in the table below, and quantum chemistry, implying semi-empirical calculations with more or less standard computer programs of properties of chemical materials. To introduce quantum mechanics in the context of chemistry, we distinguish further between the quantum laws, or the laws of discreteness, and quantum theories, which have been devised to reproduce, approximately, various experimental observations. Quantum mechanics is not a chemical theory -- not even a physical theory, but is precisely a collection of methods or algorithms applicable to calculations of systems on an atomic scale, as summarised in the following table, that might have a numerical nature or component; there is an inevitable and unavoidable error in such calculations, apart from any approximations involved in the theory that require the intervention of still further theories, that arises through the finite precision of not only the calculations but also the parameters, such as  $h$ ,  $e$  ... that were formerly known to only finite precision but now have defined values in important instances. Of methods listed in the table, five are discussed at greater or lesser length in these three chapters because of their prospective chemical applications. All theories are inadequate to some extent; even Dirac's equation that enabled a treatment of atom H fails to yield perfect agreement with experimental measurements of the hyperfine structure of spectral lines of H; any experiment on other than H, among species of prospective chemical interest, yields data that are imperfectly reproduced, even apart from the precision of the calculations and the parameters. The most accurate theories are applicable to only the simplest systems, and become absolutely intractable for application much beyond those simple or prototypical systems.

### methods of calculations within quantum mechanics and their originators

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1	matrix mechanics, Heisenberg, 1925, developed with Born and Jordan
2	symbolic method, Pauli, 1926, developed by Green, 1965
3	wave mechanics, Schroedinger, 1926

- 4 second quantisation, Dirac, 1927
  - 5 density-matrix formulation, von Neumann, 1927
  - 6 variational formulation, Jordan and Klein, 1927
  - 7 pilot-wave formulation, proposed by de Broglie, 1927; developed by Bohm 1952
  - 8 relativistic quantum mechanics, Dirac, 1928
  - 9 phase-space formulation, Wigner, 1932
  - 10 octonionic quantum mechanics, Jordan, 1933
  - 11 quaternionic quantum mechanics, Birkhoff and von Neumann, 1936
  - 12 path-integral formulation, Feynman, 1948, after Wiener, 1926, and Dirac, 1933
  - 13 Hamilton-Jacobi formulation, Leacock and Padgett, 1983
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The creation of important methods of quantum mechanics was a major development of theoretical physics during the twentieth century; throughout the development of theoretical physics, forces of two types have played an exceptional role -- the restoring force of simple harmonic motion proportional to the linear displacement from an equilibrium condition and the force in the Kepler problem proportional to an inverse squared distance. For this reason, even though our interest is chemically oriented, we devote much attention in this chapter to the treatment of an harmonic oscillator and, in chapter 2, a hydrogen atom, as a Kepler system, for which exact algebraic solutions are practicable within a limited frame and as a basis of a quantum-mechanical treatment of complicated systems. The latter fascination of theoretical physics reflected critical optical experiments, namely involving the emission and absorption of light, which became a basis for the practice of spectrometry that plays a crucial role in all chemistry. The Kepler problem encompasses both gravitation, of minor direct interest in chemistry, and coulombic attraction between particles of opposite electric charge; the effective range of the Coulomb potential energy is infinite because a photon has no rest mass. Whereas an harmonic oscillator is a fiction, devoid of physical or chemical material existence but of invaluable significance in view of its role as a prototype for the quantization of fields, a hydrogen atom is arguably the basis of all chemistry, consistent with Prout's hypothesis that was a major influence on Rutherford in his pioneering experiments on nuclear structure. For these reasons these chapters contain many sections devoted to harmonic oscillators and the hydrogen atom in their various aspects. Although the duality of particle and wave character that Einstein recognised in his treatment of the photoelectric effect led de Broglie to propose an analogous duality for a moving particle, this idea is important in quantum physics but plays little or no direct role in quantum mechanics even though it was the impetus for Schroedinger to develop wave mechanics.

Initiated with the qualitative observation by William Wollaston in Cambridge, 1802, of dark lines within the visible spectrum of light emitted by the sun that became the basis of seeking to delineate the quantum laws of nature, the most sensitive and crucial experiments to precede the development of those theories involved the measurement of optical spectra, in which discrete lines appeared and of which the wave lengths or their inverses might be fitted to simple formulae, such as four lines in the Balmer series in atomic spectra of H in 1885 and the Deslandres table in molecular spectra of C<sub>2</sub> in 1891; that the prototypical calculations in these chapters have a close connexion with spectrometric aspects is appropriate for this reason, and, at various points in the derivation or interpretation of the results, we mention these pertinent aspects. In 1924 before his original derivation of quantum mechanics, Heisenberg recognised that the observable properties of a (free) atomic or molecular system are the energies of its states -- or, precisely, their energy differences -- and the intensities of transitions between those states; any properties of a particular method of quantum mechanics are artefacts of that method and not a general feature of quantum mechanics. Dirac wrote subsequently that

*"it is important to remember that science is concerned only with observable things..."*

A system on an atomic scale, which might be amenable to calculation with some quantum-mechanical method, differs from a system on a macroscopic scale in that every experiment on a microscopic system results in an interaction that disturbs the properties of the system; this condition imposes a limitation on the power of observation that implies that there exist observations that can not be made simultaneously, which in turn implies an indeterminacy subject to Heisenberg's criteria that provide a quantitative expression of the fact that, even in a pure state, non-commuting observable quantities are immeasurable simultaneously. With a system on an atomic scale is associated a [Hilbert] space of infinite dimension, a set of observable quantities, a set of states -- some discrete and some continuous, and measurements according to which one might evaluate an observable quantity related to various states of that system. The dynamics of a system on an atomic scale treat the variation of either the observable properties -- according to Heisenberg's approach -- or the states -- according to Schroedinger's approach -- that do not vary with time. In these chapters our primary concern is with the stationary states of a system, not with the temporal variation of those states; the stationary aspect implies not a lack of movement of any particle but that the probability distribution is constant in time.

All quantum mechanics seems to be based on a postulate of a commutator -- a term originated by Dirac, such as a commutator of position and momentum variables that Heisenberg deduced and that Dirac directly recognised to be the key to quantum mechanics, namely the dependence of multiplicative relations on the order of the factors,  $ab \neq ba$ ; on this basis, we undertake calculations according to various algorithms of quantum mechanics -- which is intrinsically a collection of mathematical methods to treat systems on an atomic scale, as opposed to quantum physics that is a branch of physics that is concerned with experiments on matter and energy at the atomic level and their interpretation, because the laws that are deduced from the behaviour of macroscopic objects fail to operate adequately in an atomic realm. The canonical linear harmonic oscillator is a system that is amenable to treatment with several methods or algorithms of quantum mechanics; we treat this system according to rigorous matrix mechanics with explicit matrices to represent physical quantities, then according to rigorous wave mechanics in both coordinate and momentum representations, and eventually with Dirac's operators for creation and destruction. After a comparison of those results and a short analysis of their significance, we treat again the canonical linear harmonic oscillator according to wave mechanics in the coordinate representation and with spectral parameters, for comparison with another harmonic oscillator according to Davidson's formula for potential energy; we generate the characteristic parameters of the putative vibrational and rotational spectra of these two putative oscillators -- their frequencies and their intensities -- for their comparison. As an exact application of pioneer wave mechanics in the coordinate representation to an atomic system comprising one atomic nucleus and one electron, we treat the hydrogen atom, generating accurately the atomic energies, amplitude functions and absorption spectrum for both discrete and continuous transitions within the limitations of a non-relativistic approach and neglecting the nuclear motion. As an accurate application of wave mechanics in the coordinate representation to a molecular system comprising two atomic nuclei and one electron, we treat the dihydrogen molecular cation, calculating in an approximate manner the energy of the system as a function of internuclear distance. On the basis of these direct calculations and the deductions therefrom, we discuss the relation between quantum mechanics and molecular structure, concluding with some pedagogical ramifications. We explain how molecular structure in a classical sense is formally incompatible with quantum mechanics. Quantum-mechanical methods are nevertheless applicable to treat the structures and properties of molecules and matter, on the basis of approximations well defined, in the form of quantum-chemical calculations of a semi-empirical nature such that the electrons but not the associated atomic nuclei are treated with wave-mechanical methods. To facilitate these applications we include procedures that originated with Professor H. Huber and his students in a spirit of *transparent quantum chemistry*. Upon such a foundation, one might proceed to use other purely numerical software designed specifically to generate numerical values of diverse properties of molecules and materials of

varied extent but that is opaque to the user.

Beginning early in the twentieth century, spectroscopists attributed the band spectra in the infrared region emitted by diatomic molecules to "quantum vibration and rotation modes" of the molecules. Because of these simple motions, band spectra offered a convenient first phenomenon to which to apply not only the first quantum theory of molecules by Bjerrum in 1912 but also the formulations of the new quantum mechanics in 1926. In 1920 Kemble distinguished explicitly between the frequencies of photons, in the spectra of atoms and molecules for instance, and the frequencies of periodic motions in these systems -- there is not necessarily a relation. In his first paper, completed in Cambridge in 1926 May, J. R. Oppenheimer presented a derivation of the frequencies and relative intensities of the observable spectral lines on the basis of Dirac's new quantum commutator algebra [*Proceedings of the Cambridge Philosophical Society*, 1926], followed by a paper on the intensities of lines in the emission spectrum of the H atom. At the same time L. Mensing published a similar derivation utilizing matrix mechanics, as did E. Fues utilizing wave mechanics. Analyses of Oppenheimer's paper and of its historical and scientific contexts offer insight into the then new quantum mechanics and its utilization and reception during this brief period of competing formalisms, and into the characteristic features of Oppenheimer's later style of research and publication. Subsequent considerations of quantum mechanics and molecular structure confirmed that diatomic molecules offer a special case in that the atomic nuclei are distinguishable from the electrons such that an unique internuclear separation can be established.

We ignore Planck's derivation of a formula that expresses the distribution of frequency of radiation from a black body, which is continuous -- hence showing directly no quantum characteristic, because that formula is equally derived without assumption of discrete or discontinuous process (T. H. Boyer, *Physical Review*, 182, 1374 - 1382, 1969); with a known value of the Boltzmann constant that is equal to ideal-gas constant divided by Avogadro constant, a value for Planck's constant is determinable from

Wien's displacement law, discovered in 1893,  $\nu_{\max} = \frac{\alpha k T}{h}$ , in which  $\nu_{\max}$  is the frequency of light at

which occurs the maximum spectral flux per unit frequency/Hz,  $\frac{\alpha k}{h} = 1.034561890 \times 10^{11} \text{ Hz K}^{-1}$  at temperature  $T$  and  $\alpha = 2.821439$ .

An important conclusion of these calculations and their explanation, worthy of reiteration, is that quantum mechanics is not a chemical theory, not even a physical theory, but a collection of mathematical procedures or algorithms that one might apply to solve problems on an atomic scale. For this reason, the exploration, with mathematical software, of quantum mechanics applied to prototypical systems is particularly appropriate.

## 1.1 the meaning of quantum

### 1.11 quantum laws and quantum theories

The universe comprises a sum of matter and radiation; that these constituents are interconvertible is immaterial for practical chemistry -- the preparation and analysis of chemical substances and their mixtures. Matter might be stationary or in motion, relative to an observer, but radiation is always in motion: even though there are cavities that contain radiation, for instance as standing waves of microwave radiation within a reflex klystron or in a laser cavity for visible light, we consider the radiation to be in a continuous motion without frictional loss, reflected between one end of a cavity and another, even though subject to loss at each reflexion. Experiments have been designed and performed to take advantage of the duration of that transit back and forth across a cavity. Both matter and radiation have their electric and magnetic aspects: with radiation, as visible light for instance, is associated an electromagnetic field, which exists even in the absence of matter; radiation from the sun as centre of our solar system, whether as radio waves or visible light or xrays, thus reaches planet earth through the



intervening electromagnetic field in a vacuum – i.e. the virtual absence of matter. Likewise, macroscopic matter, in which the atomic centres on a microscopic scale comprise positively charged atomic nuclei and their surrounding negatively charged electrons, can bear a net electric charge, such as a plate of an electrical capacitor or a piece of dielectric material subjected to friction according to a triboelectric effect, or a magnetic dipolar moment, such as a bar of iron or iron oxide; matter in a form of a microscopic entity such as a molecule can analogously bear a net electric charge or a net electric or magnetic dipolar moment; other electric and magnetic moments exist, of which the electric quadrupolar moment is likely most generally important. An electric charge that is stationary with respect to an observer generates an electric field whereas an electric charge that is in motion relative to an observer generates also a magnetic field. A magnetic field can exist without a perceptibly moving charge, for instance, in the vicinity of a piece of iron below a critical temperature known as a Curie point, cf chapter 18 on the dielectric and magnetic properties of chemical matter.

Although, on a conventional or macroscopic scale, both matter and radiation seem continuous and to be capable of subdivision or attenuation *ad libitum*, on a microscopic or atomic scale both matter and radiation are found experimentally to comprise discrete units; such a discrete unit might be called a *quantum*, or described as the result of its discrete nature. The word quantum is adapted from latin *quantus*, meaning how much; in English, a quantum signifies a chunk, a small unit of a quantity. The discrete unit of matter we call a molecule -- a single atom by itself is merely a molecule with a single atomic centre or atomic nucleus. The discrete unit of radiation we call a photon, a term proposed by G. N. Lewis in 1926 to signify a carrier of radiant energy; Einstein's interpretation of the photoelectric effect in 1905 was the first substantive recognition of the discreteness of radiation. Chemists typically work with neither a single molecule nor a single photon, but only ensembles of these entities of sufficiently large number. For most practical purposes, we can consider a (small) molecule to have dimensions typically of order  $10^{-9}$  m or 1 nm, but in principle a piece of matter as large as a diamond claimed to be the size of a coconut, or a single crystal of ordinary salt NaCl as large as a football, or a wide sheet of polyethene, might constitute a single molecule according to conventional chemical criteria. Likewise, for most practical purposes, we can ignore any internal structure of a photon, but in a chemical context a molecule is usefully considered to be composed of atomic nuclei and their surrounding electrons that exist, collectively, in states of discrete or continuous energy depending on the distribution of electronic density in the vicinity of the atomic nuclei and the history of the sample. According to conventional definitions, an atomic nucleus in a stable or enduring molecular system bears a net positive electric charge, whereas each associated external electron bears a negative charge; an atomic nucleus is characterized also with a particular value of intrinsic angular momentum, parity, electric quadrupolar moment and other properties that become significant in measurements of spectra based on nuclear magnetic resonance, for instance. Although atomic nuclei have manifolds of excited states, characterized by their energy, angular momentum and other properties, for most chemical purposes such conditions are immaterial, but one significant application enables Moessbauer spectra -- whereby small variations of the energies of states of an atomic nucleus respond to the environment of that atomic centre. The fact that atomic nuclei consist of subnuclear particles, most simply viewed as protons and neutrons, is immaterial for most chemical purposes.

Matter comprises materials, in condensed or dense phases, and molecules. A molecule exists rigorously only in an isolated state, such as in an hypothetical ideal gas at a small density or the constituents of interstellar clouds, density  $\sim 5$  molecules  $\text{mL}^{-1}$ , and in an absence of external fields -- which never occurs; to an approximation of extent variable, depending on both the chemical nature of a sample and the nature of an experimental measurement on that sample, a (small) molecule might, however, seem to exist also within a condensed phase -- a solid or liquid state of aggregation, mesophase or compressed gas. Within a molecule there exist only atomic nuclei and electrons -- hence no atoms, but, near and surrounding an atomic nucleus, an atomic centre is observable that might resemble an

isolated atom of the same atomic number, except the case of hydrogen; an atomic nucleus designated  ${}_Z^A\text{M}$  of a chemical element of symbol M is usefully deemed to comprise  $Z$  protons and  $A - Z$  neutrons, but the subsidiary structure of a proton or neutron, or other aspect of what constitutes an atomic nucleus, is typically of little concern in chemistry. The discrete properties of a molecule or a photon number at least five according to the table below: four of them, which conform to macroscopic descriptions, are inertial mass, electric charge, total energy and linear momentum. A further property has the dimensions of a physical quantity called action, or angular momentum, or possibly something else; this property is generally known as angular momentum, which implies a rotation of some object, but the nature of what might be rotating is uncertain. Mass, charge and energy are scalar quantities, but linear momentum and angular momentum (or whatever other quantity might pertain) are vectorial quantities.

**Table** *Quantum laws or laws of discreteness of molecules and photons*

<u>property</u>	<u>molecule</u>	<u>photon</u>
charge / $ e $	$0, \pm 1, \pm 2, \pm 3, \dots$	0
mass / $u$	$\sim 1, \sim 2, \sim 3, \dots$	0
energy	$E \sim E_{tr} + E_{rot} + E_{vib} + E_{elec} + \dots$	$E = h \nu$
linear momentum	$ \vec{p}  =  m \vec{v} $	$ p  = \frac{h}{\lambda}$
angular momentum / $\frac{h}{2\pi}$	$ J  = 0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \dots$	1

These properties are all directly observable from experiment; for instance, not only the discreteness of electric charge but also a value of electronic charge, at present defined as  $e = -1.602176634 \times 10^{-19} \text{ C}$ , were determined in Millikan's experiment with drops of oil in an electric field or other much more sophisticated measurement.

With each property is associated a *law of conservation*, such as the conservation of net electric charge or conservation of energy. According to Noether's theorem that is a rationalization of experimental observations, with each law of conservation is associated a symmetry; each conserved quantity implies a symmetry or shift invariance. A symmetry is a variation of some property of a system that leaves the physical description of that system unaltered; symmetry is a fundamental attribute of the natural world that enables one to investigate particular aspects of a physical system in isolation. An assumption that space is homogeneous, or possesses translational symmetry, yields the property that the linear momentum of a system closed and isolated is invariant as the system moves, so that one can examine separately the motion of the centre of mass and the internal motion of the system. An assumption that space is isotropic, or possesses rotational symmetry, implies analogously that the total angular momentum of such a system is constant. Noether's theorem is applicable to conservations of linear and angular momentum, energy and net electric charge of a closed or isolated system, as follows. A conservation of linear momentum arises from an invariance to a displacement of the symmetry of spatial translation, or translational invariance; a conservation of angular momentum arises from an invariance to a displacement of a symmetry of rotation or angle, or rotational invariance. A conservation of energy arises from a symmetry of translation in time; no such conservation applies directly to mass -- to only the composite of mass and energy. Conservation of net electric charge arises from an invariant gauge transformation or the shift invariance of electric current.

We consider each property in turn. A photon bears neither rest mass nor charge, but a (small) molecule of particular isotopic composition bears a rest mass or inertial mass that is nearly an integer in

terms of unified atomic mass unit, u, or dalton, Da; a large crystal of salt or that enormous diamond might have a mass of order kilogram, which corresponds to  $\sim 10^{27}$  u and for which any relation to an integer is meaningless. A molecular entity can bear a net electric charge, of value 0 for a net neutral molecule, or  $\pm 1, \pm 2, \dots$  for a molecular ion such as  $\text{NO}^+$  or  $\text{OH}^-$  or  $\text{Ca}^{2+}$ , in units of the charge  $e$  on a proton, which is the same magnitude as the charge on a single electron but of opposite sign. The intrinsic energy  $E$  of a photon is directly proportional to the frequency  $\nu$  of an associated electromagnetic wave; the factor  $h$  of proportionality in  $E = h \nu$  is known as Planck's constant, defined as  $h = 6.626\,070\,15 \times 10^{-34}$  J s. A molecule might exist in a state of discrete energy, although a continuum of internal energies is possible under various conditions; apart from the intrinsic mass energy and the internal states of atomic nuclei, that molecular energy is conventionally subdivided approximately into classical contributions of translation, or external kinetic energy, rotation of the molecule as a whole about an internal axis, internal vibrations of atomic centres, and electronic energy; each such contribution to the total energy might also appear to assume discrete values, and vibrational and electronic energy might be considered to have kinetic and potential contributions. A photon moves in vacuo at speed  $c$  independent of its frequency, but its linear momentum  $p$  is inversely proportional to wave length  $\lambda$  of its associated electromagnetic wave; the factor of proportionality in  $p = \frac{h}{\lambda}$  between momentum and inverse wave length is again Planck's constant. For a molecule confined to an enclosed space, its linear momentum, taken as a product of its mass and velocity, assumes discrete values, but the linear momentum of a free molecule, for instance in an interstellar cloud, takes continuous values. A photon has unit angular momentum in terms of Dirac's constant, which is Planck's constant  $h$  divided by  $2 \pi$ , independent of frequency or wave length; a photon is thus rigorously a boson, or particle to which Bose-Einstein statistics pertain, rather than a fermion that conforms to Fermi-Dirac statistics. A single molecule has total angular momentum in integer or half-integer multiples of  $\frac{h}{2 \pi}$ ; including the effects of intrinsic nuclear angular momentum, a molecule is thus either a boson if it possess zero or integer total angular momentum in terms of  $\frac{h}{2 \pi}$ , such as free  $^{12}\text{C}^{16}\text{O}$  in its state of least energy, or a fermion, if it possess  $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$  units of angular momentum in terms of  $\frac{h}{2 \pi}$ , such as  $^3\text{He}$ . The external kinetic energy of a molecule is related to its linear momentum, which affects only indirectly the internal energy of which one might measure a change during absorption or emission of a photon. The angular momentum of a molecule is, in contrast, of great importance in relation to radiative processes; not only the total angular momentum as a vectorial quantity takes discrete values, such as 0, 1, 2, ... in unit of  $\frac{h}{2 \pi}$ , but also a component of angular momentum along a particular axis, generally assigned to axis  $z$ , takes discrete values of interval 1 unit. For instance, for total angular momentum 3 units, in terms of  $\frac{h}{2 \pi}$ , the component takes values from -3 to 3, so -3, -2, -1, 0, 1, 2, 3 in the same unit. The total angular momentum of a photon is 1 unit, and its projections are only -1 and 1, not 0; these values might be roughly associated with circularly polarized light, rotation clockwise or anticlockwise, for instance. Like energy, angular momentum can, in the absence of friction, be neither created nor destroyed, but might be exchanged between particles or between a particle and radiation; this conservation of angular momentum is considered to be a direct consequence of the isotropy of space, i.e. the fact that empty space has the same properties in all directions.

These properties of charge on an atom or molecule are

$\pm 1, \pm 2, \pm 3, \dots$  in units of  $e$ . For mass, the possible values for neutral molecules are positive integers 1, 2, 3, ... as *mass numbers*, but these values are only approximately integers in terms of unified atomic mass unit or dalton, and two molecules of the same total mass number, such as 28 for both  $^{12}\text{C}^{16}\text{O}$  at  $27.99491461956 \pm 0.00000000016$  u and  $^{14}\text{N}_2$  at  $28.00614800956 \pm 0.00000000124$  u, have slightly disparate actual masses. As the mass of an electron,  $m_e = (5.48579909065 \pm 0.00000000016) 10^{-4}$  u, is much smaller than the mass of any stable atomic nucleus, the mass of a molecular ion accordingly differs only slightly from that of the corresponding neutral atom or molecule. For the energy of an isolated small molecule with multiple atomic centres, the vibrational contributions to the total energy might be described in terms of integers 0, 1, 2, 3, ..., but the energy depends on these values in a linear manner only poorly for small values of these quantum numbers; for only a diatomic molecule is a vibrational quantum number rigorously defined. The energy of overall molecular rotation is formally only approximately separable from energy due to angular momenta in other forms, including intrinsic electronic and nuclear angular momenta, or from vibration, and the energy of electronic excitation of atoms or molecules is generally not expressible in terms of simple relations involving integers; atomic H or other system having only one electron is exceptional in this regard. A quantum number for linear momentum is generally of no practical interest, whereas quantum numbers for angular momentum, that assume integer or half-integer values in terms of the Dirac constant, are important: the internal state of a molecule, hence excluding its external kinetic energy, might be defined uniquely in terms of its total internal energy, relative to the energy of the ground state of least internal energy, and its total angular momentum.

These attributes constitute the quantum laws of nature, or, more precisely, the laws of discreteness. To obtain results consistent with these laws, one might either adapt classical theories of newtonian mechanics and electricity and magnetism and impose the quantization near the end of the calculation, or formulate new theories that are designed specifically to yield automatically these effects. Of the latter type, there are many quantum theories, any of which is more or less approximate and more or less irrelevant to a particular situation; these theories have been devised pragmatically to reproduce some perceived properties of microscopic systems, but no theory yet devised, in the light of these experimental facts, is accepted to be either generally accurate or universally practicable. The first quantum theory is supposedly that of Planck (1900) who derived a formula to describe the spectral distribution of radiation emitted by a *black body*, but that distribution of radiant energy is absolutely continuous: accordingly, no theory requiring a discreteness is necessary; Boyer (1969, and subsequent papers) reported an alternative derivation that is devoid of such a postulate. Einstein's treatment (1905) of the photoelectric effect, in which the kinetic energy of electrons ejected from a metallic surface illuminated with light of varied frequency increases linearly with that frequency beyond a particular frequency that becomes a threshold, of which the corresponding energy is called the work function of that surface, was an innovation at the time of its publication, but is trivial in the light of the concurrent or subsequent recognition of the laws of discreteness of molecules or matter and photons, according to the table above; rather than influencing the number of electrons or electric current measurable on illuminating a surface, the frequency of the incident light affects only the kinetic energy of the electrons. Like the distribution of energy emitted by a *black body*, the kinetic energy of the electrons that escape the surface for an energy exceeding that threshold energy varies continuously with the frequency of incident light, and so is not formally a quantum theory of radiation. The next theory, by Niels Yannicksen Bjerrum (1912), was strongly influenced by the observation of spectral lines of diatomic molecular samples in the mid-infrared region. Niels Henrik David Bohr (1913, 1915) originally sought to produce a mathematical derivation concerning the structure of an atom following the account of Rutherford's nuclear atom; its relation to

the visible emission spectra of H was an afterthought. These theories of both Bjerrum and Bohr are incorrect, worthy of only historical interest, and are a distraction from succeeding quantum theories.

As Max Born and Werner Heisenberg asserted in 1924, a proper physical description of microscopic particles in motion must be concerned with their mechanics, of which the quintessential variables are position, momentum, angular momentum and energy as a function of time; quantum mechanics must hence involve those quantities, but for an hypothetical system in one spatial dimension angular momentum is irrelevant. As P. A. M. Dirac recognised directly in 1925 on reading a paper of Heisenberg, the *fundamental postulate of quantum mechanics* is

$$p_j q_k - q_k p_j = [p_j, q_k] = -\frac{i h}{2 \pi} \delta_{j, k},$$

in which  $p_j$  and  $q_k$  are components of conjugate variables momentum and position, respectively;

according to a frame of cartesian axes,  $j, k$  might pertain to  $x, y$  and  $z$  axes;  $i = \sqrt{-1}$  is the imaginary unit;  $h$  denotes Planck's constant;  $\delta_{j, k}$  denotes Kronecker's delta function, equal to 1 if  $j = k$  and 0 otherwise.

Notation  $[p_j, q_k]$  implies a [commutator](#), as defined to its left in the above expression; with  $j = k$  and  $\delta_{j, k} = 1$ , components  $p_j$  and  $q_j$  fail to commute, or their commutator does not vanish, unlike for ordinary numerical or algebraic quantities. In one dimension this relation becomes simply

$$p q - q p = [p, q] = -\frac{i h}{2 \pi}.$$

This postulate has neither proof nor definitive derivation: its justification is that its application yields results in various formalisms that generate values of quantities comparable with experiment. This relation implies both de Broglie's relation, as outlined in section 1.25, and Heisenberg's principle of indeterminacy: a simultaneous measurement of the momentum  $p$  and position  $q$  of a particle must be inaccurate, such that the product of the uncertainty  $\Delta p$  of momentum and the uncertainty  $\Delta q$  of position in the direction of motion has a minimum value:  $\Delta p \Delta q \geq \frac{h}{4 \pi}$ ; this relation is derived in section 1.24.

The interpretation of an analogous relation  $\Delta E \Delta t \geq \frac{h}{4 \pi}$  requires care because no operator represents time; time can not be a dynamical variable because such a variable implies a variation with time, thereby excluding time itself. A third relation involves a product of angle and angular momentum.

In developing what became matrix mechanics, Heisenberg's intention was to avoid involving unobservable quantities in his derivation, such as the circular orbits of an electron postulated by Bohr in his incorrect and misleading derivation for the hydrogen atom. Although each hamiltonian operator applied in succeeding sections includes a term for kinetic energy, generally expressed as  $\frac{p^2}{2 m}$ , no internal motion involving a kinetic energy is observable in an atomic or other system; the discrete properties of each system directly observable experimentally in principle are the differences of total energy on an interaction of the system with light, and the intensity of a transition from one state to another, as recognised explicitly by Heisenberg in 1924. In applying quantum mechanics to a molecular system, one customarily -- but not invariably -- treats separately and consecutively the electronic and nuclear motions following the approximate separation of those motions according to Born and Oppenheimer in 1927 -- cf section 3.91 in chapter 3, but, perhaps ironically, no such motion is directly observable.

According to pioneer quantum mechanics applied in two forms, and additionally with Dirac's operators, we proceed to apply this postulate to deduce some observable properties of an hypothetical canonical linear harmonic oscillator. Quantities of two kinds, among others, that conform naturally to

such a relation are a matrix and a differential operator with the associated variable: the former quantity forms directly the basis of matrix mechanics; the latter quantity, with either

$$q \rightarrow \bar{q} \quad \text{and} \quad p \rightarrow -\frac{i h}{2 \pi} \frac{\partial}{\partial q}$$

in terms of coordinate  $q$ , or in terms of linear momentum  $p$ ,

$$p \rightarrow \bar{p} \quad \text{and} \quad q \rightarrow \frac{i h}{2 \pi} \frac{\partial}{\partial p}$$

in which  $\bar{p}$  and  $\bar{q}$  denote ordinary multiplicative quantities, forms in either case a basis of wave mechanics, in either a coordinate or a momentum representation, respectively. Another quantity that might obey the commutation law is a quaternion, which is a hypercomplex number, as outlined in section group 1.8. Other quantities, such as Dirac's operators for creation and destruction, might be designed to obey this commutation formula. Other quantum theories, such as Dirac's relativistic quantum mechanics, quantum electrodynamics et cetera, are little employed directly by chemists, although significant applications exist, and quantum-chemical calculations within relativistic wave mechanics are occasionally practised with valuable results.

### 1.12 particle and wave

In *Annales de Physique* **3** (series 10), 22 - 128, 1925, Louis, duc de Broglie postulated that, because *particles of light*, that G. N. Lewis named photons in 1926, have properties like those of massive particles such as momentum, material particles of rest mass not zero might also exhibit properties like those of a wave, subject to experimental test. For such a particle of light, its mass  $m$  would hence be related to its angular frequency  $\omega$  as

$$m = \frac{h \omega}{2 \pi c^2}$$

and momentum

$$p = \frac{h \omega}{2 \pi c} = \frac{h k}{2 \pi}$$

in which appear Planck constant  $h$  and speed of light in vacuo  $c$ , with wavenumber  $k = \frac{2 \pi}{\lambda}$  and wave length  $\lambda$ ;  $p$  and  $k$  are formally vectorial quantities. According to Einstein's special relativity, the mass of a particle moving at speed  $v$  is, with  $\beta = \frac{v}{c}$ ,

$$m = \frac{m_0}{\sqrt{1 - \beta^2}}$$

in terms of its mass  $m_0$  at rest relative to an observer. We introduce a rest frequency  $\omega_0 = \frac{m_0 c^2}{\frac{h}{2 \pi}}$  so that

$\omega = \frac{\omega_0}{\sqrt{1 - \beta^2}}$ . The frequency  $\omega$  of a wave hence transforms to a velocity of a particle as

$$v = c \sqrt{1 - \left( \frac{\omega_0}{\omega} \right)^2}$$

with wavenumber

$$k = \frac{m v}{\frac{h}{2 \pi}} = \frac{m c}{\frac{h \omega}{2 \pi}} \sqrt{\frac{\omega^2 - \omega_0^2}{\omega^2}} = \frac{\omega}{c} \sqrt{1 - \left(\frac{\omega_0}{\omega}\right)^2} = \frac{v \omega}{c^2}$$

The phase velocity becomes

$$v_p = \frac{c^2}{v}$$

so that on direct differentiation we derive

$$\frac{\partial}{\partial k} \omega = \left( \frac{\partial}{\partial \omega} k \right)^{-1} = \left( \frac{1}{c \sqrt{1 - \left(\frac{\omega_0}{\omega}\right)^2}} \right)^{-1} = v = v_g$$

This group velocity is thus identical to the velocity of the particle, and

$$v_p v_g = c^2$$

exactly as for electromagnetic propagation in a dispersive medium. These phase and group velocities become equal only if  $m_0 = 0$ , appropriate to a photon in vacuo.

The basis of the model *pilot wave* of de Broglie is hence that the motion of a particle corresponds to the motion of a localised wave packet, or *pilot wave*, assembled from waves in a set covering frequency or energy in a narrow range, and propagating at the particle velocity. de Broglie's derivation is fully relativistic throughout. Whereas Davisson and Germer might be credited with a verification of the de Broglie wave length, the objective of their experiment was distinct. Sir George P. Thomson, son of Sir Joseph J. Thomson who identified the electron, undertook research with the explicit intention to verify the relativistic dependence of wave length,

$$\lambda = \frac{h}{m_0 v} \sqrt{1 - \frac{v^2}{c^2}}$$

by acceleration of electrons in a beam from small to large energies and measuring the corresponding diffraction pattern as a function of energy. Whereas Sir Joseph J. Thomson became Nobel laureate in physics for identifying an electron as a particle, his son became Nobel laureate in physics for discovering that an electron acts as a wave. Sir George P. Thomson considered, however, that a wave of this sort differs from a wave of water or sound in that the energy is located only where the electron is detected: "the rest of it is a kind of phantom. Once the particle has appeared, the wave disappears like a dream when a sleeper awakes". Whereas a point particle and its matter wave are both real and distinct physical entities according to the pilot-wave theory of de Broglie and as extended by Bohm, according to standard quantum mechanics particles and waves are considered to be the same entities, connected by wave-particle duality.

We thank Professor J. D. Hey for making this description available.

## 1.2 canonical linear harmonic oscillator

### 1.21 harmonic oscillator

As a basis for a consideration of concept molecular structure, we consider the simplest system, despite being hypothetical, that conforms fully to quantum-mechanical principles and that was involved in the first application of a quantum theory, by Planck to the spectral distribution of radiation from a 'black body', even though this application was subsequently proved superfluous. This harmonic

oscillator is the most powerful and widely used single model in physical science, but no such physical system exists explicitly. We then proceed to further aspects of underlying principles and prevailing practices.

According to classical mechanics, the characteristic of an harmonic oscillator is that its frequency of oscillation is independent of the amplitude of oscillation; in contrast, according to quantum mechanics, the characteristic of an harmonic oscillator is that between adjacent discrete states of defined energy there exists a constant difference of energy. An harmonic oscillator is formally a *boson* as it lacks intrinsic angular momentum. Although there exist multiple functions of potential energy  $V$  in their dependence on a displacement coordinate consistent with the latter property, a constant difference of energy, for the *canonical linear harmonic oscillator*, this function is quadratic in displacement  $q$  from an equilibrium position, at  $q = 0$ , at which potential energy is conventionally set to zero,

$$V(q) = \frac{k_e q^2}{2} ;$$

therein appears parameter  $k_e$  called an harmonic force coefficient that is a factor of proportionality in Hooke's law of restoring force for such a displacement,

$$\underline{F} = -k_e \underline{q} .$$

with vector notation for  $\underline{F}$  and  $\underline{q}$  that we henceforth suppress. This condition of a restoring force directly and linearly proportional to a displacement from an equilibrium position independent of the amplitude of that displacement produces, on displacement, an oscillation called [simple harmonic motion](#). The most fundamental quantity in classical mechanics pertaining to the dynamics of a system is its lagrangian  $L$ , defined for a newtonian system as a difference of kinetic  $T$  and potential  $V$  energies;  $L = T - V$ . The use of this equation might avoid the involvement of forces, which are vectorial quantities for which the direction and sense might cause complications. An important formula in a lagrangian analysis or derivation is this Euler-Lagrange formula,

$$\frac{\partial}{\partial t} \left( \frac{\partial}{\partial \dot{q}} L \right) = \frac{\partial}{\partial q} L$$

in which the inner derivative is of  $L$  with respect to  $\dot{q} = \frac{\partial}{\partial t} q$ , a velocity, and analogously  $\dot{p}$  implies

a rate of change of momentum  $\frac{\partial}{\partial t} p$ , implying a force; this notation with raised point  $\dot{\phantom{x}}$  to indicate a temporal derivative originated with Newton. This lagrangian formulation of mechanics is useful because therein [Newton's equations of motion](#) become *covariant* in that they assume the same form in coordinates of any system; for instance, the preceding formula is valid even if coordinates are not orthogonal.

The total energy of a [conservative](#) dynamical system, for which the potential energy is independent of time, is a sum of kinetic and potential energies. The hamiltonian for a classical canonical linear harmonic oscillator of mass  $\mu$  and momentum  $p$  as a sum of kinetic and potential energies is

$$H = T + V = \frac{p^2}{2\mu} + \frac{1}{2} k_e q^2 ;$$

from the canonical relations we find

$$\frac{\partial}{\partial p} H = \dot{q} = \frac{p}{\mu} , \quad - \left( \frac{\partial}{\partial q} H \right) = \dot{p} = -k_e q$$

Solution of these differential equations that comprise a set yields



$$q(t) = q_0 \cos\left(\sqrt{\frac{k_e}{\mu}} t + \phi\right)$$

with phase  $\phi$  that might be determined from initial conditions. We expect to obtain approximately this solution of the quantum-mechanical harmonic oscillator in the limit of large energy, which provides a test of our solution of that problem.

For a point particle moving in a [cartesian](#) space of three dimensions with axes denoted  $x, y, z$ , the equations of motion according to the hamiltonian formalism are analogous to those above,

$$\begin{array}{lll} \frac{\partial}{\partial x} H = -(\dot{p})_x & \frac{\partial}{\partial y} H = -(\dot{p})_y & \frac{\partial}{\partial z} H = -(\dot{p})_z \\ \frac{\partial}{\partial p_x} H = \dot{x} & \frac{\partial}{\partial p_y} H = \dot{y} & \frac{\partial}{\partial p_z} H = \dot{z} \end{array}$$

in which  $p_x$  is called the momentum conjugate to  $x$ , et cetera. When a derivative such as  $\dot{x} = 0$ , the conjugate momentum  $p_x$  is constant.

We present, according to quantum mechanics, three approaches to the solution of the energies of discrete states and possible transitions between these states appropriate to absorption or emission involving a transition moment of type electric dipole. Considering this harmonic oscillator to be a boson, we apply quantum mechanics in various non-relativistic approximations.

## 1.22 canonical linear harmonic oscillator according to matrix mechanics

> **restart:**

When Heisenberg was developing matrix mechanics, he bore heavily in mind that the observable quantities associated with discrete atoms or small molecules were the frequencies of spectral lines and their intensities. His effort was devoted first to an anharmonic oscillator, because for this system the frequency of the absorbed or emitted light differs from the frequency of the oscillator, enabling a more critical test of a theory than for an harmonic oscillator. Heisenberg's derivation is complicated, more so because he lacked knowledge of matrix algebra and had to discover the law of matrix multiplication by experiment. For this reason, we treat here the simpler case of a canonical linear harmonic oscillator, applying not only methods of linear algebra in matrix mechanics, but, in succeeding sections, also differential equations in wave mechanics, section 1.23, and an original calculus with Dirac's operators, section 1.24. The required concepts of matrices and the skills in working with them might be acquired through study of chapter 6 on linear algebra; the most important properties of a matrix concern its addition, multiplication, special types comprising null, unit and constant matrices, hermitian and unitary matrices, and its transformation and diagonalization. A matrix might serve in a function, such as  $f(A)$  for which  $f(x)$  is a polynomial so that  $f(A)$  becomes a polynomial in matrix  $A$ . Matrices of infinite rank occur in matrix mechanics, but we assume that all reasonable results can be taken over matrices from infinite to finite rank without difficulty. Matrix mechanics commonly involves matrices that are [hermitian](#), such that hermitian [adjoint](#)  $A^t$  of matrix  $A$  is obtained on interchanging rows and columns and taking the [complex conjugate](#) of each element, and [unitary](#), such that its hermitian adjoint matrix is equal to its [inverse](#) --  $A^t = A^{-1}$ . With each observable quantity is hence associated a square hermitian matrix that might be generated from the mechanical variables pertinent to the system, such as the position or coordinate  $q$  and the momentum  $p$  of a particle; matrices in a set  $Q_1, Q_2, \dots, Q_n; P_1, P_2, \dots, P_n$ , hence for coordinates and momenta respectively, that satisfy the rules of commutation in the form of Heisenberg's uncertainty commutator

$$-- Q_j Q_k - Q_k Q_j = 0; \quad P_j P_k - P_k P_j = 0; \quad P_j Q_k - Q_k P_j = -\frac{i h}{2 \pi} \delta_{j, k} E,$$

in which  $\delta_{j,k}$  denotes the [Kronecker delta](#) function and  $\mathbf{E}$  is a unit matrix, render hamiltonian matrix  $\mathbf{H}$ . Observable values are sought as  $\mathbf{H}(\mathbf{P}_j, \mathbf{P}_k, \dots, \mathbf{Q}_j, \mathbf{Q}_k, \dots)$  that is a function of momenta and coordinate matrices and that is diagonal; those diagonal values then constitute the measurable values of energy of the system.

A geometric picture that is common in quantum mechanics is a [Hilbert space](#), such that a state function becomes a state vector in that space of infinite dimensions: each dimension corresponds to one row of the matrix with one column that describes the state; the component of the state vector along that axis of the Hilbert space is numerically equal to the corresponding element of the matrix. Varied orientations of the axes in a Hilbert space correspond to varied choices of a representation; for instance, the energy representation corresponds to choosing axes such that a state vector oriented along one of these axes is an eigenstate of the hamiltonian; in general vector  $a_\alpha$  has component  $a_{\alpha k}$  along an axis that corresponds to energy eigenvalue  $E_k$ . The diagonal matrix elements of an operator that has diagonal form are just the eigenvalues of that operator; if the form of the operator be not diagonal, the diagonal matrix elements are the expectation values of operators for states that are normalised.

For the canonical linear harmonic oscillator, Hooke's law relates restoring force  $-k_e q$ , with force coefficient  $k_e$  and displacement  $q$  from equilibrium, to a product, according to [Newton's second law of motion](#), of inertial mass  $\mu$  and acceleration in derivative form  $\frac{\partial^2}{\partial t^2} q$ ,

$$F = -k_e q = \mu \frac{\partial^2}{\partial t^2} q$$

According to matrix mechanics (Max Born, *Atomic Physics*), each physical quantity has a representative [matrix](#). For this equation to be applicable to a system described by means of matrix mechanics, each element of matrix  $\mathbf{Q}$  must separately obey this equation. With

$$\omega_0 = \sqrt{\frac{k_e}{\mu}},$$

in which  $\omega_0$  is a parameter with dimension radial frequency, a solution of the differential equation,

$$\frac{d^2}{dt^2} q(t) + \omega_0^2 q(t) = 0,$$

for a particular element  $q_{n,m}$  of the coordinate matrix is

$$q_{n,m}(t) = q_{0,n,m} e^{-i\omega_{n,m}t}$$

in which parameter  $q_{0,n,m}$  or  $\omega_{n,m}$  is called a *constant of the motion* that implies a constant of integration of the equations of motion of a dynamical system. As a condition that the preceding formula be indeed a solution of the differential equation, that formula requires that

$$(\omega_0^2 - \omega_{n,m}^2) q_{n,m} = 0.$$

We verify these deductions with a direct calculation. For this differential equation,

> **de := diff(q[n,m](t),t\$2) + omega[0]^2\*q[n,m](t) = 0;**

$$de := \frac{d^2}{dt^2} q_{n,m}(t) + \omega_0^2 q_{n,m}(t) = 0 \quad (5.1)$$

a prospective solution is

```
> sol := q[n,m](t) = q0[n,m]*exp(-I*omega[n,m]*t);
```

$$sol := q_{n,m}(t) = q0_{n,m} e^{-I\omega_{n,m}t} \quad (5.2)$$

which we verify on substituting into the differential equation,

```
> des := subs(sol, de);
```

$$des := \frac{\partial^2}{\partial t^2} \left( q0_{n,m} e^{-I\omega_{n,m}t} \right) + \omega_0^2 q0_{n,m} e^{-I\omega_{n,m}t} = 0 \quad (5.3)$$

and evaluating, which yields this condition.

```
> cond := simplify(des);
```

$$cond := e^{-I\omega_{n,m}t} q0_{n,m} \left( \omega_0^2 - \omega_{n,m}^2 \right) = 0 \quad (5.4)$$

Because  $e^{-i\omega_{n,m}t}$  can never be zero for finite time, we eliminate it from that product to generate the expression claimed above.

```
> cond := q0[n,m]*(-omega[n,m]^2 + omega[0]^2) = 0;
```

$$cond := q0_{n,m} \left( \omega_0^2 - \omega_{n,m}^2 \right) = 0 \quad (5.5)$$

A condition either that the amplitude quantity  $q_{n,m} = 0$  or that  $\omega_{n,m} = \pm \omega_0$  hence signifies that the only non-vanishing elements  $q_{n,m}$  of coordinate matrix  $\mathbf{Q}$  are those for which

$$\omega_{n,m} = \omega_0 \quad \text{or} \quad \omega_{n,m} = -\omega_0.$$

Because numbering of matrix elements is arbitrary, we apply a convention that a condition  $\omega_{n,m} = \omega_0$  corresponds to emission of a photon as this oscillator passes from one energy state numbered  $n$  to another numbered  $m = n - k$ , whereas a condition  $\omega_{n,m} = -\omega_0$  corresponds to absorption of a photon in a transition from one state numbered  $n$  to another numbered  $m = n + k$ . Because  $m, n$  and  $k$  are indices to number the rows and columns of a matrix, and their differences, these quantities are naturally integers, *whence quantization arises*, although there is no restriction of a matrix to a finite order. We hence form these elements such that

$$q_{n,n+k} = q0_{n,n+k} e^{-i\omega_{n,n+k}t} \quad \text{or} \quad q_{n,n-k} = q0_{n,n-k} e^{-i\omega_{n,n-k}t} \quad \text{if} \quad m = n \pm k$$

and

$$q_{n,m} = 0 \quad \text{otherwise.}$$

A direct solution of the original differential equation yields a formula equivalent to that in **sol** above, but in a less convenient form,

```
> dsolve(de, q[n,m](t));
```

$$q_{n,m}(t) = \_C1 \sin(\omega_0 t) + \_C2 \cos(\omega_0 t) \quad (5.6)$$

as two independent solutions and their associated constants of integration; we can express the latter result in terms of a single trigonometric function by including a phase factor  $\phi$ ,

```
> q[n,m](t) = \_C3*cos(omega[0]*t + phi);
```

$$q_{n,m}(t) = \_C3 \cos(\omega_0 t + \phi) \quad (5.7)$$

so that the two constants of integration required for the differential equation of second order are  $_C3$  and  $\phi$ . Alternatively, we might convert the trigonometric functions to exponential form,

```
> lhs(%) = collect(convert(rhs(%), exp), exp);
```

$$q_{n,m}(t) = \left( \frac{I_{-C1}}{2} + \frac{-C2}{2} \right) e^{-I\omega_0 t} + \left( -\frac{I_{-C1}}{2} + \frac{-C2}{2} \right) e^{I\omega_0 t} \quad (5.8)$$

as a sum of two independent exponential functions of which the form is more complicated than the preceding formula; for this reason, we prefer the solution derived above.

```
> restart:
```

```
> with(LinearAlgebra):
```

We hence define the [elements](#) of an infinite matrix  $\mathbf{Q}$  to represent [coordinate](#)  $q$  with non-zero elements  $q_{n,m}$  for  $m = n \pm k$  up to  $m = \text{dimm}$ , and display this matrix up to a specified size. We choose first  $k = 1$ , and a matrix of order 12 for our purpose.

```
> k := 1:
```

```
dim := 12:
```

```
interface( rtablesize = 15 ):
```

```
> Q := Matrix(dim, (n, m) -> if m = n+k then
                                q0[n-1,m-1]*exp(-I*omega[0]*t);
                                elif m = n-k then
                                q0[n-1, m-1]*exp(I*omega[0]*t);
                                else 0;
                                end if);
```

$$Q := \begin{bmatrix} 0, q\theta_{0,1} e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \end{bmatrix}, \quad (5.9)$$

$$\begin{bmatrix} q\theta_{1,0} e^{I\omega_0 t}, 0, q\theta_{1,2} e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, q\theta_{2,1} e^{I\omega_0 t}, 0, q\theta_{2,3} e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, q\theta_{3,2} e^{I\omega_0 t}, 0, q\theta_{3,4} e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, q\theta_{4,3} e^{I\omega_0 t}, 0, q\theta_{4,5} e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, q\theta_{5,4} e^{I\omega_0 t}, 0, q\theta_{5,6} e^{-I\omega_0 t}, 0, 0, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, q\theta_{6,5} e^{I\omega_0 t}, 0, q\theta_{6,7} e^{-I\omega_0 t}, 0, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, q\theta_{7,6} e^{I\omega_0 t}, 0, q\theta_{7,8} e^{-I\omega_0 t}, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, q\theta_{8,7} e^{I\omega_0 t}, 0, q\theta_{8,9} e^{-I\omega_0 t}, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, q\theta_{9,8} e^{I\omega_0 t}, 0, q\theta_{9,10} e^{-I\omega_0 t}, 0 \end{bmatrix},$$

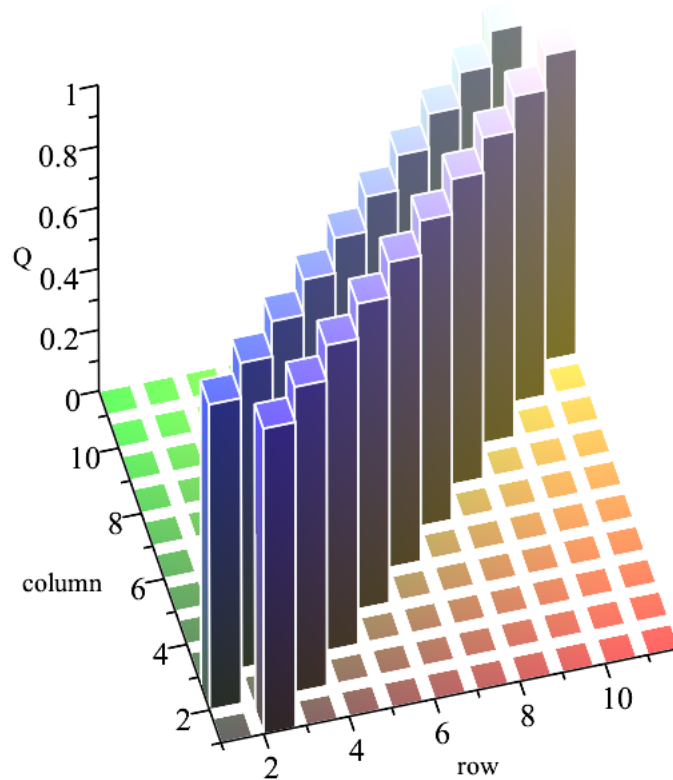
$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, q\theta_{10,9} e^{I\omega_0 t}, 0, q\theta_{10,11} e^{-I\omega_0 t} \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, q\theta_{11,10} e^{I\omega_0 t}, 0 \end{bmatrix}]$$

We show the *form*, which is tridiagonal, of the coordinate matrix in this figure.

```
> Qm := Matrix(dimn=k, shape=symmetric):
  for j to dimn-2*k do
    Qm[j+k, j] := 1:
  end do:
plots[matrixplot](Qm, axes=frame, titlefont=[TIMES,BOLD,14],
  title="form of coordinate matrix", gap=1/4, heights=histogram,
  orientation=[-105,40], labels=["row","column","Q"]);
```

form of coordinate matrix



As momentum is defined as a product of mass and velocity, so  $p = \mu \left( \frac{\partial}{\partial t} q \right)$ , momentum matrix  $\mathbf{P}$  has elements

$$p_{n,m} = \mu \left( \frac{\partial}{\partial t} q_{n,m} \right),$$

**> P := mu\*map(diff, Q, t);**

$$P := \begin{bmatrix} \left[ 0, -I\mu q\theta_{0,1} \omega_0 e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ I\mu q\theta_{1,0} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{1,2} \omega_0 e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, I\mu q\theta_{2,1} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{2,3} \omega_0 e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, I\mu q\theta_{3,2} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{3,4} \omega_0 e^{-I\omega_0 t}, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, I\mu q\theta_{4,3} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{4,5} \omega_0 e^{-I\omega_0 t}, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, I\mu q\theta_{5,4} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{5,6} \omega_0 e^{-I\omega_0 t}, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, I\mu q\theta_{6,5} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{6,7} \omega_0 e^{-I\omega_0 t}, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, I\mu q\theta_{7,6} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{7,8} \omega_0 e^{-I\omega_0 t}, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, I\mu q\theta_{8,7} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{8,9} \omega_0 e^{-I\omega_0 t}, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, I\mu q\theta_{9,8} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{9,10} \omega_0 e^{-I\omega_0 t} \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, I\mu q\theta_{10,9} \omega_0 e^{I\omega_0 t}, 0, -I\mu q\theta_{10,11} \omega_0 e^{-I\omega_0 t} \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, I\mu q\theta_{11,10} \omega_0 e^{I\omega_0 t}, 0 \right] \end{bmatrix} \quad (5.10)$$

so that the momentum matrix has the same form, tridiagonal with zero along the principal diagonal, as the coordinate matrix. Both **P** and **Q** are hermitian matrices because they represent physically measurable dynamical variables. The total energies are the sum of kinetic and potential contributions,

$$W = T + V = \frac{p^2}{2\mu} + \frac{k_e q^2}{2} = \frac{p^2}{2\mu} + \frac{\mu \omega_0^2 q^2}{2},$$

**> W := simplify((P.P)/(2\*mu) + mu\*omega[0]^2\*Q.Q/2);**

$$W := \begin{bmatrix} \left[ \mu q\theta_{0,1} \omega_0^2 q\theta_{1,0}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, \mu \omega_0^2 (q\theta_{0,1} q\theta_{1,0} + q\theta_{1,2} q\theta_{2,1}), 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, \mu \omega_0^2 (q\theta_{1,2} q\theta_{2,1} + q\theta_{2,3} q\theta_{3,2}), 0, 0, 0, 0, 0, 0, 0, 0 \right], \end{bmatrix} \quad (5.11)$$

$$\begin{aligned}
& \left[ 0, 0, 0, \mu \omega_0^2 (q\theta_{2,3} q\theta_{3,2} + q\theta_{3,4} q\theta_{4,3}), 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{3,4} q\theta_{4,3} + q\theta_{4,5} q\theta_{5,4}), 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{4,5} q\theta_{5,4} + q\theta_{5,6} q\theta_{6,5}), 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{5,6} q\theta_{6,5} + q\theta_{6,7} q\theta_{7,6}), 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{6,7} q\theta_{7,6} + q\theta_{7,8} q\theta_{8,7}), 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{7,8} q\theta_{8,7} + q\theta_{8,9} q\theta_{9,8}), 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{8,9} q\theta_{9,8} + q\theta_{9,10} q\theta_{10,9}), 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \mu \omega_0^2 (q\theta_{9,10} q\theta_{10,9} + q\theta_{10,11} q\theta_{11,10}), 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \mu q\theta_{10,11} \omega_0^2 q\theta_{11,10} \right]
\end{aligned}$$

yielding a matrix with non-zero elements only along the principal diagonal; quantities  $q\theta_{n,m}$  that originate as constants of integration in the solution of the differential equation remain to be defined. For this purpose we apply the commutation relation that expresses the fundamental postulate of quantum mechanics, with commutator  $[p, q]$ ,

$$p q - q p = -\frac{i h}{2 \pi},$$

in which  $\frac{h}{2 \pi}$  denotes Dirac's constant, equal to Planck's constant  $h$  divided by  $2 \pi$ . With matrices  $\mathbf{Q}$  for coordinate and  $\mathbf{P}$  for momentum, this relation becomes

$$\mathbf{P} \mathbf{Q} - \mathbf{Q} \mathbf{P} = -\frac{i h}{2 \pi} \mathbf{E}$$

in which  $\mathbf{E}$  on the right side denotes a unit matrix; the result of the calculation of matrices on the left side must be a diagonal matrix because the temporal derivative of  $\mathbf{P} \mathbf{Q} - \mathbf{Q} \mathbf{P}$  must vanish. We form a matrix for the commutator

$$[p, q] = p q - q p$$

on the left side.

**> commut := simplify(P.Q - Q.P);**

$$commut := \left[ \left[ -2 I \mu q\theta_{1,0} \omega_0 q\theta_{0,1}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \right. \quad (5.12)$$

$$\begin{aligned}
& \left[ 0, 2 I \mu \omega_0 (q\theta_{0,1} q\theta_{1,0} - q\theta_{1,2} q\theta_{2,1}), 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 2 I \mu \omega_0 (q\theta_{1,2} q\theta_{2,1} - q\theta_{2,3} q\theta_{3,2}), 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 2 I \mu \omega_0 (q\theta_{2,3} q\theta_{3,2} - q\theta_{3,4} q\theta_{4,3}), 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{3,4} q\theta_{4,3} - q\theta_{4,5} q\theta_{5,4}), 0, 0, 0, 0, 0, 0, 0 \right],
\end{aligned}$$

$$\begin{aligned}
& [0, 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{4,5} q\theta_{5,4} - q\theta_{5,6} q\theta_{6,5}), 0, 0, 0, 0, 0, 0], \\
& [0, 0, 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{5,6} q\theta_{6,5} - q\theta_{6,7} q\theta_{7,6}), 0, 0, 0, 0, 0, 0], \\
& [0, 0, 0, 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{6,7} q\theta_{7,6} - q\theta_{7,8} q\theta_{8,7}), 0, 0, 0, 0, 0], \\
& [0, 0, 0, 0, 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{7,8} q\theta_{8,7} - q\theta_{8,9} q\theta_{9,8}), 0, 0, 0, 0], \\
& [0, 0, 0, 0, 0, 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{8,9} q\theta_{9,8} - q\theta_{9,10} q\theta_{10,9}), 0, 0, 0], \\
& [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 2 I \mu \omega_0 (q\theta_{9,10} q\theta_{10,9} - q\theta_{10,11} q\theta_{11,10}), 0, 0], \\
& [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 2 I \mu q\theta_{11,10} \omega_0 q\theta_{10,11}] ]
\end{aligned}$$

Because both the energy and the commutator have no dependence on time, we set equal the amplitude factors with related indices of row and column, in accordance with the principle of microscopic reversibility, so that  $q\theta_{n,m} = q\theta_{m,n}$ .

```

> for m from 0 to dimm do
  for n from m to dimm do
    q0[n,m] := q0[m,n];
  end do;
end do;

```

We apply the commutation formula to form these equations, simplifying the left sides on dividing by a common factor

$$-\frac{2 i h}{2 \pi \mu \omega_0},$$

and also replace the radial frequency  $\omega_0$  by  $2 \pi \nu_0$ ,

```

> omega[0] := 2*Pi*nu[0];

```

$$\omega_0 := 2 \pi \nu_0 \quad (5.13)$$

to produce these conditions,

```

> for i to dimm-k do
  eq[i] := simplify(commut[i,i]/(-2*I*mu*omega[0])) =
    -I*h/(2*Pi)/(-2*I*mu*omega[0]);
end do;

```

$$eq_1 := q\theta_{0,1}^2 = \frac{h}{8 \pi^2 \mu \nu_0}$$

$$eq_2 := -q\theta_{0,1}^2 + q\theta_{1,2}^2 = \frac{h}{8 \pi^2 \mu \nu_0}$$

$$eq_3 := -q\theta_{1,2}^2 + q\theta_{2,3}^2 = \frac{h}{8 \pi^2 \mu \nu_0}$$



$$\begin{aligned}
eq_4 &:= -q\theta_{2,3}^2 + q\theta_{3,4}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_5 &:= -q\theta_{3,4}^2 + q\theta_{4,5}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_6 &:= -q\theta_{4,5}^2 + q\theta_{5,6}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_7 &:= -q\theta_{5,6}^2 + q\theta_{6,7}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_8 &:= -q\theta_{6,7}^2 + q\theta_{7,8}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_9 &:= -q\theta_{7,8}^2 + q\theta_{8,9}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_{10} &:= -q\theta_{8,9}^2 + q\theta_{9,10}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_{11} &:= -q\theta_{9,10}^2 + q\theta_{10,11}^2 = \frac{h}{8\pi^2\mu v_0}
\end{aligned} \tag{5.14}$$

which we solve sequentially,

```

> for j to dimm-k do
    q0[j-1,j+k-1] := op(select(has, [sqrt(rhs(isolate(eq[j],
                                                q0[j-1,j+k-1]^2)))]), -1));
end do;

```

$$q\theta_{0,1} := \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}}}{4\pi}$$

$$q\theta_{1,2} := \frac{\sqrt{\frac{h}{\mu v_0}}}{2\pi}$$

$$q\theta_{2,3} := \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}}}{4\pi}$$

$$\begin{aligned}
q\theta_{3,4} &:= \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}}}{2\pi} \\
q\theta_{4,5} &:= \frac{\sqrt{10} \sqrt{\frac{h}{\mu v_0}}}{4\pi} \\
q\theta_{5,6} &:= \frac{\sqrt{3} \sqrt{\frac{h}{\mu v_0}}}{2\pi} \\
q\theta_{6,7} &:= \frac{\sqrt{14} \sqrt{\frac{h}{\mu v_0}}}{4\pi} \\
q\theta_{7,8} &:= \frac{\sqrt{\frac{h}{\mu v_0}}}{\pi} \\
q\theta_{8,9} &:= \frac{3\sqrt{2} \sqrt{\frac{h}{\mu v_0}}}{4\pi} \\
q\theta_{9,10} &:= \frac{\sqrt{5} \sqrt{\frac{h}{\mu v_0}}}{2\pi} \\
q\theta_{10,11} &:= \frac{\sqrt{22} \sqrt{\frac{h}{\mu v_0}}}{4\pi}
\end{aligned} \tag{5.15}$$

and display as our matrix to represent displacement coordinate  $q$ .

```

> Q := map(simplify, Q):
'Q' = SubMatrix(Q, [1..dim-k],[1..dim-k]);

```

$$Q = \begin{bmatrix} \sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t} \\ 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}}}{4\pi}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \end{bmatrix}, \tag{5.16}$$

$$\begin{aligned}
& \left[ \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi}, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi}, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, \frac{\sqrt{10} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, \frac{\sqrt{10} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, \frac{\sqrt{3} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi}, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, \frac{\sqrt{3} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, \frac{\sqrt{14} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, \frac{\sqrt{14} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{\pi}, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{\pi}, 0, \frac{3\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, \frac{3\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, \frac{\sqrt{5} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi} \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{5} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0 \right]
\end{aligned}$$

We extract the constant part of the amplitude factors to be a multiplicand of the entire matrix.

```
> 'Q' = sqrt(h/(mu*nu[0]))/(2*Pi)&*map(simplify, map(x -> x*2*
```

**Pi/sqrt(h/(mu\*nu[0])), rhs(%))];**

$$Q = \left( \frac{\sqrt{\frac{h}{\mu v_0}}}{2\pi} \right) \&^* \left[ \left[ 0, \frac{\sqrt{2} e^{-2I\pi v_0 t}}{2}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \right. \\ \left[ \frac{\sqrt{2} e^{2I\pi v_0 t}}{2}, 0, e^{-2I\pi v_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, e^{2I\pi v_0 t}, 0, \frac{\sqrt{6} e^{-2I\pi v_0 t}}{2}, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, \frac{\sqrt{6} e^{2I\pi v_0 t}}{2}, 0, \sqrt{2} e^{-2I\pi v_0 t}, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, \sqrt{2} e^{2I\pi v_0 t}, 0, \frac{\sqrt{10} e^{-2I\pi v_0 t}}{2}, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, \frac{\sqrt{10} e^{2I\pi v_0 t}}{2}, 0, \sqrt{3} e^{-2I\pi v_0 t}, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, \sqrt{3} e^{2I\pi v_0 t}, 0, \frac{\sqrt{14} e^{-2I\pi v_0 t}}{2}, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, \frac{\sqrt{14} e^{2I\pi v_0 t}}{2}, 0, 2 e^{-2I\pi v_0 t}, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 2 e^{2I\pi v_0 t}, 0, \frac{3\sqrt{2} e^{-2I\pi v_0 t}}{2}, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, \frac{3\sqrt{2} e^{2I\pi v_0 t}}{2}, 0, \sqrt{5} e^{-2I\pi v_0 t} \right], \\ \left. \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \sqrt{5} e^{2I\pi v_0 t}, 0 \right] \right]$$
(5.17)

According to the latter manipulation and recalling that the rows and the columns of this matrix **Q** number from zero so that the element topmost and leftmost is  $q_{0,0}$ , the numerical coefficients of

$$\frac{\sqrt{\frac{h}{\mu v_0}} e^{-2\pi I v_0 t}}{2\pi} \text{ in } q_{n,n+1} \text{ along the superdiagonal in matrix } \mathbf{Q} \text{ are } \sqrt{\frac{n+1}{2}} \text{ and the}$$

numerical coefficients of  $\frac{\sqrt{\frac{h}{\mu v_0}} e^{2\pi i v_0 t}}{2\pi}$  in  $q_{n+1,n}$  along the subdiagonal in matrix **Q** are also

$\sqrt{\frac{n+1}{2}}$ . We display the submatrix of energy for which the truncated matrices for **P** and **Q** are valid.

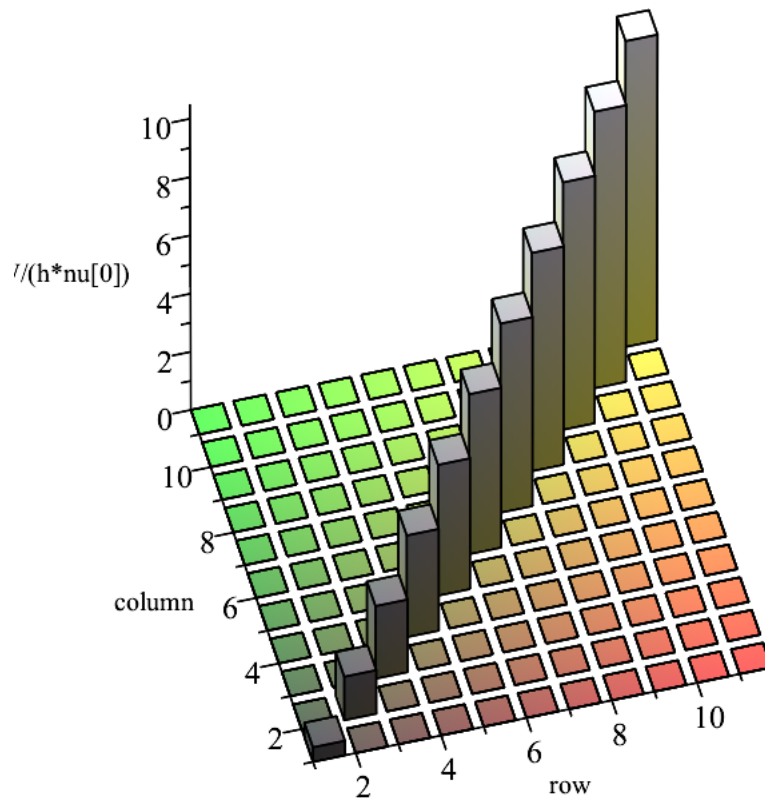
```
> 'W' = map(eval, SubMatrix(W, [1..dim-1],[1..dim-1]));
```

$$W = \begin{bmatrix} \left[ \frac{h v_0}{2}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, \frac{3 h v_0}{2}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, \frac{5 h v_0}{2}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, \frac{7 h v_0}{2}, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, \frac{9 h v_0}{2}, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, \frac{11 h v_0}{2}, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, \frac{13 h v_0}{2}, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, \frac{15 h v_0}{2}, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, \frac{17 h v_0}{2}, 0, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{19 h v_0}{2}, 0, 0 \right], \\ \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{21 h v_0}{2}, 0 \right] \end{bmatrix} \quad (5.18)$$

A plot of this energy matrix shows this simple form.

```
> plots[matrixplot](rhs(%)/(h*nu[0]), axes=frame, titlefont=[TIMES,
BOLD,14],
title="form of energy matrix", gap=1/4, heights=histogram,
orientation=[-105,40], labels=["row","column","W/(h*nu[0])"]);
```

### form of energy matrix



We calculate the intensity of the absorption spectrum for the canonical isotropic harmonic oscillator in three spatial dimensions and in its ground state, for which  $n = 0$ , as a dimensionless oscillator strength or  $f$  value dependent on the square of an electric dipolar moment  $e q$ ,

$$f = \frac{3 \cdot 8 \mu \pi^2}{3 h e^2} e^2 q^2$$

for the transition from state with  $n = 0$  to a state with  $n = 1$ , for which the applicable matrix element is

$$q_{0,1} = \frac{\sqrt{\frac{2 h}{\mu v_0}} e^{-2 I \pi v_0 t}}{4 \pi}$$

but represented as  $Q_{1,2}$  in the matrix above because for *Maple* the matrix elements must number from unity, not zero.

```
> f := 3*simplify(8/3*mu*Pi^2/h/e^2*e*Q[1,2]*subs(I=-I,e*Q[1,2])*nu[0]);
```

$$f := 1 \quad (5.19)$$

As the sum of all oscillator strengths for transitions in absorption from the ground state is unity for three spatial dimensions, this value is consistent with that definition because only one transition, from  $n = 0$  to  $n = 1$ , is possible from that state as  $q_{0,i} = 0$  for  $i \neq 1$ . The external factor 3 in the numerator of the latter formula for  $f$  results from a calculation in three spatial dimensions, although the oscillation is

effectively in only one dimension.

For  $q_{n,m} \neq 0$  for  $m = n \pm k$  with  $k = 1$ , the energies of discrete states are hence independent of time and take values

$$E_n = W_{n,n} = \left( n + \frac{1}{2} \right) h \nu_0,$$

in which appear quantum number  $n$ , Planck's constant  $h$  and circular frequency  $\nu_0$ . According to absorption or emission as a transition involving an electric dipole, for which the electric dipolar moment is  $e q$ , the only possible transitions with  $k = 1$  are those for which  $n - m = \pm 1$ . When  $n = 0$ , this oscillator has *residual energy*

$$E_0 = W_{0,0} = \frac{h \nu_0}{2}.$$

whereas, according to classical mechanics, there is no residual energy. In accordance with the fact that  $V \rightarrow \infty$  as  $q \rightarrow \infty$ , so that  $E \rightarrow \infty$  as  $n \rightarrow \infty$ , and assuming mass  $\mu$  to be independent of kinetic energy, there are only discrete states, spaced equidistantly and numbering uncountably, with no continuum.

We repeat this calculation with  $k = 2$ . Redefining the [elements](#) of an infinite matrix  $Q$  to represent [coordinate](#)  $q$  with non-zero elements  $q_{n,m}$  for  $m = n \pm k$  up to  $m = \text{dim}m$ , we choose here  $k = 2$ , and display this matrix of order 12.

```
> k := 2:
  Q := Matrix(dim, (n, m) -> if m = n+k then
    q0[n-1,m-1]*exp(-I*omega[0]*t);
  elif m = n-k then
    q0[n-1, m-1]*exp(I*omega[0]*t);
  else 0;
  end if);
```

$$Q := \begin{bmatrix} 0, 0, q\theta_{0,2} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \\ 0, 0, 0, q\theta_{1,3} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \\ q\theta_{0,2} e^{2I\pi\nu_0 t}, 0, 0, 0, q\theta_{2,4} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0, 0, 0, 0 \\ 0, q\theta_{1,3} e^{2I\pi\nu_0 t}, 0, 0, 0, q\theta_{3,5} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0, 0, 0, 0 \\ 0, 0, q\theta_{2,4} e^{2I\pi\nu_0 t}, 0, 0, 0, q\theta_{4,6} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0, 0, 0 \\ 0, 0, 0, q\theta_{3,5} e^{2I\pi\nu_0 t}, 0, 0, 0, q\theta_{5,7} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0, 0 \\ 0, 0, 0, 0, q\theta_{4,6} e^{2I\pi\nu_0 t}, 0, 0, 0, q\theta_{6,8} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0 \\ 0, 0, 0, 0, 0, q\theta_{5,7} e^{2I\pi\nu_0 t}, 0, 0, 0, q\theta_{7,9} e^{-2I\pi\nu_0 t}, 0, 0, 0, 0, 0 \end{bmatrix}, \quad (5.20)$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, q\theta_{6,8} e^{2I\pi v_0 t}, 0, 0, 0, q\theta_{8,10} e^{-2I\pi v_0 t}, 0 \end{bmatrix},$$

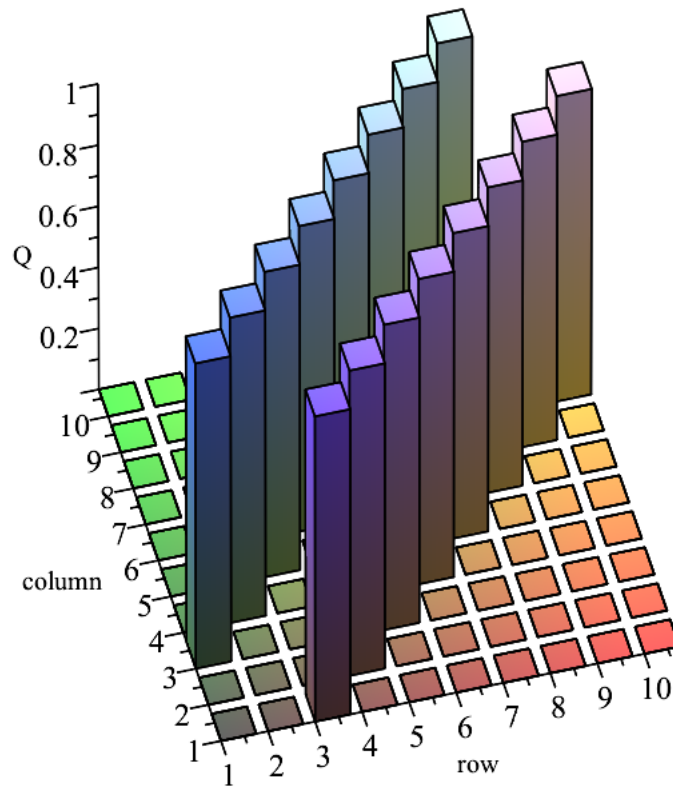
$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, q\theta_{7,9} e^{2I\pi v_0 t}, 0, 0, 0, q\theta_{9,11} e^{-2I\pi v_0 t} \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, q\theta_{8,10} e^{2I\pi v_0 t}, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, q\theta_{9,11} e^{2I\pi v_0 t}, 0, 0 \end{bmatrix}$$

We show the *form* of the coordinate matrix in this figure, again having only two non-zero diagonals, but separated by three zero diagonals.

```
> Qm := Matrix(dim=2*k, shape=symmetric):
  for j to dim-2*k do
    Qm[j+k, j] := 1:
  end do:
plots[matrixplot](Qm, axes=frame, titlefont=[TIMES,BOLD,14],
  title="form of coordinate matrix", gap=1/4, heights=histogram,
  orientation=[-105,40], labels=["row","column","Q"]);
form of coordinate matrix
```



As above, we form momentum matrix **P** with



$$p = \mu \left( \frac{\partial}{\partial t} q \right) \text{ for each element.}$$

$$p_{n,m} = \mu \left( \frac{\partial}{\partial t} q_{n,m} \right).$$

**> P := mu\*map(diff, Q, t);**

$$P := \begin{bmatrix} 0, 0, -2 \operatorname{Im} q \theta_{0,2} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \\ 0, 0, 0, -2 \operatorname{Im} q \theta_{1,3} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0, 0, 0, 0, 0, 0 \\ 2 \operatorname{Im} q \theta_{0,2} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{2,4} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0, 0, 0, 0 \\ 0, 2 \operatorname{Im} q \theta_{1,3} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{3,5} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0, 0, 0, 0 \\ 0, 0, 2 \operatorname{Im} q \theta_{2,4} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{4,6} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0, 0, 0 \\ 0, 0, 0, 2 \operatorname{Im} q \theta_{3,5} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{5,7} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0, 0 \\ 0, 0, 0, 0, 2 \operatorname{Im} q \theta_{4,6} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{6,8} \pi v_0 e^{-2i\pi v_0 t}, 0, 0, 0 \\ 0, 0, 0, 0, 0, 2 \operatorname{Im} q \theta_{5,7} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{7,9} \pi v_0 e^{-2i\pi v_0 t}, 0, 0 \\ 0, 0, 0, 0, 0, 0, 2 \operatorname{Im} q \theta_{6,8} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{8,10} \pi v_0 e^{-2i\pi v_0 t}, 0 \\ 0, 0, 0, 0, 0, 0, 0, 2 \operatorname{Im} q \theta_{7,9} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0, -2 \operatorname{Im} q \theta_{9,11} \pi v_0 e^{-2i\pi v_0 t} \\ 0, 0, 0, 0, 0, 0, 0, 0, 2 \operatorname{Im} q \theta_{8,10} \pi v_0 e^{2i\pi v_0 t}, 0, 0, 0 \\ 0, 0, 0, 0, 0, 0, 0, 0, 0, 2 \operatorname{Im} q \theta_{9,11} \pi v_0 e^{2i\pi v_0 t}, 0, 0 \end{bmatrix} \quad (5.21)$$

The total energies are the sum of kinetic and potential contributions,

$$W = T + V = \frac{p^2}{2\mu} + \frac{k_e q^2}{2} = \frac{p^2}{2\mu} + \frac{\mu \omega_0^2 q^2}{2}.$$

**> W := simplify((P.P)/(2\*mu) + mu\*omega[0]^2\*Q.Q/2);**

$$W := \begin{bmatrix} 4 \mu q \theta_{0,2}^2 \pi^2 v_0^2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \\ 0, 4 \mu q \theta_{1,3}^2 \pi^2 v_0^2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \\ 0, 0, 4 \pi^2 \mu v_0^2 (q \theta_{0,2}^2 + q \theta_{2,4}^2), 0, 0, 0, 0, 0, 0, 0, 0, 0 \end{bmatrix} \quad (5.22)$$

$$\begin{aligned}
& \left[ 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{1,3}^2 + q\theta_{3,5}^2), 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{2,4}^2 + q\theta_{4,6}^2), 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{3,5}^2 + q\theta_{5,7}^2), 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{4,6}^2 + q\theta_{6,8}^2), 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{5,7}^2 + q\theta_{7,9}^2), 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{6,8}^2 + q\theta_{8,10}^2), 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 4 \pi^2 \mu v_0^2 (q\theta_{7,9}^2 + q\theta_{9,11}^2), 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 4 \mu q\theta_{8,10}^2 \pi^2 v_0^2, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 4 \mu q\theta_{9,11}^2 \pi^2 v_0^2 \right]
\end{aligned}$$

yields again a diagonal matrix in which still appear integration constants  $q\theta_{n,m}$ .

As above, we apply the commutation relation,

$$p q - q p = -\frac{i h}{2 \pi}.$$

by forming a matrix for the commutator

$$[p, q] = p q - q p$$

on the left side.

**> commut := simplify(P.Q - Q.P);**

$$commut := \left[ \left[ -4 I \mu q\theta_{0,2}^2 \pi v_0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \right.$$

**(5.23)**

$$\begin{aligned}
& \left[ 0, -4 I \mu q\theta_{1,3}^2 \pi v_0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 4 I \pi \mu v_0 (q\theta_{0,2}^2 - q\theta_{2,4}^2), 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{1,3}^2 - q\theta_{3,5}^2), 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{2,4}^2 - q\theta_{4,6}^2), 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{3,5}^2 - q\theta_{5,7}^2), 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{4,6}^2 - q\theta_{6,8}^2), 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{5,7}^2 - q\theta_{7,9}^2), 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{6,8}^2 - q\theta_{8,10}^2), 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 4 I \pi \mu v_0 (q\theta_{7,9}^2 - q\theta_{9,11}^2), 0, 0 \right],
\end{aligned}$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 4 I \mu q \theta_{8,10}^2 \pi v_0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 4 I \mu q \theta_{9,11}^2 \pi v_0 \end{bmatrix}]$$

Because both the energy and the commutator have no dependence on time, we set equal the corresponding amplitude factors, so that  $q \theta_{n,m} = q \theta_{m,n}$ , although this setting is already imposed with this command above.

```
> for m from 0 to dimm do
  for n from m to dimm do
    q0[n,m] := q0[m,n];
  end do;
end do;
```

We apply the commutation formula to form these equations, simplifying the left sides on dividing by a common factor

$$-\frac{i h}{\pi \mu \omega_0},$$

and also replacing radial frequency  $\omega_0$  by  $2 \pi v_0$  involving circular frequency  $v_0$ , to yield these conditions,

```
> omega[0] := 2*Pi*nu[0];
for i to dimm-k do
  eq[i] := simplify(commut[i,i]/(-2*I*mu*omega[0])) =
    -I*h/(2*Pi)/(-2*I*mu*omega[0]);
end do;
```

$$\omega_0 := 2 \pi v_0$$

$$eq_1 := q \theta_{0,2}^2 = \frac{h}{8 \pi^2 \mu v_0}$$

$$eq_2 := q \theta_{1,3}^2 = \frac{h}{8 \pi^2 \mu v_0}$$

$$eq_3 := -q \theta_{0,2}^2 + q \theta_{2,4}^2 = \frac{h}{8 \pi^2 \mu v_0}$$

$$eq_4 := -q \theta_{1,3}^2 + q \theta_{3,5}^2 = \frac{h}{8 \pi^2 \mu v_0}$$

$$eq_5 := -q \theta_{2,4}^2 + q \theta_{4,6}^2 = \frac{h}{8 \pi^2 \mu v_0}$$

$$eq_6 := -q \theta_{3,5}^2 + q \theta_{5,7}^2 = \frac{h}{8 \pi^2 \mu v_0}$$

$$\begin{aligned}
eq_7 &:= -q\theta_{4,6}^2 + q\theta_{6,8}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_8 &:= -q\theta_{5,7}^2 + q\theta_{7,9}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_9 &:= -q\theta_{6,8}^2 + q\theta_{8,10}^2 = \frac{h}{8\pi^2\mu v_0} \\
eq_{10} &:= -q\theta_{7,9}^2 + q\theta_{9,11}^2 = \frac{h}{8\pi^2\mu v_0}
\end{aligned} \tag{5.24}$$

which we solve sequentially,

```

> for j to dimm-k do
    q0[j-1,j+k-1] := op(select(has, [sqrt(rhs(isolate(eq[j],
        q0[j-1,j+k-1]^2)))]), -1));
end do:

```

and display as our matrix to represent displacement coordinate  $q$ ,

```

> Q := map(simplify, Q):
'Q' = SubMatrix(Q, [1..dimm-k],[1..dimm-k]);

```

$$Q = \begin{bmatrix} \left[ \begin{array}{c} \sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t} \\ 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0, 0, 0, 0, 0, 0 \end{array} \right], \\ \left[ \begin{array}{c} \sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t} \\ 0, 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0, 0, 0, 0, 0 \end{array} \right], \\ \left[ \begin{array}{c} \sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t} \\ \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, 0, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi}, 0, 0, 0, 0, 0 \end{array} \right], \\ \left[ \begin{array}{c} \sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t} \\ 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, 0, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi}, 0, 0, 0, 0 \end{array} \right], \\ \left[ \begin{array}{c} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t} \\ 0, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, 0, 0, \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0, 0 \end{array} \right], \end{bmatrix} \tag{5.25}$$

$$\begin{aligned}
& \left[ 0, 0, 0, \frac{\sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, 0, 0, \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{4\pi}, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi}, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, \frac{\sqrt{6} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{4\pi}, 0, 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{-2i\pi v_0 t}}{2\pi} \right], \\
& \left[ 0, 0, 0, 0, 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{2} \sqrt{\frac{h}{\mu v_0}} e^{2i\pi v_0 t}}{2\pi}, 0, 0 \right]
\end{aligned}$$

**> 'Q' = sqrt(h/(mu\*nu[0]))/(2\*Pi)\*map(simplify, map(x -> x\*2\*  
Pi/sqrt(h/(mu\*nu[0])), rhs(%)));**

$$\begin{aligned}
Q = & \left( \frac{\sqrt{\frac{h}{\mu v_0}}}{2\pi} \right) \& * \left[ \left[ 0, 0, \frac{\sqrt{2} e^{-2i\pi v_0 t}}{2}, 0, 0, 0, 0, 0, 0, 0 \right], \right. \\
& \left[ 0, 0, 0, \frac{\sqrt{2} e^{-2i\pi v_0 t}}{2}, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ \frac{\sqrt{2} e^{2i\pi v_0 t}}{2}, 0, 0, 0, e^{-2i\pi v_0 t}, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, \frac{\sqrt{2} e^{2i\pi v_0 t}}{2}, 0, 0, 0, e^{-2i\pi v_0 t}, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, e^{2i\pi v_0 t}, 0, 0, 0, \frac{\sqrt{6} e^{-2i\pi v_0 t}}{2}, 0, 0, 0 \right], \\
& \left. \left[ 0, 0, 0, e^{2i\pi v_0 t}, 0, 0, 0, \frac{\sqrt{6} e^{-2i\pi v_0 t}}{2}, 0, 0 \right] \right]
\end{aligned} \tag{5.26}$$

$$\begin{bmatrix} 0, 0, 0, 0, \frac{\sqrt{6}}{2} e^{2I\pi v_0 t}, 0, 0, 0, \sqrt{2} e^{-2I\pi v_0 t}, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, \frac{\sqrt{6}}{2} e^{2I\pi v_0 t}, 0, 0, 0, \sqrt{2} e^{-2I\pi v_0 t} \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, \sqrt{2} e^{2I\pi v_0 t}, 0, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, \sqrt{2} e^{2I\pi v_0 t}, 0, 0 \end{bmatrix}$$

According to the latter manipulation and recalling that the rows and columns of matrix **Q** number from

zero, the numerical coefficients of  $\frac{\sqrt{\frac{h}{\mu v_0}} e^{-2\pi I v_0 t}}{2\pi}$  in  $q_{n, n+2}$  along the superdiagonal in matrix **Q**

increase with  $n$  as  $\sqrt{\frac{n+1}{2}}$  for  $n$  even and  $\sqrt{\frac{n}{2}}$  for  $n$  odd; the numerical coefficients of

$\frac{\sqrt{\frac{h}{\mu v_0}} e^{2\pi I v_0 t}}{2\pi}$  in  $q_{n, n-2}$  along the subdiagonal in matrix **Q** are correspondingly  $\sqrt{\frac{n-1}{2}}$

for  $n$  even and  $\sqrt{\frac{n-2}{2}}$  for  $n$  odd. We display the submatrix of energy for which the truncated matrices for **P** and **Q** are valid.

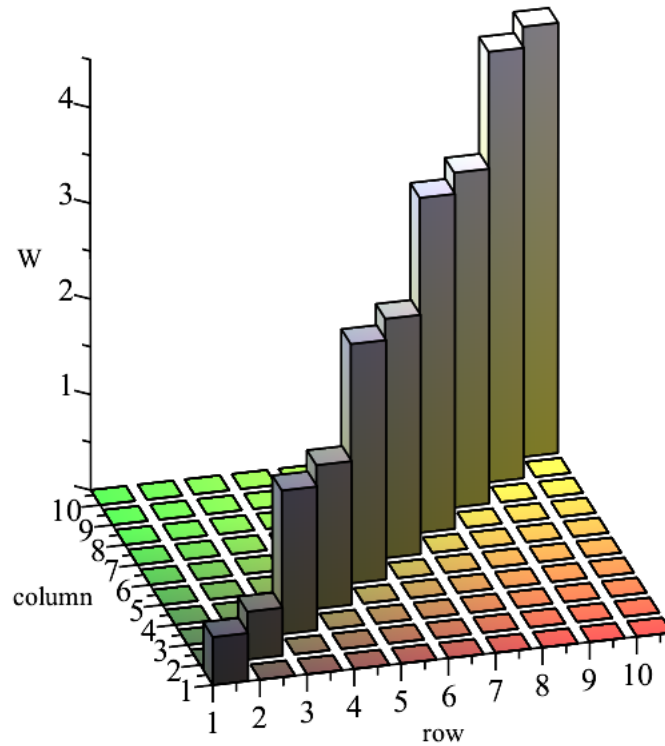
```
> 'W' = map(eval, SubMatrix(W, [1..dim-1],[1..dim-1]));
```

$$W = \begin{bmatrix} \frac{h v_0}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{h v_0}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{3 h v_0}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{3 h v_0}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{5 h v_0}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{5 h v_0}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{7 h v_0}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{7 h v_0}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{9 h v_0}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{9 h v_0}{2} \end{bmatrix} \quad (5.27)$$

A plot of this energy matrix shows this simple form.

```
> plots[matrixplot](rhs(%)/(h*nu[0]), axes=frame, titlefont=[TIMES,
BOLD,14],
    title="form of energy matrix", gap=1/4, heights=histogram,
    orientation=[-105,65], labels=["row","column","W"]);
```

### form of energy matrix



Rotate this plot to show that for each value of energy two adjacent states have an equal amount; this property is described as degeneracy, such that two quantum states have the same energy and properties that are identical apart from the choice or numbering of subscripts. For this choice  $k=2$ , the state of least energy with  $n=0$  or  $n=1$  has still

$$E_0 = W_{0,0} = \frac{h \nu_0}{2}$$

and the separation of energy between states of adjacent disparate energy is still  $h \nu_0$ , but two each adjacent states share a common energy. Transitions according to an electric dipolar moment are, however, still possible only between states of adjacent energies, so from  $n=2$  to either  $n=0$  in emission or  $n=4$  in absorption, or from  $n=3$  to either  $n=1$  in emission or  $n=5$  in absorption, and so forth.

The fact that matrices  $\mathbf{P}$  and  $\mathbf{Q}$  fail to commute results from the discreteness of the states, according to the numbering of their rows and columns. Empirical evidence, such as the discrete lines in optical spectra, require the development of a mechanics that treats discrete states; non-commuting matrices have precisely the required mathematical feature to incorporate this discreteness into mechanics. The

commutator  $\mathbf{P} \mathbf{Q} - \mathbf{Q} \mathbf{P} = -\frac{i h}{2 \pi} \mathbf{E}$ , in which  $\mathbf{E}$  denotes a unit matrix, is consistent with the difference of

the action integral,  $\int p dq = n h$ , between two successive states being invariably  $h$ ; that action integral through one period of a motion is thereby quantized to the unit of Planck's constant  $h$  except for an additive constant. Setting that constant equal to zero generates the quantum conditions of Bohr and



Sommerfeld; for the canonical linear harmonic oscillator as solved above, the additive constant is  $\frac{1}{2} h$ . The physical meaning of the non-commutativity of the matrices is the quantization of the physical states.

### e1.21 exercise

Apply the procedure in section 1.22 for  $k = n - m = 3$ , to show that three adjacent states share a common energy, but transitions are possible only between states with adjacent and unlike energies.

### e1.22 exercise

Given a real operator  $A$  satisfying this quadratic equation of least order,

$$A^2 - 3A + 2 = 0$$

find eigenvalues and eigenvectors of  $A$  and show that  $A$  corresponds to an observable property.

### 1.23 canonical linear harmonic oscillator according to wave mechanics

> restart:

A fundamental postulate of quantum mechanics, arising from the correspondence principle, is that each classical dynamical variable that relates to the motion of a particle, whether free or otherwise, is representable with a linear operator. Operator  $A$  is linear if, for functions  $f$  and  $g$  and scalar  $c$ ,

$$A(f+g) = Af + Ag \quad \text{and} \quad A(c f) = c A f.$$

Examples of such operators are [multiplicative](#) operators such as 3 or differential operators such as  $\frac{\partial}{\partial x}$ .

An operator that represents a physical observable must be [hermitian](#) so that its [eigenvalues](#) and [expectation values](#) are real. The observable properties of a quantum system are functions of the position observables,  $q$ , and the momentum observables,  $p$ . According to wave mechanics, a physical quantity might be represented with a differential operator; to every observable there corresponds an operator, which might be an ordinary scalar or vectorial quantity. To conform to the fundamental postulate of quantum mechanics for a single particle in one dimension with assumed cartesian coordinates, known as Heisenberg's commutation relation,

$$p q - q p = - \frac{i h}{2 \pi} ,$$

we select either  $p$  or  $q$  to be a differential operator and the other corresponding quantity to remain just an ordinary algebraic quantity. For the momentum representation we choose

$$q \rightarrow i \frac{h \left( \frac{\partial}{\partial p} \right)}{2 \pi}$$

and  $p$  remains an algebraic quantity; for the coordinate representation we alternatively choose

$$p \rightarrow -i \frac{h \left( \frac{\partial}{\partial q} \right)}{2 \pi}$$

and  $q$  remains an algebraic quantity. In either case, this formula for the commutator,

$$[p, q] = p q - q p$$

holds if we provide an operand for either differential operator  $\frac{\partial}{\partial p}$  or  $\frac{\partial}{\partial q}$ ; this operand,  $\chi(p)$  or  $\psi(q)$

respectively, is called an amplitude function.  $\chi(p)$  is only indirectly a Fourier transform of  $\psi(q)$ , and vice versa, and specifically in cartesian coordinates, as we demonstrate below -- in other coordinate

systems, an alternative transformation is applicable; all information within  $\psi(q)$  is thus likewise within  $\chi(p)$ , and both represent merely the content of a hamiltonian that enables their calculation. The general operand  $\Psi(q, t)$  as a wave function must be subject to not only a spatial derivative, such as  $\frac{\partial}{\partial q}$ , but also a temporal derivative,  $\frac{\partial}{\partial t}$ . With the temporal dimension there is an associated differential operator:

$$\frac{i h}{2 \pi} \frac{\partial}{\partial t}$$

In what follows we examine the properties of operands without temporal dependence; although we introduce these properties here before our first calculation according to wave mechanics that involves the canonical linear harmonic oscillator, they are absolutely general: their scope is in no way limited to this particular application or system.

In multiple dimensions with (cartesian) components  $q_j, p_j$ , the corresponding commutators become [  $q_j, q_k] = 0, [p_j, p_k] = 0, [p_j, q_k] = -i \frac{h}{2 \pi} \delta_{j, k}$  in which  $\delta$  denotes the [Kronecker delta](#) function:  $\delta = 1$  when  $j = k$  and 0 otherwise.

As a mathematical function, within wave mechanics, that serves as an operand of differential operators, an amplitude function  $\psi(q)$  or wave function  $\psi(q, t)$  in a coordinate representation in one spatial dimension, or equivalently  $\chi(p)$  in a momentum representation equivalent to one spatial dimension, in either case generally including a temporal dependence, must conform to these technical properties [E. C. Kemble, *The Fundamental Principles of Quantum Mechanics*, McGraw-Hill, New York USA, 1937], expressed in terms of  $\psi(q)$ :

- the physical state of a particle is described as fully as practicable with complex wave function  $\psi(q, t)$ , but that function merely reflects the content of a hamiltonian, or other, operator according to which that function might be defined or evaluated;
- that wave function  $\psi(q, t)$  and at least its first spatial derivative,  $\frac{\partial}{\partial q} \psi(q, t)$ , must be continuous and remain finite for all values of  $q$ , except at an infinite discontinuity in potential energy  $V(q)$ ; in the latter case,  $\psi(q)$  must be analytic at each point at which  $V(q)$  is analytic; only  $|\psi(q, t)|^2$  must be singly valued;
- for bound states, amplitude function  $\psi(q)$  and all its derivatives must tend to zero more rapidly than  $q$  to any negative power; the theory of distributions is required for elements of the continuous spectrum;
- amplitude function  $\psi(q)$  and all its derivatives must be absolutely and quadratically convergent for all  $q$ , and for continuous functions they must be square integrable on any finite interval;
- amplitude function  $\psi(q)$  must be associated with a continuous flux of probability  $\psi(q)^2$ , and this flux must be continuous across any boundary on which  $V(q)$  be continuous;
- amplitude function  $\psi(q)$  must satisfy a condition that it must admit orthonormal -- i.e. orthogonal and normalised -- eigenfunctions in a complete set, which are required to establish that the series of expansion of terms involving terms such as  $H^n \psi(q)$  have a meaning well defined;

- a quantity that is physically observable is represented with an hermitian operator  $F$  that is linear; such an hermitian operator satisfies a condition  $\int \psi(q)_1^* F \psi(q)_2 dq = \int \psi(q)_2 (F \psi(q)_1)^* dq$ , in which  $\psi(q)^*$  denotes a complex conjugate according to which  $i = \sqrt{-1}$  in  $\psi(q)$  becomes replaced in  $\psi(q)^*$  with  $-i$  anywhere that it occurs in  $\psi(q)$ ;
- the possible result of an observation of physically observable quantity  $F$  represented with linear hermitian operator  $F$  is any eigenvalue  $f_j$  of  $F$ , for which  $F \psi(q)_j = f_j \psi(q)_j$ ; if  $\psi(q)_j$  be an eigenfunction of  $F$ , a measurement of  $F$  certainly yields a value  $f_j$ ;
- an average or expectation value  $\langle F \rangle$  of any physically observable quantity  $F$  that corresponds to an operator  $F$  is calculated with  $\langle F \rangle = \int_{-\infty}^{\infty} \psi(q)^* F \psi(q) dq$ ; use of this formula is practical only if  $\psi(q)$  be normalised, such that  $\int_{-\infty}^{\infty} \psi(q)^* \psi(q) dq = 1$ ; such normalisation enables  $\psi(q)$  to be interpreted as a probability amplitude such that a particle with which that amplitude function is associated is certain to be found somewhere; otherwise, for unnormalised  $\psi(q)$ ,  $\langle F \rangle = \int_{-\infty}^{\infty} \psi(q)^* F \psi(q) dq / \int_{-\infty}^{\infty} \psi(q)^* \psi(q) dq$ ; in the latter most general form to calculate an average or expectation value, if  $\psi(q)$  be normalised, the denominator is unity; such an expectation value is the expected mean of measurements in a sequence on the observable quantity;
- depending on whether one employs the coordinate or the momentum representation of wave mechanics, involving either  $p$  or  $q$  as a differential operator respectively, and any functional thereof, becomes a differential operator; for a amplitude function with a temporal dependence, the operator corresponding to energy  $E$  is  $\frac{i h}{2 \pi} \frac{\partial}{\partial t}$ ;
- wave function  $\Psi(q, t)$  dependent on both spatial and temporal variables is a solution of Schroedinger's equation dependent on time,  $H(q, t) \Psi(q, t) = \frac{i h}{2 \pi} \frac{\partial}{\partial t} \Psi(q, t)$ , in which

$H(q, t)$  denotes an hamiltonian operator; this operator is derived from a classical hamiltonian expressed in cartesian coordinates according to the correspondences between quantities and operators appropriate to wave mechanics in a particular representation, either coordinate or momentum; for a particle subject to a field of only conservative forces, the classical hamiltonian is simply a sum of kinetic and potential energies, which is inapplicable to an electrically charged particle in a magnetic field for instance. If one assume the validity of this Schroedinger equation, the allowed values of energy and angular momentum and the wave functions all arise from its solution.

For either the coordinate representation or the momentum representation in a cartesian system, extension to three spatial dimensions is obvious. If a particle to be treated according to wave mechanics be other than a boson with no intrinsic angular momentum, further properties of that amplitude function or wave function are applicable.

In one dimension, Schroedinger's equation dependent on spatial,  $q$ , and temporal,  $t$ , variables is hence

$$\frac{i h \left( \frac{\partial}{\partial t} \Psi(q, t) \right)}{2 \pi} = - \frac{h^2 \left( \frac{\partial^2}{\partial q^2} \Psi(q, t) \right)}{8 \pi^2 \mu} + V(q) \Psi(q, t)$$

Whereas the kinetic energy is expressed classically as  $\frac{p^2}{2m}$ , when  $p$  becomes an operator  $-i \frac{h}{2\pi}$

$\frac{\partial}{\partial q}$  according to the basis of wave mechanics, this operator operates twice to produce  $-\frac{h^2}{4\pi^2} \frac{\partial^2}{\partial q^2}$  rather than involving the square of a first derivative. The presence of a first derivative

in time but second derivative in spatial coordinate imposes that this equation is relativistically incorrect. If  $V(q)$  be independent of time, these variables become separable so that we express wave function  $\Psi(q, t)$  as a product of an amplitude functions and temporal function.

$$\Psi(q, t) = \psi(q) \tau(t)$$

Substituting that product into the above equation and dividing by  $\Psi(q, t)$  yields

$$\frac{i h \left( \frac{d}{dt} \tau(t) \right)}{2 \pi \tau(t)} = - \frac{h^2 \left( \frac{d^2}{dq^2} \psi(q) \right)}{8 \pi^2 \mu \psi(q)} + V(q)$$

This equation implies that each side is equal to a constant, which we denote  $W$ , and which has the dimensions of energy. The differential equation on the left side is

$$\frac{i h \left( \frac{d}{dt} \tau(t) \right)}{2 \pi \tau(t)} = W$$

which has as its solution

$$\tau(t) = e^{-\frac{i \cdot 2 \pi W t}{h}}$$

because  $\overline{\tau(t)} \tau(t) = 1$  as the electron must be found somewhere at any time;  $\overline{\tau(t)}$  is the complex conjugate of  $\tau(t)$  in which  $i$  is replaced with  $-i$ . The solution of the differential equation on the right side,

$$-\frac{h^2 \left( \frac{d^2}{dq^2} \psi(q) \right)}{8 \pi^2 \mu \psi(q)} + V(q) = W$$

or

$$-\frac{h^2 \left( \frac{d^2}{dq^2} \psi(q) \right)}{8 \pi^2 \mu} + V(q) \psi(q) = W \psi(q)$$

depends on the nature of the potential energy; for a canonical linear harmonic oscillator,  $V(q) = \frac{1}{2}$

$k q^2$ . We proceed to solve the radial equation with this potential energy.

According to wave mechanics, the energies of a system in a stationary state are solutions of Schroedinger's equation independent of time. For such a system, the coordinate representation is generally preferable to the momentum representation because the potential energy is generally expressed

more readily in terms of a coordinate than a momentum; we solve the system in momentum space below our solution in coordinate space. Wave function  $\Psi(q, t)$  might contain a phase factor  $e^{i\alpha}$ , which for a system of charged particles implies the conservation of electric charge.

For the canonical linear harmonic oscillator, the function for potential energy is hence expressed as a quadratic dependence on displacement variable  $q$ ,

$$V(q) = \frac{k q^2}{2} .$$

The hamiltonian  $H(q)$  corresponding to the total energy of the system is thus a sum of kinetic,  $T(q)$ , and potential,  $V(q)$ , energies,

$$H(q) = T(q) + V(q) = \frac{p^2}{2 \mu} + \frac{k q^2}{2}$$

into which we substitute for momentum this differential operator according to the coordinate

representation,  $p \rightarrow -i \frac{h}{2 \pi} \left( \frac{\partial}{\partial q} \right)$ ; for a particle of effective mass  $\mu$  subjected to a displacement  $q$ , the operator for kinetic energy in one dimension is accordingly expressed as

$$T(q) = - \frac{h^2 \left( \frac{\partial^2}{\partial q^2} \right)}{8 \pi^2 \mu} ,$$

and the hamiltonian, dependent on coordinate  $q$  but independent of time, becomes

$$H(q) = - \frac{h^2 \left( \frac{\partial^2}{\partial q^2} \right)}{8 \pi^2 \mu} + \frac{k q^2}{2} .$$

Note that this expression contains a second derivative,  $\frac{\partial^2}{\partial q^2}$ , rather than a first derivative squared,

$\left( \frac{\partial}{\partial q} \right)^2$ , that one might, incorrectly, expect from the analogy with the classical expression,  $\frac{p^2}{2 \mu}$ , as explained above. As only differences in potential energy matter physically, we choose the zero of the energy scale at  $q = 0$ . Energies  $W_n$  of the system are evaluated from the solutions to Schroedinger's equation incorporating this hamiltonian operator that operates on amplitude function  $\psi(q)$  as its operand,

$$H(q) \psi(q) = W \psi(q) ,$$

or

$$- \frac{h^2 \left( \frac{\partial^2}{\partial q^2} \right)}{8 \pi^2 \mu} \psi(q) + \frac{k q^2 \psi(q)}{2} = W \psi(q)$$

to yield

$$H(q) \psi_n(q) = W_n \psi_n(q) .$$

The latter relation has the form of an eigenvalue equation with  $W_n$  as that scalar proper value of eigenvalue that corresponds to a particular solution  $\psi_n(q)$  as proper function or eigenfunction and that is

independent of variable  $q$ ; quantities  $\psi_n(q)$  called amplitude functions serve accordingly as eigenfunctions or eigenvectors.

```
> with(DEtools):
  with(plots):
  with(PDEtools, declare):
  declare(psi(q), prime=q);
  assume(k > 0, mu > 0, h > 0, W > 0);
```

$\psi(q)$  will now be displayed as  $\psi$

derivatives with respect to  $q$  of functions of one variable will now be displayed with ' (8.1)

Having set assumptions on the sign of pertinent quantities, we state the resulting differential equation.

```
> ode := - h^2/(8*Pi^2*mu)*diff(psi(q), q$2) + 1/2*k*q^2*psi(q) = W*
  psi(q);
```

$$ode := -\frac{h^2}{8\pi^2\mu}(\psi'') + \frac{kq^2}{2}\psi = W\psi \quad (8.2)$$

What kind is this differential equation?

```
> odeadvisor(ode);
[[_2nd_order, _with_linear_symmetries]] (8.3)
```

This differential equation is of second order, and linear because there is no constant term that is not a factor of  $\psi(q)$ . We proceed to solve the full equation.

```
> sol := dsolve(ode, psi(q));
```

$$sol := \psi = \frac{{}_C1 \text{ WhittakerM}\left(\frac{\pi\sqrt{\mu} W}{h\sqrt{k}}, \frac{1}{4}, \frac{2\pi\sqrt{k}\sqrt{\mu} q^2}{h}\right)}{\sqrt{q}} + \frac{{}_C2 \text{ WhittakerW}\left(\frac{\pi\sqrt{\mu} W}{h\sqrt{k}}, \frac{1}{4}, \frac{2\pi\sqrt{k}\sqrt{\mu} q^2}{h}\right)}{\sqrt{q}} \quad (8.4)$$

This solution is presented in Whittaker functions because Schroedinger's equation in this coordinate has the form of Whittaker's differential equation, which is one standard differential equation in applied mathematics and its physical applications. Is this expression that contains two independent parts that arise from the solution of a differential equation of second order in derivatives, containing integration constant either  ${}_C1$  or  ${}_C2$ , a true solution? We test it.

```
> test := odetest(sol, ode);
test := 0 (8.5)
```

For any solution of Schroedinger's equation to be acceptable, the amplitude function  $\rightarrow 0$  as  $q \rightarrow \infty$  or  $q \rightarrow -\infty$ , to conform to the properties stipulated above. For these Whittaker functions, the applicable condition to enforce that asymptotic behaviour that  $\psi(q) \rightarrow 0$  as  $q \rightarrow \infty$  or  $q \rightarrow -\infty$  is that the difference of the first argument and the second argument must take non-negative half-integer values, so that the polynomial in  $q$  terminates at a particular power consistent with the quadratic convergence of the

amplitude function. We extract first the Whittaker functions,

```
> op(rhs(sol));
```

$$\frac{-C1 \text{ WhittakerM}\left(\frac{\pi \sqrt{\mu} W}{h \sqrt{k}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} q^2}{h}\right)}{\sqrt{q}}, \quad (8.6)$$

$$\frac{-C2 \text{ WhittakerW}\left(\frac{\pi \sqrt{\mu} W}{h \sqrt{k}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} q^2}{h}\right)}{\sqrt{q}}$$

then their first and second arguments,

```
> op(1, op(3, op(2, [op(rhs(sol))])), op(2, op(3, op(2, [op(rhs(sol))]))));
```

$$\frac{\pi \sqrt{\mu} W}{h \sqrt{k}}, \frac{1}{4} \quad (8.7)$$

of which we set their difference equal to a half integer, and solve for  $W$ ,

```
> W1 := solve(op(1, op(3, op(2, [op(rhs(sol))])), op(2, op(3, op(2, [op(rhs(sol))]))))=n/2, W);
Warning, solve may be ignoring assumptions on the input variables.
```

$$W1 := \frac{h \sqrt{k} (2n + 1)}{4 \pi \sqrt{\mu}} \quad (8.8)$$

which we substitute into the expressions for the amplitude function.

```
> sol := eval(sol, W=W1);
```

$$\text{sol} := \psi = \frac{-C1 \text{ WhittakerM}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} q^2}{h}\right)}{\sqrt{q}} \quad (8.9)$$

$$+ \frac{-C2 \text{ WhittakerW}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} q^2}{h}\right)}{\sqrt{q}}$$

This imposition of half-integer values of quantum number  $n$  generates the discrete energy associated with each amplitude function, which we associate with discrete values in the [spectrum](#) of this oscillator.

We separate the two contributions to this solution,

```
> psi1 := remove(has, rhs(sol), WhittakerW);
```

$$\psi1 := \frac{-C1 \text{ WhittakerM}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} q^2}{h}\right)}{\sqrt{q}} \quad (8.10)$$

```
> psi2 := remove(has, rhs(sol), WhittakerM);
```

$$\psi_2 := \frac{-C_2 \text{WhittakerW}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2\pi\sqrt{k}\sqrt{\mu}q^2}{h}\right)}{\sqrt{q}} \quad (8.11)$$

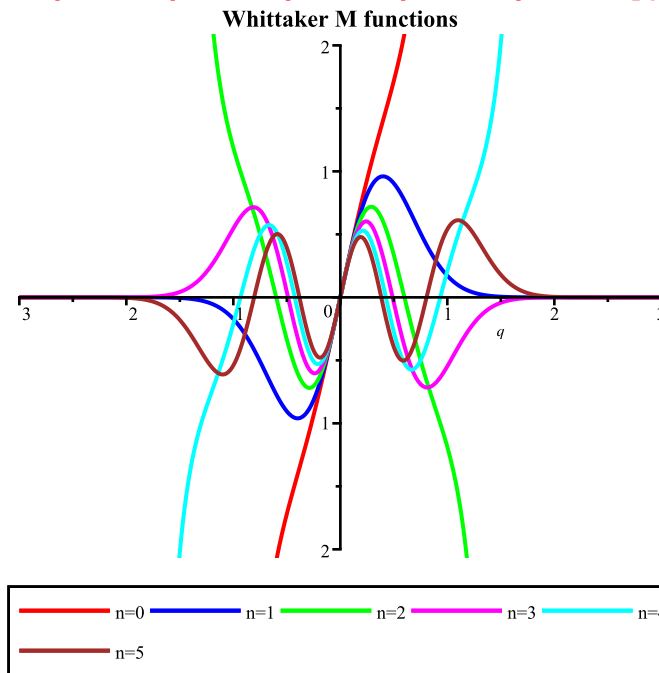
simplify them,

```
> for j from 0 to 16 do
  psi3[j] := simplify(eval(psi1, n=j), symbolic);
end do;
> for j from 0 to 16 do
  psi4[j] := simplify(eval(psi2, n=j), symbolic);
end do;
```

and plot them.

```
> plot([seq(eval(psi3[j], [_C1=1,h=1,mu=1,k=1,W=1]), j=0..5)],
  q=-3..3, -2..2, numpoints=500, title="Whittaker M functions",

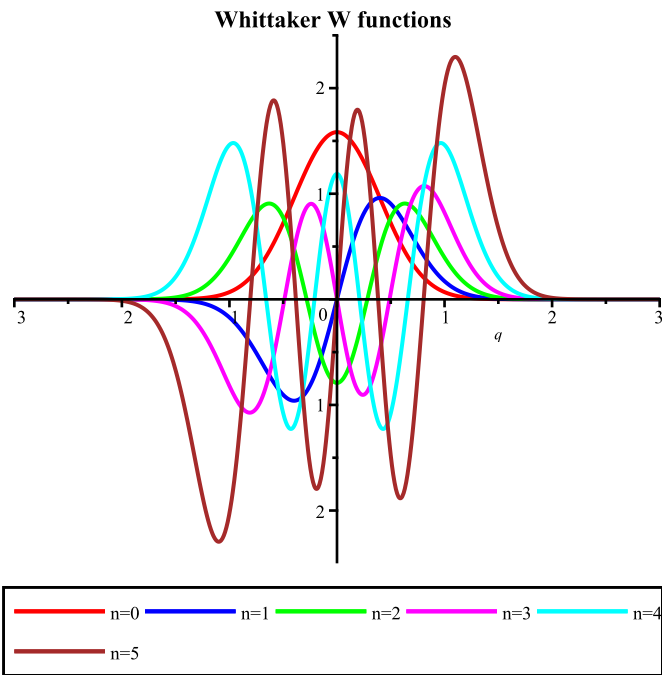
  titlefont=[TIMES,BOLD,14], colour=[red,blue,green,magenta,
  cyan,brown],
  legend=["n=0","n=1","n=2","n=3","n=4","n=5"]);
```



```
> plot([seq(eval(psi4[j], [_C2=1,h=1,mu=1,k=1,W=1]), j=0..5)],
  q=-3..3, -2.5..2.5, numpoints=500, title="Whittaker W
  functions",

  titlefont=[TIMES,BOLD,14], colour=[red,blue,green,magenta,
  cyan,brown],
  legend=["n=0","n=1","n=2","n=3","n=4","n=5"]);
```





As the contributions containing Whittaker M functions diverge for even values of index  $n$ , we discard these contributions. We retain the other, Whittaker W, contributions and convert them into arrow functions.

$$\psi := (n, q) \mapsto \psi_n^4 \quad (8.12)$$

These Whittaker functions are entirely real -- no quantity  $\sqrt{-1}$  appears within them. With  $\psi_n(q) = \overline{\psi_n(q)}$  so that each amplitude function is identical with its complex conjugate,

$$\int_{-\infty}^{\infty} \overline{\Psi_n(q)} \Psi_n(q) \, dq = \int_{-\infty}^{\infty} \Psi_n(q)^2 \, dq,$$

we thus integrate the squares of the first six amplitude functions  $\Psi_n(q)$ , expressed in  $\Psi(n, q)$  with  $n = 0 \dots 5$ , throughout all space in one dimension; we divide by a common factor  $C2^2$  to clarify the remaining expressions.

```
> Int(psi(n,q)^2/_C2^2, q=-infinity..infinity)
    = seq(simplify(int(psi(n,q)^2/_C2^2, q=-infinity..infinity)),
          n=0..7);
```

$$\int_{-\infty}^{\infty} \frac{\psi_n^2}{C2^2} dq = \left( \sqrt{\pi}, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2}, \frac{3\sqrt{\pi}}{4}, \frac{3\sqrt{\pi}}{2}, \frac{15\sqrt{\pi}}{4}, \frac{45\sqrt{\pi}}{4}, \frac{315\sqrt{\pi}}{8} \right) \quad (8.13)$$

By inspection and induction, we find that these quantities have the form  $\frac{n! \sqrt{\pi}}{\gamma^n}$ .

```
> 'seq'(n!*sqrt(Pi)/2^n, n=0..5) = seq(n!*sqrt(Pi)/2^n, n=0..7);
```

**(8.14)**

$$seq\left(\frac{n! \sqrt{\pi}}{2^n}, n=0..5\right) = \left(\sqrt{\pi}, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2}, \frac{3\sqrt{\pi}}{4}, \frac{3\sqrt{\pi}}{2}, \frac{15\sqrt{\pi}}{4}, \frac{45\sqrt{\pi}}{4}, \frac{315\sqrt{\pi}}{8}\right) \quad (8.14)$$

For the normalisation of these amplitude functions, constant  $\_C2$  of integration must be set equal to the inverse square root of these quantities.

>  $\_C2 := \text{sqrt}(2^n/(n!*\text{sqrt}(\text{Pi})))$ ;

$$\_C2 := \sqrt{\frac{2^n}{n! \sqrt{\pi}}} \quad (8.15)$$

To incorporate this result we evaluate  $\psi_n(q)$ .

```
> for j from 0 to 12 do
  psi(j,q) := eval(psi(j,q), n=j);
end do;
for j from 0 to 5 do
  psi(j,q) := eval(psi(j,q), n=j);
end do;
```

$$\psi(0, q) := \frac{2^{1/4} k^{1/8} \mu^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{1/4}}$$

$$\psi(1, q) := \frac{2^{1/4} \sqrt{\pi} q k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{3/4}}$$

$$\psi(2, q) := \frac{2 \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{h}{4} \right) 2^{3/4} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{5/4}}$$

$$\psi(3, q) := \frac{2 q 2^{3/4} \sqrt{4} \sqrt{3} \sqrt{\pi} \mu^{3/8} \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{3 h}{4} \right) k^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{3 h^{7/4}}$$

$\psi(4, q) :=$

$$\frac{4 \left( \pi^2 k \mu q^4 - \frac{3 h \pi \sqrt{k} \sqrt{\mu} q^2}{2} + \frac{3 h^2}{16} \right) 2^{3/4} \sqrt{3} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{3 h^{9/4}}$$

$$\psi(5, q) := \frac{1}{15 h^{11/4}} \left( 4 \left( \pi^2 k \mu q^4 - \frac{5 h \pi \sqrt{k} \sqrt{\mu} q^2}{2} \right) \right) \quad (8.16)$$

$$+ \frac{15 \hbar^2}{16} \left) q^{2^{3/4}} \sqrt{4} \sqrt{15} \sqrt{\pi} k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{\hbar}} \right)$$

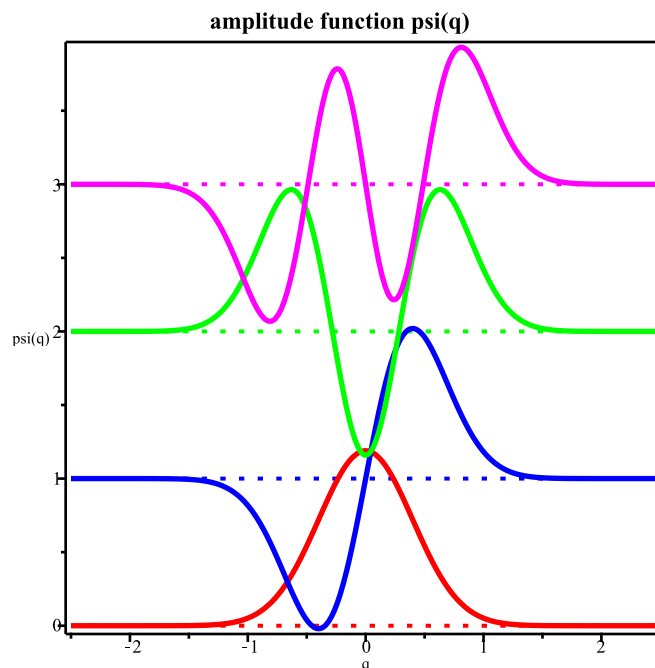
We test the validity of our normalisation over a range greater than that within which we deduced the form of the normalising factor.

```
> Int(psi(n,q)^2, q=-infinity..infinity) = seq(simplify(int(psi(n,q)
^2, q=-infinity..infinity)), n=0..10);
```

$$\int_{-\infty}^{\infty} \psi_n^2 dq = (1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1) \quad (8.17)$$

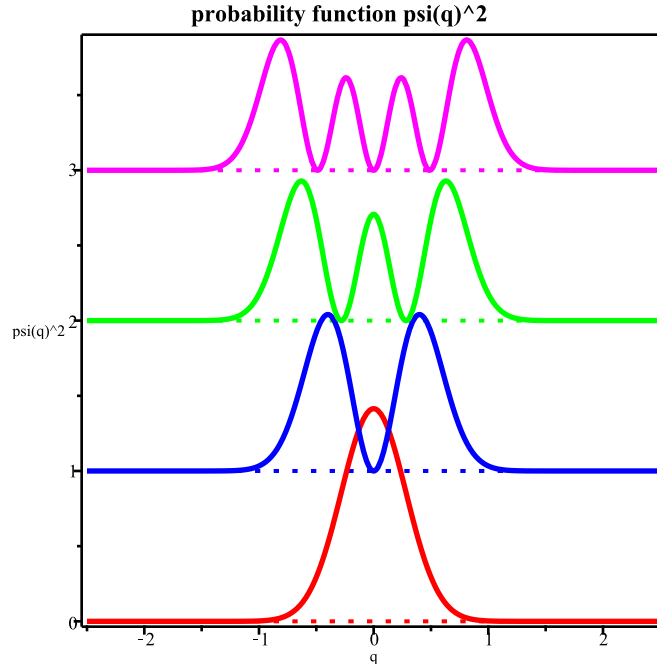
As these values are all unity, we verify that our derivation is correct. As these amplitude functions are normalised according to  $\int_{-\infty}^{\infty} \psi(q) \psi(q) dq = 1$ , one regards, following Born (1927),  $\psi(q) \psi(q) dq$  as a probability of a particular displacement between  $q$  and  $q + dq$ , as the value of the normalising integral then yields the total probability of a displacement somewhere as unity. Such an interpretation involving probability is consistent with the principle of indeterminacy. Displacing the functions one unit vertically for clarity, we plot  $\psi_n(q)$  for small values of  $n$ ; for the purpose of these plots, we take  $\hbar = k = \mu = 1$ , but such values act merely as scale factors.

```
> p1 := plot([0,1,2,3],-2.5..2.5, colour=[red,blue,green,magenta],
linestyle=[2,2,2,2]):
p2 := plot([seq(simplify(eval(psi(n,q)+n, [mu=1,k=1,h=1])),
n=0..3)], q=-2.5..2.5, thickness=[2,2,2,2],
colour=[red,blue,green,magenta]):
display([p1,p2], axes=BOXED, labels=["q","psi(q)"],
title="amplitude function psi(q)", titlefont=[TIMES,BOLD,14]
);
```



We plot also the squares of these amplitude functions.

```
> p3 := plot([0,1,2,3], -2.5..2.5, colour=[red,blue,green,magenta],
             linestyle=[2,2,2,2]):
p4 := plot([seq(simplify(eval(psi(n,q)^2+n, [mu=1,k=1,h=1])),
             n=0..3)], q=-2.5..2.5, thickness=[2,2,2,2],
             colour=[red,blue,green,magenta]):
display([p3,p4], axes=BOXED, labels=["q","psi(q)^2"],
        title="probability function psi(q)^2",
        titlefont=[TIMES,BOLD,14]);
```



We examine the forms of  $\psi_0(q)$ ,

```
> 'psi'[0]*^(q)^ = psi(0,q);
```

$$\psi_0(q) = \frac{2^{1/4} k^{1/8} \mu^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{1/4}} \quad (8.18)$$

$\psi_1(q)$ ,

```
> 'psi'[1]*^(q)^ = psi(1,q);
```

$$\psi_1(q) = \frac{2^{1/4} \sqrt{\pi} q k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{3/4}} \quad (8.19)$$

$\psi_2(q)$ ,

```
> 'psi'[2]*^(q)^ = psi(2,q);
```

$$\psi_2(q) = \frac{2 \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{h}{4} \right) 2^{3/4} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{5/4}} \quad (8.20)$$

and  $\psi_3(q)$ .

```
> 'psi'[3]*^(q) = factor(psi(3,q));
```

$$\psi_3(q) = \frac{q 2^{3/4} \sqrt{4} \sqrt{3} \sqrt{\pi} \mu^{3/8} \left( 4 \pi \sqrt{k} \sqrt{\mu} q^2 - 3 h \right) k^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{6 h^{7/4}} \quad (8.21)$$

We observe that, apart from numerical and physical constants and parameters, these amplitude functions comprise an exponential factor of gaussian type and a coordinate  $q$  in a finite series with terms in alternating even or odd positive powers up to  $q^n$ ; the latter terminating series is a further consequence of the choice of a half integer value of the difference between the first and second arguments of the Whittaker functions. If, instead of using Whittaker functions above, we convert to Hermite functions, we find them to have a common factor comprising a gaussian function, of form  $e^{-q^2}$ , which arises also in the asymptotic expansion above; we then require that the first argument of these Hermite functions be a non-negative integer so that each function becomes a polynomial of finite order of the same non-negative integer. For the resulting amplitude functions in terms of Hermite polynomials, we obtain exactly the same plots of  $\psi_n(q)$  and  $\psi_n(q)^2$  as above.

Are these amplitude functions orthogonal? We integrate their product over all space in one dimension.

```
> Int('psi(1,q)''psi(0,q)', q=-infinity..infinity)
= int(psi(1,q)*psi(0,q), q=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(1, q) \psi(0, q) dq = 0 \quad (8.22)$$

```
> Int('psi(2,q)''psi(0,q)', q=-infinity..infinity)
= int(psi(2,q)*psi(0,q), q=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(2, q) \psi(0, q) dq = 0 \quad (8.23)$$

```
> Int('psi(3,q)''psi(0,q)', q=-infinity..infinity)
= int(psi(3,q)*psi(0,q), q=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(3, q) \psi(0, q) dq = 0 \quad (8.24)$$

We test whether our amplitude functions are eigenfunctions of the hamiltonian operator, for which purpose we must ensure that the coordinate variable is the first argument; we hence define an amplitude function in a slightly altered form.

```
> for j from 1 to 5 do
  psi[q](q,j) := psi(j,q);
end do;
```

$$\Psi_q(q, 1) := \frac{2 \cdot 2^{1/4} \sqrt{\pi} q k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{3/4}}$$

$$\Psi_q(q, 2) := \frac{2 \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{h}{4} \right) 2^{3/4} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{h^{5/4}}$$

$$\Psi_q(q, 3) := \frac{2 q 2^{3/4} \sqrt{4} \sqrt{3} \sqrt{\pi} \mu^{3/8} \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{3 h}{4} \right) k^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{3 h^{7/4}}$$

$$\Psi_q(q, 4) :=$$

$$\frac{4 \left( \pi^2 k \mu q^4 - \frac{3 h \pi \sqrt{k} \sqrt{\mu} q^2}{2} + \frac{3 h^2}{16} \right) 2^{3/4} \sqrt{3} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}}}{3 h^{9/4}}$$

$$\Psi_q(q, 5) := \frac{1}{15 h^{11/4}} \left( 4 \left( \pi^2 k \mu q^4 - \frac{5 h \pi \sqrt{k} \sqrt{\mu} q^2}{2} \right. \right. \quad (8.25)$$

$$\left. \left. + \frac{15 h^2}{16} \right) q 2^{3/4} \sqrt{4} \sqrt{15} \sqrt{\pi} k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} \right)$$

We calculate  $\frac{H\Psi_q(q, j)}{\Psi_q(q, j)}$ ,

```
> j := 'j':
for j from 1 to 5 do
  simplify(collect((-h^2/(8*Pi^2*mu)*diff(psi[q](q,j),q$2)
    + 1/2*k*q^2*psi[q](q,j))/psi[q](q,j), mu), symbolic)
;
end do;
```

$$\frac{3 h \sqrt{k}}{4 \pi \sqrt{\mu}}$$

$$\frac{5 h \sqrt{k}}{4 \pi \sqrt{\mu}}$$

$$\frac{7 h \sqrt{k}}{4 \pi \sqrt{\mu}}$$

$$\frac{7 h \sqrt{k}}{4 \pi \sqrt{\mu}}$$

$$\frac{7 h \sqrt{k}}{4 \pi \sqrt{\mu}}$$

$$\frac{7 h \sqrt{k}}{4 \pi \sqrt{\mu}}$$

$$\frac{9 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}}, \frac{11 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}} \quad (8.26)$$

of which the results are clearly equal to the energies calculated above as  $W1$ .

**> seq(eval(W1, n=j), j=1..5);**

$$\frac{3 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}}, \frac{5 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}}, \frac{7 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}}, \frac{9 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}}, \frac{11 \hbar \sqrt{k}}{4 \pi \sqrt{\mu}} \quad (8.27)$$

Amplitude functions  $\psi_q(q, j)$  are thus eigenfunctions of the hamiltonian operator with eigenvalues  $(n + \frac{1}{2}) \frac{h}{2 \pi} \sqrt{\frac{k}{\mu}}$ . We undertake an analogous test for momentum operator  $p \rightarrow -i \frac{h}{2 \pi} \frac{\partial}{\partial q}$ .

**> for j from 1 to 5 do**

**simplify(collect(-I\*h/(2\*Pi)\*diff(psi[q](q,j),q)/psi[q](q,j),  
mu), symbolic);**  
**end do;**

$$\begin{aligned} & \frac{\frac{1}{2} (2 \pi \sqrt{k} \sqrt{\mu} q^2 - \hbar)}{\pi q} \\ & \frac{I \sqrt{k} \sqrt{\mu} q (4 \pi \sqrt{k} \sqrt{\mu} q^2 - 5 \hbar)}{4 \pi \sqrt{k} \sqrt{\mu} q^2 - \hbar} \\ & - \frac{\frac{1}{2} (-8 \pi^2 k \mu q^4 + 18 \hbar \pi \sqrt{k} \sqrt{\mu} q^2 - 3 \hbar^2)}{\pi q (4 \pi \sqrt{k} \sqrt{\mu} q^2 - 3 \hbar)} \\ & \frac{I \sqrt{k} q \sqrt{\mu} (-16 \pi^2 k \mu q^4 + 56 \hbar \pi \sqrt{k} \sqrt{\mu} q^2 - 27 \hbar^2)}{-16 \pi^2 k \mu q^4 + 24 \hbar \pi \sqrt{k} \sqrt{\mu} q^2 - 3 \hbar^2} \\ & \frac{\frac{1}{32} (32 \pi^3 k^3 \mu^3 q^6 - 160 \pi^2 k \mu q^4 \hbar + 150 \hbar^2 \pi \sqrt{k} \sqrt{\mu} q^2 - 15 \hbar^3)}{q \left( \pi^2 k \mu q^4 - \frac{5 \hbar \pi \sqrt{k} \sqrt{\mu} q^2}{2} + \frac{15 \hbar^2}{16} \right) \pi} \quad (8.28) \end{aligned}$$

Apart from an alternating real and imaginary nature, these results contain a dependence on displacement variable  $q$ ; these amplitude functions are hence *not* eigenfunctions of the momentum operator.

In general, to evaluate an *expectation value* of some observable property  $O$  of a system with which is associated amplitude function  $\psi_j(x)$  involves this integral,

$$O_j = \int_{-\infty}^{\infty} \overline{\psi_j(x)} O \psi_j(x) dx$$

in which  $\overline{\psi_j(x)}$  denotes a complex conjugate of  $\psi_j(x)$ . For a *matrix element* of some property  $O$  involving two states, with which amplitude functions  $\psi_j(x)$  and  $\psi_k(x)$  are associated, the corresponding integral is

$$O_{j,k} = \int_{-\infty}^{\infty} \overline{\psi_j(x)} O \psi_k(x) dx$$

As a particular instance, we evaluate a matrix element of  $q$  between states with  $n=0$  and  $n=1$ , which we denote  $q_{1,0}$ , through an integral

$$q_{1,0} = \int_{-\infty}^{\infty} \overline{\psi_1(q)} q \psi_0(q) dq,$$

which is expressed as  $\langle 1 | q | 0 \rangle$  according to Dirac's notation introduced in section 1.24. In this integral for a real quantity  $q_{1,0}$ , we take the complex conjugate of  $\psi_1(q)$ , denoted  $\overline{\psi_1(q)}$  or  $\psi_1(q)^*$  and best formed as **subs(I = -I,  $\psi_1(q)$ )** rather than using **conjugate()**, but, because these amplitude functions of an harmonic oscillator as derived above have no imaginary part, this refinement is superfluous here.

```
> Int('psi(1,q)*q*psi(0,q)', q=-infinity..infinity) =
    simplify(int(psi(1,q)*q*psi(0,q), q=-infinity..infinity),
    symbolic);
```

$$\int_{-\infty}^{\infty} \psi(1, q) q \psi(0, q) dq = \frac{\sqrt{h}}{2 \sqrt{\pi} k^{1/4} \mu^{1/4}} \quad (8.29)$$

We evaluate matrix elements  $\langle n+1 | q | n \rangle$  for  $n$  in a sequence  $[0, 12]$ , suppressing the constant

symbolic factor  $\frac{\sqrt{h}}{\mu^{1/4} k^{1/4}}$  that appears in the preceding result,

```
> smef := sqrt(h)/(k^(1/4)*mu^(1/4)*sqrt(Pi));
sme := [seq(simplify(int(psi(n+1,q)*q*psi(n,q),
    q=-infinity..infinity),symbolic)/smef, n=0..11)];
```

$$smef := \frac{\sqrt{h}}{\sqrt{\pi} k^{1/4} \mu^{1/4}}$$

$$sme := \left[ \frac{1}{2}, \frac{\sqrt{2}}{2}, \frac{\sqrt{3}}{2}, 1, \frac{\sqrt{5}}{2}, \frac{\sqrt{6}}{2}, \frac{\sqrt{7}}{2}, \sqrt{2}, \frac{3}{2}, \frac{\sqrt{10}}{2}, \frac{\sqrt{11}}{2}, \sqrt{3} \right] \quad (8.30)$$

which has the form of this sequence of numerical coefficients of  $\frac{\sqrt{h}}{\mu^{1/4} k^{1/4}}$ .

```
> 'seq'(sqrt('n'+1)/2, n=0..12) = seq(sqrt(n+1)/2, n=0..11);
```

$$seq\left(\frac{\sqrt{n+1}}{2}, n=0..12\right) = \left(\frac{1}{2}, \frac{\sqrt{2}}{2}, \frac{\sqrt{3}}{2}, 1, \frac{\sqrt{5}}{2}, \frac{\sqrt{6}}{2}, \frac{\sqrt{7}}{2}, \sqrt{2}, \frac{3}{2}, \frac{\sqrt{10}}{2}, \frac{\sqrt{11}}{2}, \sqrt{3}\right), \quad (8.31)$$



$$\sqrt{3})$$

This result shows that the matrix elements increase with  $n$  according to  $\sqrt{\frac{n+1}{2}}$ .

We test matrix elements between the state with  $n = 0$  and other states up to  $n = 11$ .

```
> sme := [seq(simplify(int(psi(n+1,q)*q*psi(0,q),
q=-infinity..infinity),symbolic)/smef, n=0..11)];
```

$$sme := \left[ \frac{1}{2}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right] \quad (8.32)$$

These results indicate that matrix elements of  $q$  are not zero only if values of  $n$  differ by precisely one unit.

For the analogous quantity  $\langle 1 | \frac{1}{q} | 0 \rangle$ , we calculate the first integral,

```
> Int('psi(1,q)'*1/q*'psi(0,q)', q=-infinity..infinity) =
simplify(int(psi(1,q)*1/q*psi(0,q), q=-infinity..infinity),
symbolic);
```

$$\int_{-\infty}^{\infty} \frac{\Psi(1, q) \Psi(0, q)}{q} dq = \frac{2 \sqrt{\pi} k^{-1/4} \mu^{-1/4}}{\sqrt{h}} \quad (8.33)$$

and  $\langle n+1 | q^{-1} | n \rangle$  for  $n$  in the same sequence  $[0, 12]$ , suppressing the constant symbolic factor

$$\frac{\mu^{\frac{1}{4}} k^{\frac{1}{4}}}{\sqrt{h}},$$

```
> sme1 := [seq(simplify(int(psi(n+1,q)*1/q*psi(n,q),
q=-infinity..infinity),symbolic)/(mu^(1/4)*k^(1/4)*sqrt(Pi))*
sqrt(h), n=0..11)];
```

$$sme1 := \left[ 2, 0, \frac{2\sqrt{3}}{3}, 0, \frac{2\sqrt{5}}{5}, 0, \frac{2\sqrt{7}}{7}, 0, \frac{2}{3}, 0, \frac{2\sqrt{11}}{11}, 0 \right] \quad (8.34)$$

This sequence has a curious property of alternate members of the sequence having zero value, which we reproduce with this formula,  $\frac{1}{\sqrt{n+1}} (1 - (-1)^{n+1})$ .

```
> [seq(1/sqrt(n+1)*(1-(-1)^(n+1)), n=0..11)];
```

$$\left[ 2, 0, \frac{2\sqrt{3}}{3}, 0, \frac{2\sqrt{5}}{5}, 0, \frac{2\sqrt{7}}{7}, 0, \frac{2}{3}, 0, \frac{2\sqrt{11}}{11}, 0 \right] \quad (8.35)$$

We form a matrix with elements  $\langle n+1 | q | n \rangle / (\sqrt{h} \left( \frac{k}{\mu} \right)^{\frac{1}{4}})$ ,

```
> with(LinearAlgebra):
interface( rtablesize = 17 );
```

```

Mq := Matrix(16,16, shape=symmetric):
> for n from 0 to 14 do
  Mq[n+2,n+1] := simplify(int(psi(n+1,q)*q*psi(n,q),
    q=-infinity..infinity)/sqrt(h)*(mu^(1/4)*k^(1/4)),symbolic):
end do:
> Mq;

```

$$\begin{bmatrix}
 0, \frac{1}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \\
 \left[ \frac{1}{2\sqrt{\pi}}, 0, \frac{\sqrt{2}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, \frac{\sqrt{2}}{2\sqrt{\pi}}, 0, \frac{\sqrt{3}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, \frac{\sqrt{3}}{2\sqrt{\pi}}, 0, \frac{1}{\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, \frac{1}{\sqrt{\pi}}, 0, \frac{\sqrt{5}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, \frac{\sqrt{5}}{2\sqrt{\pi}}, 0, \frac{\sqrt{6}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, 0, \frac{\sqrt{6}}{2\sqrt{\pi}}, 0, \frac{\sqrt{7}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, 0, 0, \frac{\sqrt{7}}{2\sqrt{\pi}}, 0, \frac{\sqrt{2}}{\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{2}}{\sqrt{\pi}}, 0, \frac{3}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, 0, 0, 0, 0, \frac{3}{2\sqrt{\pi}}, 0, \frac{\sqrt{10}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{10}}{2\sqrt{\pi}}, 0, \frac{\sqrt{11}}{2\sqrt{\pi}}, 0, 0, 0, 0 \right], \\
 \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{11}}{2\sqrt{\pi}}, 0, \frac{\sqrt{3}}{\sqrt{\pi}}, 0, 0, 0 \right],
 \end{bmatrix} \tag{8.36}$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{3}}{\sqrt{\pi}}, 0, \frac{13\sqrt{2}}{4\sqrt{\pi}}, 0, 0 \\ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{13\sqrt{2}}{4\sqrt{\pi}}, 0, \frac{7\sqrt{2}}{2\sqrt{\pi}}, 0 \\ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{7\sqrt{2}}{2\sqrt{\pi}}, 0, \frac{15\sqrt{2}}{4\sqrt{\pi}} \\ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{15\sqrt{2}}{4\sqrt{\pi}}, 0 \end{bmatrix}$$

which is tridiagonal with zero along the principal diagonal and non-zero values in the superdiagonal and subdiagonal. We invert this matrix

**> Mqil := map(simplify, SubMatrix(1/Mq, 1..10,1..10));**

$$Mqil := \left[ \left[ 0, 2\sqrt{\pi}, 0, -\frac{2\sqrt{\pi}\sqrt{6}}{3}, 0, \frac{4\sqrt{\pi}\sqrt{30}}{15}, 0, -\frac{8\sqrt{\pi}\sqrt{35}}{35}, 0, \frac{16\sqrt{\pi}\sqrt{70}}{105} \right], \quad (8.37) \right.$$

$$\left[ 2\sqrt{\pi}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right],$$

$$\left[ 0, 0, 0, \frac{2\sqrt{3}\sqrt{\pi}}{3}, 0, -\frac{4\sqrt{\pi}\sqrt{15}}{15}, 0, \frac{4\sqrt{\pi}\sqrt{70}}{35}, 0, -\frac{16\sqrt{\pi}\sqrt{35}}{105} \right],$$

$$\left[ -\frac{2\sqrt{\pi}\sqrt{6}}{3}, 0, \frac{2\sqrt{3}\sqrt{\pi}}{3}, 0, 0, 0, 0, 0, 0, 0 \right],$$

$$\left[ 0, 0, 0, 0, 0, \frac{2\sqrt{5}\sqrt{\pi}}{5}, 0, -\frac{2\sqrt{\pi}\sqrt{210}}{35}, 0, \frac{8\sqrt{\pi}\sqrt{105}}{105} \right],$$

$$\left[ \frac{4\sqrt{\pi}\sqrt{30}}{15}, 0, -\frac{4\sqrt{\pi}\sqrt{15}}{15}, 0, \frac{2\sqrt{5}\sqrt{\pi}}{5}, 0, 0, 0, 0, 0 \right],$$

$$\left[ 0, 0, 0, 0, 0, 0, 0, \frac{2\sqrt{7}\sqrt{\pi}}{7}, 0, -\frac{4\sqrt{\pi}\sqrt{14}}{21} \right],$$

$$\left[ -\frac{8\sqrt{\pi}\sqrt{35}}{35}, 0, \frac{4\sqrt{\pi}\sqrt{70}}{35}, 0, -\frac{2\sqrt{\pi}\sqrt{210}}{35}, 0, \frac{2\sqrt{7}\sqrt{\pi}}{7}, 0, 0, 0 \right],$$

$$\left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{2\sqrt{\pi}}{3} \right],$$

$$\left[ \frac{16\sqrt{\pi}\sqrt{70}}{105}, 0, -\frac{16\sqrt{\pi}\sqrt{35}}{105}, 0, \frac{8\sqrt{\pi}\sqrt{105}}{105}, 0, -\frac{4\sqrt{\pi}\sqrt{14}}{21}, 0, \frac{2\sqrt{\pi}}{3}, 0 \right]$$

We form the corresponding matrix of  $\langle n+1 | \frac{1}{q} | n \rangle$  directly from integrals of the amplitude functions, which requires several sequences of integrals.

```
> Mqi := Matrix(16,16, shape=symmetric):
> for n from 0 while n+1<16 do
    Mqi[n+2,n+1] := simplify(int(psi(n+1,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
for n from 0 while n+3<16 do
    Mqi[n+4,n+1] := simplify(int(psi(n+3,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
for n from 0 while n+5<16 do
    Mqi[n+6,n+1] := simplify(int(psi(n+5,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
for n from 0 while n+7<16 do
    Mqi[n+8,n+1] := simplify(int(psi(n+7,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
for n from 0 while n+9<16 do
    Mqi[n+10,n+1] := simplify(int(psi(n+9,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
for n from 0 while n+11<16 do
    Mqi[n+12,n+1] := simplify(int(psi(n+11,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
for n from 0 while n+13<16 do
    Mqi[n+14,n+1] := simplify(int(psi(n+13,q)*1/q*psi(n,q),
        q=-infinity..infinity)*sqrt(h)/(mu^(1/4)*k^(1/4)),symbolic):
end do:
```

The resulting matrix, of which we show this submatrix,

```
> Mqi2 := map(simplify, SubMatrix(Mqi, 1..10,1..10));
```

$$Mqi2 := \begin{bmatrix} \left[ 0, 2\sqrt{\pi}, 0, -\frac{2\sqrt{\pi}\sqrt{6}}{3}, 0, \frac{4\sqrt{\pi}\sqrt{30}}{15}, 0, -\frac{8\sqrt{\pi}\sqrt{35}}{35}, 0, \frac{16\sqrt{\pi}\sqrt{70}}{105} \right], \\ \left[ 2\sqrt{\pi}, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \\ \left[ 0, 0, 0, \frac{2\sqrt{3}\sqrt{\pi}}{3}, 0, -\frac{4\sqrt{\pi}\sqrt{15}}{15}, 0, \frac{4\sqrt{\pi}\sqrt{70}}{35}, 0, -\frac{16\sqrt{\pi}\sqrt{35}}{105} \right], \end{bmatrix} \quad (8.38)$$

$$\begin{aligned}
& \left[ -\frac{2\sqrt{\pi}\sqrt{6}}{3}, 0, \frac{2\sqrt{3}\sqrt{\pi}}{3}, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, \frac{2\sqrt{5}\sqrt{\pi}}{5}, 0, -\frac{2\sqrt{\pi}\sqrt{210}}{35}, 0, \frac{8\sqrt{\pi}\sqrt{105}}{105} \right], \\
& \left[ \frac{4\sqrt{\pi}\sqrt{30}}{15}, 0, -\frac{4\sqrt{\pi}\sqrt{15}}{15}, 0, \frac{2\sqrt{5}\sqrt{\pi}}{5}, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, \frac{2\sqrt{7}\sqrt{\pi}}{7}, 0, -\frac{4\sqrt{\pi}\sqrt{14}}{21} \right], \\
& \left[ -\frac{8\sqrt{\pi}\sqrt{35}}{35}, 0, \frac{4\sqrt{\pi}\sqrt{70}}{35}, 0, -\frac{2\sqrt{\pi}\sqrt{210}}{35}, 0, \frac{2\sqrt{7}\sqrt{\pi}}{7}, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{2\sqrt{\pi}}{3} \right], \\
& \left[ \frac{16\sqrt{\pi}\sqrt{70}}{105}, 0, -\frac{16\sqrt{\pi}\sqrt{35}}{105}, 0, \frac{8\sqrt{\pi}\sqrt{105}}{105}, 0, -\frac{4\sqrt{\pi}\sqrt{14}}{21}, 0, \frac{2\sqrt{\pi}}{3}, 0 \right]
\end{aligned}$$

which has matrix elements of value identical to those of the matrix obtained on inverting the matrix containing elements  $\langle n+1 | q | n \rangle$ . The matrix that we obtain on inverting the matrix with elements  $\langle n+1 | \frac{1}{q} | n \rangle$ ,

**> Mq2 := map(simplify, SubMatrix(1/Mqi, 1..10,1..10));**  
**Mq2 :=**

**(8.39)**

$$\begin{aligned}
& \left[ \left[ 0, \frac{1}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0, 0 \right], \right. \\
& \left[ \frac{1}{2\sqrt{\pi}}, 0, \frac{\sqrt{2}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, \frac{\sqrt{2}}{2\sqrt{\pi}}, 0, \frac{\sqrt{3}}{2\sqrt{\pi}}, 0, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, \frac{\sqrt{3}}{2\sqrt{\pi}}, 0, \frac{1}{\sqrt{\pi}}, 0, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, \frac{1}{\sqrt{\pi}}, 0, \frac{\sqrt{5}}{2\sqrt{\pi}}, 0, 0, 0, 0 \right], \\
& \left[ 0, 0, 0, 0, \frac{\sqrt{5}}{2\sqrt{\pi}}, 0, \frac{\sqrt{6}}{2\sqrt{\pi}}, 0, 0, 0 \right],
\end{aligned}$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, \frac{\sqrt{6}}{2\sqrt{\pi}}, 0, \frac{\sqrt{7}}{2\sqrt{\pi}}, 0, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, \frac{\sqrt{7}}{2\sqrt{\pi}}, 0, \frac{\sqrt{2}}{\sqrt{\pi}}, 0 \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, \frac{\sqrt{2}}{\sqrt{\pi}}, 0, \frac{3}{2\sqrt{\pi}} \end{bmatrix},$$

$$\begin{bmatrix} 0, 0, 0, 0, 0, 0, 0, 0, 0, \frac{3}{2\sqrt{\pi}}, 0 \end{bmatrix}$$

```
> Equal(Mq2, map(simplify, SubMatrix(Mq, 1..10,1..10)));
true
```

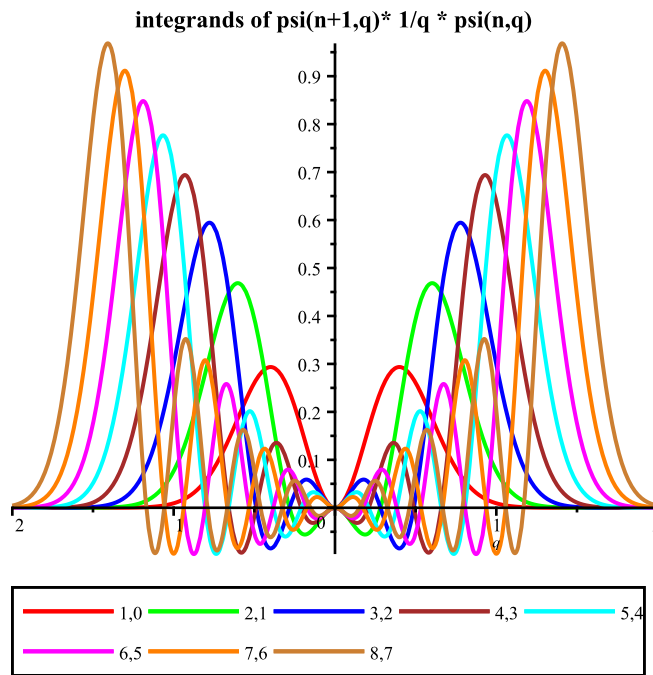
(8.40)

is identical with the original matrix containing elements  $\langle n+1 | q | n \rangle$ . Because  $\sqrt{35}$  might appear in matrix **Mqi1** as  $\sqrt{7} \sqrt{5}$  the corresponding test of equality might fail, despite the equality of the matrices.

The significance of these results is that, when one seeks to calculate matrix elements of a quantity for which direct integration is impractical, one might, for only this canonical linear harmonic oscillator, alternatively calculate through integration the reciprocal of that quantity and then invert the corresponding matrix. Although the number of states of discrete energy of the canonical linear harmonic oscillator is uncountable, and thus the matrices of these quantities are formally of infinite order, for the purposes here a submatrix of appropriate order suffices.

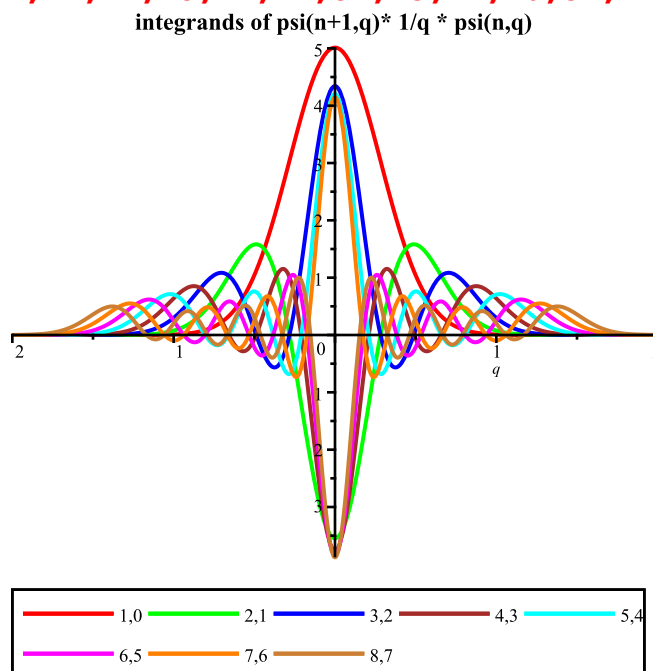
We plot the integrands these integrals that yield the mutually reciprocal matrix elements, first  $\psi(n+1, q) q \psi(n, q)$ ,

```
> plot([seq(eval(psi(n+1,q)*q*psi(n,q), [mu=1,k=1,h=1]), n=0..7)],
q=-2..2,
colour=[red,green,blue,brown,cyan,magenta,coral,gold],
title="integrands of psi(n+1,q)* 1/q * psi(n,q)", titlefont=
[TIMES,BOLD,14],
legend=["1,0","2,1","3,2","4,3","5,4","6,5","7,6","8,7"]);
```



and then first  $\psi(n+1, q) \frac{1}{q} \psi(n, q)$ ; for odd values of  $m = n$ , other integrals are non-zero, as shown in the matrix of  $\langle n+1 | \frac{1}{q} | n \rangle$  above.

```
> plot([seq(eval(psi(n+1,q)*1/q*psi(n,q), [mu=1,k=1,h=1]), n=0..7)],
       q=-2..2,
       colour=[red,green,blue,brown,cyan,magenta,coral,gold],
       title="integrands of psi(n+1,q)* 1/q * psi(n,q)", titlefont=
       [TIMES,BOLD,14],
       legend=["1,0","2,1","3,2","4,3","5,4","6,5","7,6","8,7"]);
```



To the spatial part of the amplitude functions  $\psi(j, q)$ , we include the temporal factor,

$$\tau(t) = e^{-\frac{i \cdot 2\pi W t}{h}}, \text{ which with } W(n) = \left(n + \frac{1}{2}\right) h v_0 \text{ becomes, for } n = 0, 1, 2, 3, \text{ to form } \eta(j, q, t) \\ = \psi(j, q) \tau(j, t),$$

$$> \text{ eta}(0, q, t) := \text{ psi}(0, q) * \text{ eval}(\exp(-I * 2 * \text{ Pi} * W * t / h), W = 1/2 * h * \text{ nu}[0]);$$

$$\eta(0, q, t) := \frac{2^{1/4} k^{1/8} \mu^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} e^{-I \pi v_0 t}}{h^{1/4}} \quad (8.41)$$

$$> \text{ eta}(1, q, t) := \text{ psi}(1, q) * \text{ eval}(\exp(-I * 2 * \text{ Pi} * W * t / h), W = 3/2 * h * \text{ nu}[0]);$$

$$\eta(1, q, t) := \frac{2^{1/4} \sqrt{\pi} q k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} e^{-3 I \pi v_0 t}}{h^{3/4}} \quad (8.42)$$

$$> \text{ eta}(2, q, t) := \text{ psi}(2, q) * \text{ eval}(\exp(-I * 2 * \text{ Pi} * W * t / h), W = 5/2 * h * \text{ nu}[0]);$$

$$\eta(2, q, t) := \frac{2 \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{h}{4} \right) 2^{3/4} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} e^{-5 I \pi v_0 t}}{h^{5/4}} \quad (8.43)$$

$$> \text{ eta}(3, q, t) := \text{ psi}(3, q) * \text{ eval}(\exp(-I * 2 * \text{ Pi} * W * t / h), W = 7/2 * h * \text{ nu}[0]);$$

$$\eta(3, q, t) := \quad (8.44)$$

$$\frac{2 q 2^{3/4} \sqrt{4} \sqrt{3} \sqrt{\pi} \mu^{3/8} \left( \pi \sqrt{k} \sqrt{\mu} q^2 - \frac{3 h}{4} \right) k^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} e^{-7 I \pi v_0 t}}{3 h^{7/4}}$$

$$> \text{ eta}(4, q, t) := \text{ psi}(4, q) * \text{ eval}(\exp(-I * 2 * \text{ Pi} * W * t / h), W = 9/2 * h * \text{ nu}[0]);$$

$$\eta(4, q, t) := \frac{1}{3 h^{9/4}} \left( 4 \left( \pi^2 k \mu q^4 - \frac{3 h \pi \sqrt{k} \sqrt{\mu} q^2}{2} \right. \right. \\ \left. \left. + \frac{3 h^2}{16} \right) 2^{3/4} \sqrt{3} \mu^{1/8} k^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} e^{-9 I \pi v_0 t} \right) \quad (8.45)$$

$$> \text{ eta}(5, q, t) := \text{ psi}(5, q) * \text{ eval}(\exp(-I * 2 * \text{ Pi} * W * t / h), W = 11/2 * h * \text{ nu}[0]);$$

$$\eta(5, q, t) := \frac{1}{15 h^{11/4}} \left( 4 \left( \pi^2 k \mu q^4 - \frac{5 h \pi \sqrt{k} \sqrt{\mu} q^2}{2} \right. \right. \\ \left. \left. + \frac{15 h^2}{16} \right) q 2^{3/4} \sqrt{4} \sqrt{15} \sqrt{\pi} k^{3/8} \mu^{3/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} q^2}{h}} e^{-11 I \pi v_0 t} \right) \quad (8.46)$$

The corresponding matrix elements become



```
> Int(conjugate('eta(1,q,t)')*q*'eta(0,q,t)', q=-infinity..infinity)
=
simplify(int(subs(I=-I, eta(1,q,t))*q*eta(0,q,t), q=-infinity..
infinity),
symbolic);
```

$$\int_{-\infty}^{\infty} \overline{\eta(1, q, t)} q \eta(0, q, t) dq = \frac{e^{2I\pi v_0 t} \sqrt{h\sim}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}} \quad (8.47)$$

```
> Int(conjugate('eta(2,q,t)')*q*'eta(1,q,t)', q=-infinity..infinity)
=
simplify(int(subs(I=-I, eta(2,q,t))*q*eta(1,q,t), q=-infinity..
infinity), symbolic);
```

$$\int_{-\infty}^{\infty} \overline{\eta(2, q, t)} q \eta(1, q, t) dq = \frac{e^{2I\pi v_0 t} \sqrt{h\sim} \sqrt{2}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}} \quad (8.48)$$

```
> Int(conjugate('eta(3,q,t)')*q*'eta(2,q,t)', q=-infinity..infinity)
=
simplify(int(subs(I=-I, eta(3,q,t))*q*eta(2,q,t), q=-infinity..
infinity), symbolic);
```

$$\int_{-\infty}^{\infty} \overline{\eta(3, q, t)} q \eta(2, q, t) dq = \frac{e^{2I\pi v_0 t} \sqrt{h\sim} \sqrt{3}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}} \quad (8.49)$$

Relative to the corresponding matrix elements calculated above, these expressions contain an additional multiplicand  $e^{2I\pi v_0 t}$ ,

```
> smet := [seq(simplify(int(eta(j+1,q,t)*q*eta(j,q,t),
q=-infinity..infinity),symbolic), j=0..4)];
```

$$smet := \left[ \frac{e^{-4I\pi v_0 t} \sqrt{h\sim}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}}, \frac{e^{-8I\pi v_0 t} \sqrt{h\sim} \sqrt{2}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}}, \frac{e^{-12I\pi v_0 t} \sqrt{h\sim} \sqrt{3}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}}, \frac{e^{-16I\pi v_0 t} \sqrt{h\sim}}{\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}}, \right. \quad (8.50)$$

$$\left. \frac{e^{-20I\pi v_0 t} \sqrt{5} \sqrt{h\sim}}{2\sqrt{\pi} k\sim^{1/4} \mu\sim^{1/4}} \right]$$

but the temporal factors become eliminated from the squares of these matrix elements, with  $-\sqrt{-1}$  replacing  $\sqrt{-1}$  in one multiplicand; to such squares is related some physically meaningful quantity that is independent of time.

```
> smetsq := [seq(simplify(subs(I=-I, smet[j])*smet[j]), j=1..5)];
```

$$smetsq := \left[ \frac{h\sim}{4\pi\sqrt{k\sim}\sqrt{\mu\sim}}, \frac{h\sim}{2\pi\sqrt{k\sim}\sqrt{\mu\sim}}, \frac{3h\sim}{4\pi\sqrt{k\sim}\sqrt{\mu\sim}}, \frac{h\sim}{\pi\sqrt{k\sim}\sqrt{\mu\sim}}, \right. \quad (8.51)$$

$$\left[ \frac{5 \hbar}{4 \pi \sqrt{k} \sqrt{\mu}} \right]$$

In summary, through a solution of Schroedinger's equation independent of time for a canonical linear harmonic oscillator in the coordinate representation, thus invoking momentum as a differential operator, we have obtained discrete energies

$$E_n = \frac{\left(n + \frac{1}{2}\right) \hbar \omega_0}{2 \pi} = \left(n + \frac{1}{2}\right) \hbar \nu_0$$

in which occur angular frequency  $\omega_0 = \sqrt{\frac{k}{\mu}}$  or circular frequency  $\nu_0 = 2 \pi \omega_0$ , expressions for amplitude function  $\psi_n(q)$  in terms of Whittaker functions, and expressions for matrix elements for  $q$  that pertain to emission or absorption of a single photon in a transition between states of adjacent energies.

**> n := 'n':**

For an alternative approach, within wave mechanics, to the solution of the energies and amplitude functions for this canonical linear harmonic oscillator, we adopt the momentum representation for which

$$q \rightarrow i \frac{\hbar \left( \frac{\partial}{\partial p} \right)}{2 \pi}, \quad \text{and } p \text{ remains an algebraic quantity;}$$

We here use  $\chi(p)$  to distinguish the amplitude functions in terms of  $p$  from those  $\psi(q)$  in terms of  $q$  above. Schroedinger's equation independent of time becomes accordingly

**> ode := p^2/(2\*mu)\*chi(p) - 1/2\*k\*(h/(2\*Pi))^2\*diff(chi(p), p\$2)**  
**= W\*chi(p);**

$$ode := \frac{p^2 \chi(p)}{2 \mu} - \frac{k \hbar^2 (\chi_{p,p})}{8 \pi^2} = W \chi(p) \quad (8.52)$$

in which  $\chi_{p,p}$  implies a second derivative of  $\chi$  with respect to  $p$ . What is the kind of this differential equation?

**> odeadvisor(ode);**

**[[\_2nd\_order, \_with\_linear\_symmetries]]** (8.53)

Like the analogous version of Schroedinger's equation in the coordinate representation above, this differential equation is of second order, and [linear](#) because there is no constant term that is not a factor of  $\chi(p)$ . We proceed to solve this equation.

**> sol := dsolve(ode, chi(p));**

$$sol := \chi(p) = \frac{-CI \text{ WhittakerM}\left(\frac{\pi \sqrt{\mu} W}{\hbar \sqrt{k}}, \frac{1}{4}, \frac{2 \pi p^2}{\hbar \sqrt{k} \sqrt{\mu}}\right)}{\sqrt{p}} \quad (8.54)$$

$$+ \frac{_{C3} \text{WhittakerW}\left(\frac{\pi \sqrt{\mu_{\sim}} W_{\sim}}{h_{\sim} \sqrt{k_{\sim}}}, \frac{1}{4}, \frac{2 \pi p^2}{h_{\sim} \sqrt{k_{\sim}} \sqrt{\mu_{\sim}}}\right)}{\sqrt{p}}$$

Because this differential equation contains derivatives of second order, this equation has two independent solutions, as shown. Is this expression that contains two independent parts, each with an arbitrary parameter  $_{C1}$  or  $_{C3}$ , a true solution? We test it.

```
> test := odetest(sol, ode);
test := 0 (8.55)
```

For any solution of Schroedinger's equation to be acceptable, it must conform to the properties stipulated at the top of this section. For these Whittaker functions, the applicable condition is that the difference of the first argument and the second argument must take non-negative half-integer values.

```
> op(rhs(sol));
```

$$\frac{_{C1} \text{WhittakerM}\left(\frac{\pi \sqrt{\mu_{\sim}} W_{\sim}}{h_{\sim} \sqrt{k_{\sim}}}, \frac{1}{4}, \frac{2 \pi p^2}{h_{\sim} \sqrt{k_{\sim}} \sqrt{\mu_{\sim}}}\right)}{\sqrt{p}}, \quad (8.56)$$

$$\frac{_{C3} \text{WhittakerW}\left(\frac{\pi \sqrt{\mu_{\sim}} W_{\sim}}{h_{\sim} \sqrt{k_{\sim}}}, \frac{1}{4}, \frac{2 \pi p^2}{h_{\sim} \sqrt{k_{\sim}} \sqrt{\mu_{\sim}}}\right)}{\sqrt{p}}$$

We again extract the first and second arguments of these Whittaker functions,

```
> op(1, op(3, op(2, [op(rhs(sol))])), op(2, op(3, op(2,
[op(rhs(sol))]))));
```

$$\frac{\pi \sqrt{\mu_{\sim}} W_{\sim}}{h_{\sim} \sqrt{k_{\sim}}}, \frac{1}{4} \quad (8.57)$$

and set their difference equal to a half integer; we solve for the energy,

```
> W1 := solve(op(1, op(3, op(2, [op(rhs(sol))])) -
op(2, op(3, op(2, [op(rhs(sol))])))=n/2, W);
Warning, solve may be ignoring assumptions on the input
variables.
```

$$W1 := \frac{h_{\sim} \sqrt{k_{\sim}} (2 n + 1)}{4 \pi \sqrt{\mu_{\sim}}} \quad (8.58)$$

which we insert into the amplitude functions.

```
> sol := eval(sol, W=W1);
```

$$\text{sol} := \chi(p) = \frac{_{C1} \text{WhittakerM}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2 \pi p^2}{h_{\sim} \sqrt{k_{\sim}} \sqrt{\mu_{\sim}}}\right)}{\sqrt{p}} \quad (8.59)$$

$$+ \frac{{}_3\text{WhittakerW}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2\pi p^2}{h\sqrt{k}\sqrt{\mu}}\right)}{\sqrt{p}}$$

We separate the two contributions to this solution,

```
> chi1 := remove(has, rhs(sol), WhittakerW);
```

$$\chi^1 := \frac{{}_1\text{WhittakerM}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2\pi p^2}{h\sqrt{k}\sqrt{\mu}}\right)}{\sqrt{p}} \quad (8.60)$$

```
> chi2 := remove(has, rhs(sol), WhittakerM);
```

$$\chi^2 := \frac{{}_3\text{WhittakerW}\left(\frac{n}{2} + \frac{1}{4}, \frac{1}{4}, \frac{2\pi p^2}{h\sqrt{k}\sqrt{\mu}}\right)}{\sqrt{p}} \quad (8.61)$$

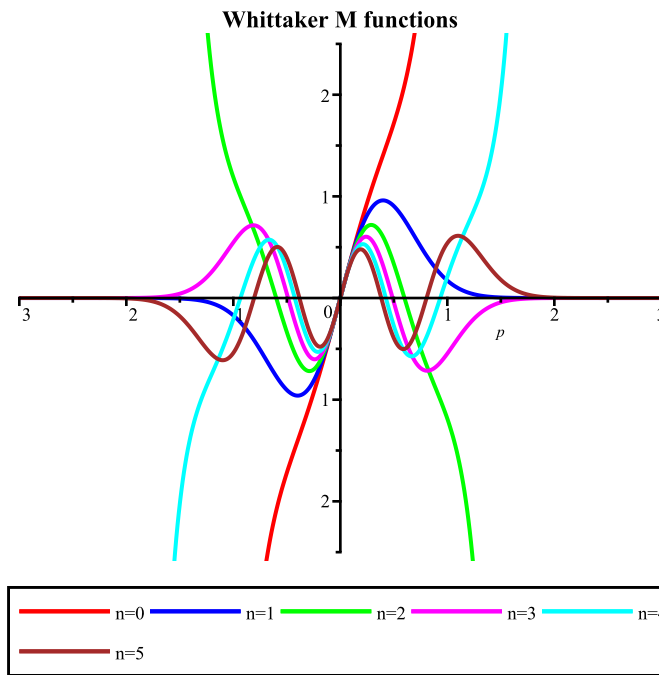
simplify them,

```
> for j from 0 to 16 do
    chi3[j] := simplify(eval(chi1, n=j), symbolic);
end do;
```

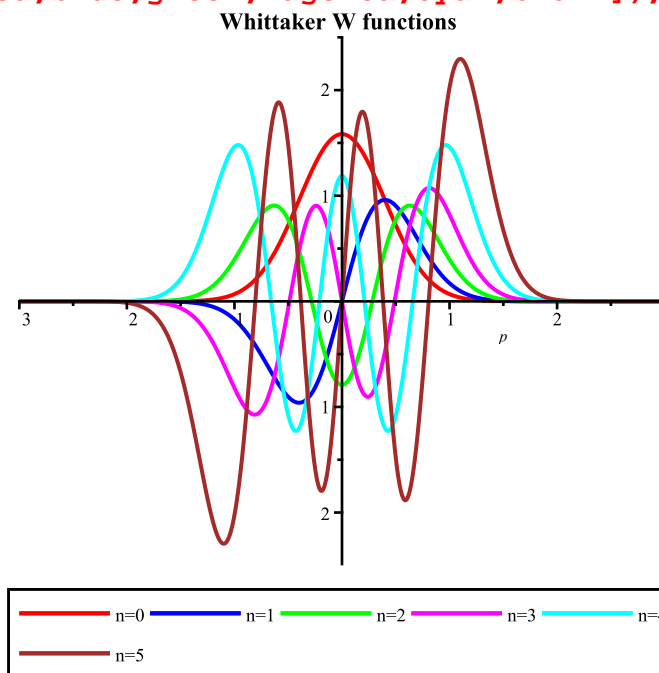
```
> for j from 0 to 16 do
    chi4[j] := simplify(eval(chi2, n=j), symbolic);
end do;
```

and plot them.

```
> plot([seq(eval(chi3[j], [_C1=1,h=1,mu=1,k=1,W=1]), j=0..5)],
    p=-3..3, -2.5..2.5, numpoints=500, title="Whittaker M
functions",
    titlefont=[TIMES,BOLD,14], legend=["n=0","n=1","n=2","n=3","n=
4","n=5"],
    colour=[red,blue,green,magenta,cyan,brown]);
```



```
> plot([seq(eval(chi4[j], [_C3=1,h=1,mu=1,k=1,W=1]), j=0..5)],
      p=-3..3, -2.5..2.5, numpoints=500, title="Whittaker W
      functions",
      titlefont=[TIMES,BOLD,14], legend=["n=0","n=1","n=2","n=3",
      "n=4","n=5"],
      colour=[red,blue,green,magenta,cyan,brown]);
```



As the contributions containing Whittaker M functions diverge for even values of index  $n$ , we discard these contributions. We convert the other, Whittaker W, contributions into arrow functions.

```
> chi := unapply(chi4[n], (n,p));
```

$$\chi := (n, p) \mapsto \chi_n^4 \quad (8.62)$$

Applying the fact that these functions are real, we integrate the first six amplitude functions  $\chi_n(p)$ , expressed in  $\chi(n, p)$  for which  $n = 0..7$ , throughout all space in one dimension; we divide by common symbolic factor  $_C3^2$  to clarify the remaining expressions.

```
> seq(simplify(int(chi(n,p)^2/_C3^2, p=-infinity..infinity)), n=0..7);
```

$$\sqrt{\pi}, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2}, \frac{3\sqrt{\pi}}{4}, \frac{3\sqrt{\pi}}{2}, \frac{15\sqrt{\pi}}{4}, \frac{45\sqrt{\pi}}{4}, \frac{315\sqrt{\pi}}{8} \quad (8.63)$$

By inspection we again deduce that these quantities have the form  $\frac{n! \sqrt{\pi}}{2^n}$ , as we test.

```
> 'seq'(n!*sqrt(Pi)/2^n, n=0..7) = seq(n!*sqrt(Pi)/2^n, n=0..7);
```

$$\text{seq}\left(\frac{n! \sqrt{\pi}}{2^n}, n=0..7\right) = \left(\sqrt{\pi}, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2}, \frac{3\sqrt{\pi}}{4}, \frac{3\sqrt{\pi}}{2}, \frac{15\sqrt{\pi}}{4}, \frac{45\sqrt{\pi}}{4}, \frac{315\sqrt{\pi}}{8}\right) \quad (8.64)$$

For normalisation of these amplitude functions constant  $_C3$  of integration must be set equal to the inverse square root of these quantities.

```
> _C3 := sqrt(2^n/(n!*sqrt(Pi)));
```

$$_C3 := \sqrt{\frac{2^n}{n! \sqrt{\pi}}} \quad (8.65)$$

To incorporate this result, we evaluate  $\psi_n(q)$ .

```
> for j from 0 to 11 do
    chi(j,p) := eval(chi(j,p), n=j);
end do;
```

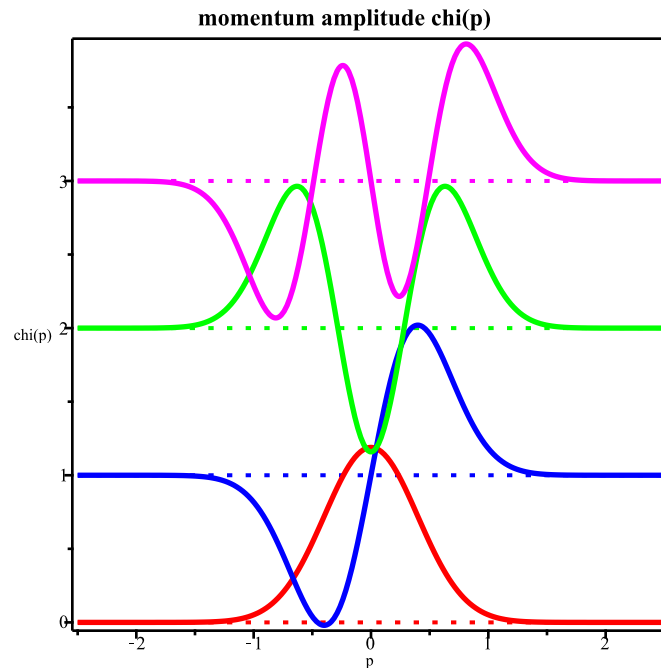
We test the validity of our normalisation over a range greater than that within which we deduced the form of the normalising factor.

```
> seq(simplify(int(chi(n,p)^2, p=-infinity..infinity)), n=0..12);
1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1
```

(8.66)

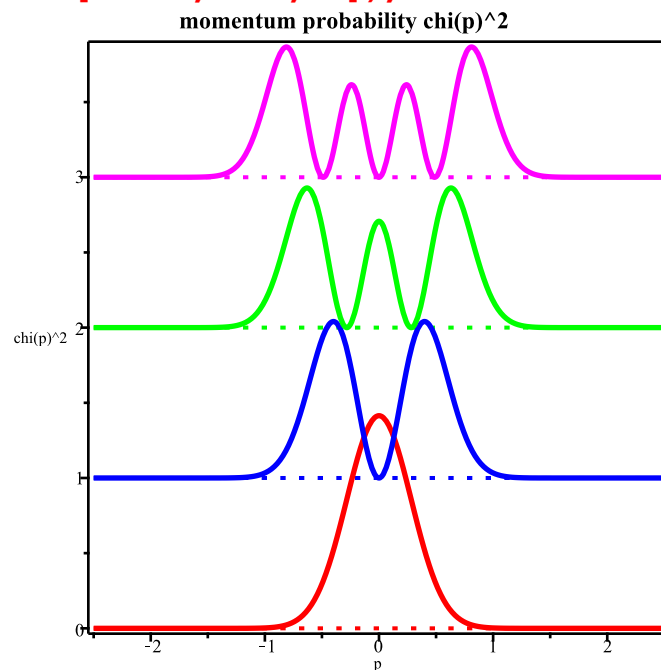
Because these values are all unity we verify that our derivation is correct. We plot  $\chi_n(p)$  for small values of  $n$ , displacing the functions vertically cumulatively one unit for clarity.

```
> p1 := plot([0,1,2,3], -2.5..2.5, colour=[red,blue,green,magenta],
    linestyle=[2,2,2,2]):
p2 := plot([seq(simplify(eval(chi(n,p)+n, [mu=1,k=1,h=1])),
    n=0..3)], p=-2.5..2.5, thickness=[2,2,2,2],
    colour=[red,blue,green,magenta]):
display([p1,p2], axes=BOXED, labels=["p","chi(p)"],
    title="momentum amplitude chi(p)", titlefont=[TIMES,BOLD,
14]);
```



We plot also the squares of these amplitude functions.

```
> p3 := plot([0,1,2,3], -2.5..2.5, colour=[red,blue,green,magenta],
             linestyle=[2,2,2,2]):
p4 := plot([seq(simplify(eval(chi(n,p)^2+n, [mu=1,k=1,h=1])),
               n=0..3)], p=-2.5..2.5, thickness=[2,2,2,2],
           colour=[red,blue,green,magenta]):
display([p3,p4], axes=BOXED, labels=["p","chi(p)^2"],
        title="momentum probability chi(p)^2",
        titlefont=[TIMES,BOLD,14]);
```



We examine the forms of  $\chi_0(p)$  for  $n = 0$ ,

```
> 'chi'[0]*^(p)^ = chi(0,p);
```

$$\chi_0(p) = \frac{2^{1/4} e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{h^{1/4} k^{1/8} \mu^{1/8}} \quad (8.67)$$

$n = 1$ ,

```
> 'chi'[1]*^(p)^ = chi(1,p);
```

$$\chi_1(p) = \frac{2^{1/4} \sqrt{\pi} p e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{h^{3/4} k^{3/8} \mu^{3/8}} \quad (8.68)$$

$n = 2$ ,

```
> 'chi'[2]*^(p)^ = chi(2,p);
```

$$\chi_2(p) = \frac{2 \left( \pi p^2 - \frac{h\sqrt{k}\sqrt{\mu}}{4} \right) 2^{3/4} e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{h^{5/4} k^{5/8} \mu^{5/8}} \quad (8.69)$$

and  $n = 3$ .

```
> 'chi'[3]*^(p)^ = chi(3,p);
```

$$\chi_3(p) = \frac{2 p 2^{3/4} \sqrt{4} \sqrt{3} \sqrt{\pi} \left( \pi p^2 - \frac{3 h\sqrt{k}\sqrt{\mu}}{4} \right) e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{3 h^{7/4} k^{7/8} \mu^{7/8}} \quad (8.70)$$

We observe that, apart from numerical and physical constants and parameters, these amplitude functions comprise an exponential factor of gaussian type and momentum  $p$  in a series with terms in alternating even or odd powers up to  $p^n$ . Are these amplitude functions orthogonal? We integrate their product over all space in one dimension.

```
> Int('chi'(0,p)*'chi'(1,p), p=-infinity..infinity)
= int(chi(0,p)*chi(1,p), p=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \chi(0,p) \chi(1,p) dp = 0 \quad (8.71)$$

```
> Int('chi'(0,p)*'chi'(2,p), p=-infinity..infinity)
= int(chi(0,p)*chi(2,p), p=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \chi(0,p) \chi(2,p) dp = 0 \quad (8.72)$$

```
> Int('chi'(0,p)*'chi'(3,p), p=-infinity..infinity)
= int(chi(0,p)*chi(3,p), p=-infinity..infinity);
```

$$(8.73)$$



$$\int_{-\infty}^{\infty} \chi(0, p) \chi(3, p) dp = 0 \quad (8.73)$$

We evaluate a matrix element of  $q$  between states with  $n=0$  and  $n=1$ , or  $q_{0,1}$ , through an integral,

$$q_{0,1} = \int_{-\infty}^{\infty} \overline{\chi_1(p)} q \chi_0(p) dp,$$

which we denote according to Dirac's notation as  $\langle 0 | q | 1 \rangle$ . In this integral for a real quantity  $q_{0,1}$ , we should take the complex conjugate of  $\chi_1(p)$ , denoted  $\overline{\chi_1(p)}$  or  $\chi_1(p)^*$ , but, because these amplitude functions of an harmonic oscillator as just derived have no imaginary part, this refinement is superfluous here. Because we are integrating with respect to  $p$ , a particular requirement of this momentum representation is that we must convert  $q$  to  $\frac{i\hbar}{2\pi} \frac{\partial}{\partial p}$ ; for this reason the integrand contains that derivative.

```
> Int('chi(1,p)'*I*h/2/Pi*Diff('chi(0,p)',p), p=-infinity..infinity)
=
simplify(int(chi(1,p)*I*h/(2*Pi)*diff(chi(0,p), p),
p=-infinity..infinity));
```

$$\int_{-\infty}^{\infty} \frac{\frac{1}{2} \chi(1, p) \hbar \left( \frac{d}{dp} \chi(0, p) \right)}{\pi} dp = \frac{-\frac{1}{2} \sqrt{\hbar}}{k^{1/4} \mu^{1/4} \sqrt{\pi}} \quad (8.74)$$

Apart from an extra factor  $-I = -\sqrt{-1}$ , that result is the same as generated above with  $\psi_n(q)$ , as expected because  $\langle 0 | q | 1 \rangle$  must be independent whether coordinate or momentum representation of the amplitude functions; the intensity of a transition according to radiation interacting with an electric dipole is proportional to the square of the modulus of this quantity, hence  $|\langle 0 | q | 1 \rangle|^2$  or alternatively expressed as  $\langle 0 | q | 1 \rangle \langle 1 | q | 0 \rangle$ . This matrix element, called a transition moment of electric dipolar type, has the sense of an electric dipolar moment, but a calculation of any such quantity might contain a phase factor of form  $e^{\sqrt{-1}(\alpha_0 - \alpha_1)}$  in which  $\alpha_0$  and  $\alpha_1$  are arbitrary; such phase factors are intrinsically unobservable, being arbitrary. Because in a construct such as  $\langle 0 | q | 1 \rangle \langle 1 | q | 0 \rangle$  such phase factors cancel, they can occur in expressions for observable quantities. In general, if such a phase factor fail to cancel, the quantity in which it might occur does not correspond to an observable property. This criterion, among others, is useful to verify whether an expression for an observable quantity be correct.

Are the other matrix elements of  $q$  also the same as above, apart from a possible factor  $I$ ? We test by calculating the first six matrix elements  $\langle n | q | n+1 \rangle$ .

```
> sme := [seq(simplify(int(chi(n,p)*I*h/(2*Pi)*diff(chi(n+1,p), p),
p=-infinity..infinity)), n=0..5)];
```

$$sme := \left[ \frac{\frac{1}{2} \sqrt{\hbar}}{k^{1/4} \mu^{1/4} \sqrt{\pi}}, \frac{\frac{1}{2} \sqrt{\hbar} \sqrt{2}}{k^{1/4} \mu^{1/4} \sqrt{\pi}}, \frac{\frac{1}{2} \sqrt{3} \sqrt{\hbar}}{k^{1/4} \mu^{1/4} \sqrt{\pi}}, \frac{I \sqrt{\hbar}}{k^{1/4} \mu^{1/4} \sqrt{\pi}}, \right] \quad (8.75)$$

$$\left[ \frac{\frac{1}{2} \sqrt{5} \sqrt{h}}{k^{1/4} \mu^{1/4} \sqrt{\pi}}, \frac{\frac{1}{2} \sqrt{h} \sqrt{6}}{k^{1/4} \mu^{1/4} \sqrt{\pi}} \right]$$

To perceive the significance of these expressions, we extract the constant factor,

```
> smef := sqrt(h)/(k^(1/4)*mu^(1/4)*sqrt(2*Pi)):
```

```
sme := simplify(map(x -> x/smef, sme))*smef;
```

$$sme := \frac{\left[ \frac{1}{2} \sqrt{2}, I, \frac{1}{2} \sqrt{6}, I\sqrt{2}, \frac{1}{2} \sqrt{10}, I\sqrt{3} \right] \sqrt{h} \sqrt{2}}{2 \sqrt{\pi} k^{1/4} \mu^{1/4}} \quad (8.76)$$

and recognise the sequence as follows.

```
> 'seq'(sqrt((n+1)/2)*I, n=0..5)*smef = seq(sqrt((n+1)/2)*I, n=0..7)
*smef;
```

$$\frac{\text{seq}\left(\frac{1}{2} \sqrt{2n+2}, n=0..5\right) \sqrt{h} \sqrt{2}}{2 \sqrt{\pi} k^{1/4} \mu^{1/4}} \quad (8.77)$$

$$= \frac{\left(\frac{1}{2} \sqrt{2}, I, \frac{1}{2} \sqrt{6}, I\sqrt{2}, \frac{1}{2} \sqrt{10}, I\sqrt{3}, \frac{1}{2} \sqrt{14}, 2I\right) \sqrt{h} \sqrt{2}}{2 \sqrt{\pi} k^{1/4} \mu^{1/4}}$$

Apart from the common factor  $I = \sqrt{-1}$ , these results are the same as for the solution of Schroedinger's equation above in the coordinate representation. This result shows that the matrix elements increase

according to  $\sqrt{\frac{n+1}{2}}$ .

We might append a temporal factor,  $e^{-\frac{i \cdot 2 \pi W t}{h}}$ , to these amplitude functions  $\chi_n(p)$  just as for the corresponding amplitude functions  $\psi_n(p)$  above.

In summary, through solution of Schroedinger's equation independent of time for a canonical linear harmonic oscillator invoking coordinate  $q$  as a differential operator,  $q \rightarrow i \frac{h \left( \frac{\partial}{\partial p} \right)}{2 \pi}$ , we have obtained discrete energies

$$E_n = \frac{\left(n + \frac{1}{2}\right) h \omega_0}{2 \pi} = \left(n + \frac{1}{2}\right) h \nu_0$$

in which angular frequency  $\omega_0 = \sqrt{\frac{k}{\mu}}$  and circular frequency  $\nu_0 = 2 \pi \omega_0$ , expressions for amplitude function  $\chi_n(p)$ , and expressions for matrix elements for  $q$  that pertain to emission or absorption of a single photon in a transition between states of adjacent energies.

To take into account that the variable conjugate to  $q$  is not  $p$  but  $\frac{p}{h}$ , so that a pure Fourier transform of  $\psi_n(q)$  fails to produce  $\chi_n(p)$ , we test the consistency between  $\psi_n(q)$  and  $\chi_n(p)$  by applying this indirect Fourier transform to  $\psi_n(q)$  that includes weighting factor  $\frac{1}{\sqrt{h}}$  ;

$$\chi_n(p) = \int_{-\infty}^{\infty} \frac{\psi_n(q) e^{-\frac{2\pi I q p}{h}}}{\sqrt{h}} dq ;$$

we calculate also a ratio of that transformed function with function  $\chi_n(p)$  calculated above directly from Schroedinger's equation, then analogously an inverse Fourier transform,

$$\psi_n(q) = \int_{-\infty}^{\infty} \frac{\chi_n(p) e^{\frac{2\pi I p q}{h}}}{\sqrt{h}} dp$$

of that result, and eventually calculate, as a test of consistency, the ratio of the latter from that second integral with the original amplitude function  $\psi_n(q)$  as already calculated directly above from Schroedinger's equation.

```
> for n from 0 to 11 do
  chi||p[n] := collect(factor(simplify(combine(int(psi(n,q)
    *exp(-2*Pi*I*q*p/h), q=-infinity..infinity)/sqrt(h), radical))
),p):
  aa[n] := collect(factor(chi||p[n])/chi(n,p), p):
  aa[n] := simplify(expand(numer(aa[n]), radical)
    /expand(denom(aa[n]), radical)):
  psi||q[n] := collect(factor(simplify(combine(int(chi||p[n]*
    exp(2*Pi*I*q*p/h), p=-infinity..infinity)/sqrt(h), radical))),
q):
  ab[n] := simplify(psi||q[n]/psi(n,q)):
  print(`n=`,n,`  ratio chi(p)t/chi(p) =`, aa[n],
    `      ratio of psi(q)t/psi(q) =`, ab[n]);
end do:

n=, 0,  ratio chi(p)t/chi(p) =, 1,  ratio of psi(q)t/psi(q) =, 1
n=, 1,  ratio chi(p)t/chi(p) =, -I,  ratio of psi(q)t/psi(q) =, 1
n=, 2,  ratio chi(p)t/chi(p) =, -1,  ratio of psi(q)t/psi(q) =, 1
n=, 3,  ratio chi(p)t/chi(p) =, I,  ratio of psi(q)t/psi(q) =, 1
n=, 4,  ratio chi(p)t/chi(p) =, 1,  ratio of psi(q)t/psi(q) =, 1
n=, 5,  ratio chi(p)t/chi(p) =, -I,  ratio of psi(q)t/psi(q) =, 1
n=, 6,  ratio chi(p)t/chi(p) =, -1,  ratio of psi(q)t/psi(q) =, 1
```

$$\begin{aligned}
n=, 7, \quad & \text{ratio } \chi(p)t/\chi(p) =, I, \quad \text{ratio of } \psi(q)t/\psi(q) =, 1 \\
n=, 8, \quad & \text{ratio } \chi(p)t/\chi(p) =, 1, \quad \text{ratio of } \psi(q)t/\psi(q) =, 1 \\
n=, 9, \quad & \text{ratio } \chi(p)t/\chi(p) =, -I, \quad \text{ratio of } \psi(q)t/\psi(q) =, 1 \\
n=, 10, \quad & \text{ratio } \chi(p)t/\chi(p) =, -1, \quad \text{ratio of } \psi(q)t/\psi(q) =, 1 \\
n=, 11, \quad & \text{ratio } \chi(p)t/\chi(p) =, I, \quad \text{ratio of } \psi(q)t/\psi(q) =, 1
\end{aligned} \tag{8.78}$$

In the above list, the ratio of  $\chi_n(p)$  calculated directly from Schroedinger's equation and of  $\chi_n(p)$  calculated as a Fourier transform of  $\psi_n(q)$  is one of the fourth roots of unity, i.e.  $\pm 1, \pm i$ ; this test of consistency proves valid in each case.

Here are the first four amplitude functions  $\chi_n(p)$  calculated directly above.

> for n from 0 to 3 do

    chi||n := collect(chi(n,p), exp);

end do;

$$\begin{aligned}
\chi^0 &:= \frac{2^{1/4} e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{h^{1/4} k^{1/8} \mu^{1/8}} \\
\chi^1 &:= \frac{2^{1/4} \sqrt{\pi} p e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{h^{3/4} k^{3/8} \mu^{3/8}} \\
\chi^2 &:= \frac{2 \left( \pi p^2 - \frac{h\sqrt{k}\sqrt{\mu}}{4} \right) 2^{3/4} e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{h^{5/4} k^{5/8} \mu^{5/8}} \\
\chi^3 &:= \frac{2 p 2^{3/4} \sqrt{4} \sqrt{3} \sqrt{\pi} \left( \pi p^2 - \frac{3 h\sqrt{k}\sqrt{\mu}}{4} \right) e^{-\frac{\pi p^2}{h\sqrt{k}\sqrt{\mu}}}}{3 h^{7/4} k^{7/8} \mu^{7/8}}
\end{aligned} \tag{8.79}$$

We observe that  $\chi_n(p)$  has the same form as  $\psi_n(q)$ , because a Fourier transform, direct or indirect, of a gaussian function yields simply another gaussian function, and that likewise a Fourier transform of a gaussian function multiplied by a polynomial yields simply another gaussian function multiplied by an analogous polynomial. We find also an extra factor  $(\sqrt{-1})^n$  in amplitude functions  $\chi_n(p)$  transformed from  $\psi_n(q)$  relative to  $\chi_n(p)$  calculated directly from Schroedinger's equation above, but this factor is immaterial because only the magnitude, as  $|\psi_n(q)|^2$  or  $|\chi_n(p)|^2$ , of the amplitude function has a physical significance; any solution of Schroedinger's equation independent of time multiplied by  $e^{ia}$ , with constant  $a$ , remains a solution of Schroedinger's equation because it is homogeneous; if the magnitude of  $a$  be other than unity, the normalisation might suffer. Apart from this complication, these results reflect

that the hamiltonian operator for the canonical linear harmonic oscillator,  $H = \frac{p^2}{2\mu} + \frac{kq^2}{2}$ , is effectively symmetric in variables  $p$  and  $q$ , which we might express as  $H = p^2 + q^2$  with modified forms of  $p$  and  $q$ .

With regard to the plots of the amplitude functions, taking as mass  $\mu$  of the oscillator that,  $m_e$ , of an electron at rest and as frequency  $\nu_0$  that of blue light, force coefficient assumes a value  $\sim 12.9 \text{ N m}^{-1}$ ; the width at half maximum stature of  $\psi_0(q)$  is  $\sim 3 \cdot 10^{-9} \text{ m}$  and the corresponding width of  $\chi_0(p)$  is  $\sim \frac{m_e c}{180}$ . That the latter value is much smaller than  $m_e c$  justifies a non-relativistic approximation in these calculations; the ratio of these two widths is  $\sim \sqrt{\frac{1}{h}}$ , as expected.

> **restart:**

The WhittakerW functions are equivalent to a product of Hermite polynomials and a gaussian function, which is a conventional expression of the amplitude function of the canonical linear harmonic oscillator in the position representation.

```
> psi[n](q) = 2^((-2*n+1)/4)*(k*mu)^(1/8)*HermiteH(n,sqrt(2*Pi/h)*
(k*mu)^(1/4)*q)
/sqrt(n!)/(h^(1/4))*exp(-Pi/h*sqrt(k*mu)*
q^2);
```

$$\psi_n(q) = \frac{2^{-\frac{n}{2} + \frac{1}{4}} (k\mu)^{1/8} \text{HermiteH}\left(n, \sqrt{2} \sqrt{\frac{\pi}{h}} (k\mu)^{1/4} q\right) e^{-\frac{\pi\sqrt{k\mu} q^2}{h}}}{\sqrt{n!} h^{1/4}} \quad (8.80)$$

The amplitude functions in the momentum representation likewise has this form.

```
> chi[n](p) = 2^((-2*n+1)/4)*HermiteH(n,sqrt(2*Pi/h)/((k*mu)^(1/4))*
p)
/sqrt(n!)/(h^(1/4))/((k*mu)^(1/8))*exp(-Pi/h/sqrt(k*
mu)*p^2);
```

$$\chi_n(p) = \frac{2^{-\frac{n}{2} + \frac{1}{4}} \text{HermiteH}\left(n, \frac{\sqrt{2} \sqrt{\frac{\pi}{h}} p}{(k\mu)^{1/4}}\right) e^{-\frac{\pi p^2}{h\sqrt{k\mu}}}}{\sqrt{n!} h^{1/4} (k\mu)^{1/8}} \quad (8.81)$$

This approach is discussed explicitly in section 1.31 for a canonical linear harmonic oscillator in spectrometric notation.

### e1.23 exercise

Using the amplitude functions generated according to the method in section 1.23, and forming matrix elements  $Mq^3_{j,k} = \langle j | q^3 | k \rangle = \int_{-\infty}^{\infty} \psi(j, q) q^3 \psi(k, q) dq$ , form a matrix of the results of the

integrations, and with inversion of that matrix as real numbers form a matrix of elements  $\langle j | q^{-3} | k \rangle$ .

## 1.24 application of Dirac's operators to a canonical linear harmonic oscillator

> restart:

We proceed to treat a canonical linear harmonic oscillator on applying operators  $a$  and  $a^\dagger$  (generally printed elsewhere as  $a$  with suffixed superscript *dagger*); here  $a^\dagger$ , which is the [adjoint](#) of  $a$ , is denoted  $b$  for practical convenience in input and output. These operators, developed by Dirac and Fock from a formalism developed by Jordan, Klein, Wigner and Dirac in 1927, operate on a state through its *ket* to diminish the population of that state in favour of an adjacent state, either of less energy -- for  $a$ , or greater energy -- for  $a^\dagger$  or  $b$  according to an index of that state; for an harmonic oscillator as a boson, i.e. having integer intrinsic angular momentum and specifically zero intrinsic angular momentum, the effect of  $a$  is thus to destroy a vibrational quantum and of  $a^\dagger$  to create a vibrational quantum. For this reason these operators are called *destruction* and *creation* operators, respectively, or *lowering* and *raising* operators, or *shift operators* in various contexts. The property of destruction or creation is most pertinent in a *quantum field* theory, or with *second quantization*, in which real particles are destroyed or created, but we retain the nomenclature here for practical purposes.

In this formalism these, and other, operators require operands, which we define as follows: a *ket* implies an abstract quantity with a vectorial sense that is supposed to signify a state of a system, which is assumed to exist, and its properties; a *bra*, which is likewise assumed to exist, as the [dual](#) of a *ket*, is a corresponding conjugate transpose vector of a ket; a state function or state vector, whether represented by  $\psi_\alpha$  or  $a_\alpha$  or  $b_\alpha$  is hence described with a ket or ket vector,  $|\alpha\rangle$  and the [hermitian adjoint](#) state as  $\psi_\alpha^\dagger$  or  $a_\alpha^\dagger$  or  $b_\alpha^\dagger$  with a bra or bra vector  $\langle \alpha |$ . Such a ket or bra is supposed to carry complete information about that physical state but in an entirely abstract sense; Dirac introduced this notation in 1939. Dirac's notation in which state function  $\psi$  is written as  $|\psi\rangle$  is convenient when we treat functions in a known set  $\psi_j$  and seek to emphasise the relations between functions with varied  $j$ ; symbol  $\psi$  is then omitted to leave  $|j\rangle$ . This notation expresses compactly integrals over all space that commonly arise in the theory or its practice, according to the following equivalences.

<u>wave mechanics</u>	<u>Dirac</u>
$\psi_j$	$ j\rangle$
$\psi_j^*$	$\langle j  $
$\int \psi_j^* A \psi_k d\tau$	$\langle j   A   k \rangle$

In the latter case  $A$  denotes some operator and integration is over all pertinent space. An [inner product](#) of two state vectors, written  $\psi_\alpha^\dagger \psi_\beta = \langle \alpha | \beta \rangle$ , is called a bracket, which is or represents a number.

Operation on a ket vector from the left with  $A$  produces another ket vector,  $A | \beta \rangle = | \beta' \rangle$ , or analogously on a bra vector from the right produces another bra vector,  $\langle \alpha | A = \langle \alpha' |$ . A matrix element of  $A$  between states  $\alpha$  and  $\beta$  is a number and is expressible as  $\langle \alpha | A | \beta \rangle = \langle \alpha | \beta' \rangle = \langle \alpha' | \beta \rangle$ . The operators  $a$  and  $b$  or  $a^\dagger$  on these ket and bra quantities are alternatively described as ladder operators to indicate their effect on stationary states: the raising operator adds a quantum of energy or angular momentum to a system, and the lowering operator removes a quantum of energy or angular momentum. In some contexts, the use of these operators is known as *second quantization*; the first quantization applies to the energies of molecules, the second to quantization of the radiation field. In our calculations the use of abstract operators is impracticable with *Maple*; an operator must invariably operate on a function. In a commutation relation, any operator must act on a function, such as a *bra* or

*ket*, whether that function be an eigenfunction of that operator is irrelevant.

If particles in some set be indistinguishable, their hamiltonian is invariant to permutations of these particles; dynamical states that differ only by a permutation of identical particles can not be distinguished with any observation. According to a postulate of symmetry related to the indistinguishability of particles, particles of which the intrinsic angular momentum is an integer multiple of  $\frac{h}{2\pi}$ , or zero, have only symmetric states, are called bosons and are subject to Bose-Einstein statistics, whereas particles of which the intrinsic angular momentum is a half odd integer multiple of  $\frac{h}{2\pi}$  have only antisymmetric states, are called fermions and are subject to Fermi-Dirac statistics; partially symmetric states do not exist. The operators for creation and destruction treated here are formally appropriate for operations on bosons.

Creation and destruction operators can act on states of particles of various types. A destruction operator decreases the number of particles in a given state by unity; a creation operator increases the number of particles in a given state by unity, and is the adjoint of the destruction operator. In many subfields of physics and chemistry in which the use of these operators, instead of amplitude functions, is known as *second quantization*, these operators can server to represent

- phonons, which are collective excitations in a periodic, elastic arrangement of atoms or molecules in condensed matter, such as a solid or some liquid, or
- plasmons that are collective excitations of electrons associated with mobile electrons in a fixed lattice of ions, or
- magnons that are produced from 'spin' waves in magnetic materials, or
- polarons produced by an electron and lattice distortion that forms a polarization field.

In each case, a wave field becomes *quantized* so that the problem is described in terms of an occupation number of a particle. In quantum chemistry and many-body theory, these creation and destruction operators might act on electron states. They can also refer specifically to ladder operators for the quantum canonical linear harmonic oscillator, as we apply in succeeding subsections. In the latter case, the raising operator is interpreted as a creation operator, adding a quantum of energy to the oscillator system, and the lowering operator is interpreted as a destruction operator, removing a quantum of energy from the oscillator system. A state of a system might be defined with the number of quanta or particles in each allowed mode; a creation or destruction operator enables particles to be added or subtracted from the physical state, and a 'vacuum' state of fixed energy constitutes the state of the system with least energy.

cf. J. S. Avery, *Creation and Annihilation Operators*, McGraw-Hill, New York, USA, 1976

To implement the required operations on quantities bra and ket, we apply procedures below that are designed for this purpose; alternative operations are practicable with the content of various commands in *Maple* package [physics](#).

### 1.241 procedures

These procedures were developed with kind assistance from G. J. Fee. This procedure **&\*** defines an operator for multiplication involving non-commuting quantities, each of which must be defined in a preceding list named **Operators**.

```
> `&*` := proc()  
    local C, CT, d, i, j, k, Largs, n, t, x;  
    option remember, system;  
    if type( [args], 'list'('And'('name', 'operator')) ) then
```

```

    ``&*``(args);
else
    t := NULL;
    C := 1;
    Largs := [args];
    n := nops(Largs);
    for i to n do
        x := Largs[i];
        if not type( x, 'operator' ) then
            C := C*x;
        elif type( x, 'name' ) then
            t := t, x;
        elif type( x, ``*`` ) then
            CT, d := selectremove( 'type', x, 'Not'('operator') );
            C := C*CT;
            if type( d, 'specfunc'('anything', ``&*``) ) then
                t := t, op(d);
            else
                t := t, d;
            end if;
        elif type( x, 'specfunc'('anything', ``&*``) ) then
            t := t, op(x);
        elif type( x, `+`) then
            return add(procname(seq(Largs[j], j=1..i-1), op(k, x),
                seq(Largs[j], j=i+1..n)), k=1..nops(x));
        else
            t := t, x;
        end if;
    end do;
    if t = NULL then
        C;
    elif nops([t]) = 1 then
        C * t;
    else
        C * procname( t );
    end if;
end if;
end proc:

```

This procedure  $\&^{\wedge}$  defines the raising of a non-commuting quantity to a non-negative integer.

```

> ``&^`` := proc(a, n)
    if type(n, 'integer') then
        if n<0 then error "inverses undefined";

```



```

    else
      if n=0 then 1;
      elif n=1 then a;
      elif n=2 then a&*a;
      else (a&^(n-1))&*a;
      end if;
    end if;
  else '`&^`'(a, n);
end if;
end proc:

```

This procedure `type/operator` distinguishes operators, which must be defined in a list of name **Operators**, from other variables or quantities.

```

> `type/operator` := proc(x)
  if member(x, Operators) then
    true;
  elif type(x, {'name', 'numeric'}) then
    false;
  elif type(x, 'function') and op(0, x) = `&*` then
    true;
  elif type(x, {'+', `*`, `^`}) then
    member(true, map(procname, [op(x)]));
  else
    false;
  end if;
end proc:

```

This procedure `&c` defines a commutator  $[a, b] = a b - b a$  between non-commuting quantities  $a$  and  $b$ .

```

> `&c` := proc(a,b)
  radsimp(a&*b - b&*a);
end proc:

```

This procedure `type/ket` distinguishes an operator  $ket = | .. >$  from other quantities.

```

> `type/ket` := proc(x)
  if type(x, 'function') and op(0, x)='ket' then
    true;
  else false;
  end if;
end proc:

```

This procedure `type/bra` distinguishes an operator  $bra = < .. |$  from other quantities.

```

> `type/bra` := proc(x)
  if type(x, 'function') and op(0, x)='bra' then
    true;
  else false;

```

```

    end if;
end proc:

```

This procedure `evalapply/&*` extends a *Maple* operator `evalapply` for purposes required with non-commutative algebra.

```

> `evalapply/&*` := proc(f,L)
    local c,g,h,i,m,n;
    n := nops(f);
    m := nops(L);
    if m <> 1 then
        error "expecting one argument";
    end if;
    h := L[1];
    c := 1;
    for i from n by -1 to 1 do
        g := op(i,f);
        if type(g, 'operator') and type(g, 'procedure') then
            h := g(h);
        else
            c := c*g;
        end if;
    end do;
    c*h;
end proc:

```

This procedure `braket2` evaluates an inner product  $\langle n | m \rangle$ , in which  $\langle n |$  is Dirac's quantity called 'bra  $n$ ' and  $| m \rangle$  is Dirac's quantity called 'ket  $m$ ', according to Kronecker's delta function, such that  $\langle n | m \rangle = 1$  for normalisation if  $n = m$  or 0 for orthogonality otherwise.

```

> braket2 := proc(x,y)
    local k1,k2,kd,c,i,ib;
    if type(x, 'bra') and type(y, 'ket') then
        k1 := op(1,x);
        k2 := op(1,y);
        kd := k1 - k2;
        if type(kd, 'integer') then
            if kd=0 then 1
            else 0;
            end if;
        else
            'procname'(args);
        end if;
    elif type(x, `*`) then
        c := 1;
        for i in x do

```

```

        if has(i, 'bra') then
            ib := i;
        else c := c*i;
        end if;
    end do;
    c*procname(ib, y);
elif type(y, `*`) then
    c := 1;
    for i in y do
        if has(i, 'ket') then
            ib := i;
        else c := c*i;
        end if;
    end do;
    c*procname(x, ib);
elif type(x, `+`) then
    map(procname, x,y);
elif type(y, `+`) then
    map2(procname, x,y);
else
    'procname'(args);
end if;
end proc:

```

This procedure `braket3` to evaluate  $\langle .. | .. \rangle$  accepts three parameters or arguments, of which the first, on the left, denotes a state according to a *bra*, the second, in the middle, is a constant or an operator, and the third, on the right, denotes a state according to a *ket*. If the second argument be an operator, that operation on the *ket* is implemented with procedure `operator/apply`; the result is sent to procedure `braket2` for further evaluation.

```

> braket3 := proc(x,r,y)
    local ry;
    ry := `operator/apply`(r, ket(y));
    factor(simplify(radsimp(braket2(bra(x), ry))));
end proc:

```

This procedure applies an operation, according to a procedure named as first argument or parameter, to a quantity named as second argument or parameter; this procedure is invoked within procedure `braket3`.

```

> `operator/apply` := proc(a,x)
    local c,h,i,n;
    if type(a, 'procedure') then
        a(x);
    elif not type(a, 'operator') then
        a*x;
    elif type(a, `*`) then
        c := 1;

```

this procedure  $\&@$  applies an operator to a ket.

This procedure enables ordering of products of operators according to an order of those operators specified in `deforder`.

```
> ordering := proc(c)
    local a,b,d1,d2,i,ia,ib,j,n;
    if type(c, constant) then
        c;
    elif
        type(c, {`+`,`*`,`^`,`^`}) then
            map(procname, c);
    elif
        type(c, `&*`) then
            n := nops(c);
            for i to n-1 do
                a := op(i, c);
                ia := op_num[a];
                if not type(ia, integer) then
                    next;
                end if;
                j := i+1;
```

```

    b := op(j, c);
    ib := op_num[b];
    if not type(ib, integer) then
        next;
    end if;
    d1 := a &c b;
    d2 := '&c`(a, b);
    if d1 = d2 then
        next;
    end if;
    if ib < ia then
        return expand(procname('&*(seq(op(k, c), k=1..i-1),
            b,a, seq(op(k, c), k=i+2..n)) -
            '&*(seq(op(k, c), k=1..i-1), d1, seq(op(k, c),
                k=i+2..n)))));
    end if;
end do;
c;
elif type(c, '&^`) then
    map(procname, c);
elif type(c, function) then
    map(procname, c);
elif type(c, name) then
    c;
else
    error "invalid expression";
end if;
end proc:

```

Warning, (in ordering) `k` is implicitly declared local

This procedure defines the order of operators desired in output expressions.

```

> deforder := proc()
    local i,a;
    global op_num;
    for i to nargs do
        a := args[i];
        if type(a, operator) then
            op_num[a] := i;
        else
            error "Argument must be an operator";
        end if;
    end do;
end proc:

```

```
op_num := table():
```

These two procedures are utilities that are essential in ordering operators according to procedure **ordering** above.

```
> `type/&*` := proc(c)
    type(c, specfunc(anything,`&*`));
end proc:
> `type/&^` := proc(c)
    type(c, specfunc(anything,`&^`));
end proc:
```

This procedure defines a commutator and sets the result equal to a specified quantity:

$$[a, b] = a b - b a = d.$$

```
> def_c := proc(a,b,d)
    `&c` (b,a) := -d;
    `&c` (a,b) := d;
end proc:
```

This procedure defines a double commutator and sets the result equal to a specified quantity:

$$[a, [b, c]] = d.$$

```
> def_2c := proc(a,b,c,d);
    `&c`(`&c` (c,b), a) := d;
    `&c`(`&c` (b,c), a) := -d;
    `&c`(a, `&c` (c,b)) := -d;
    `&c`(a, `&c` (b,c)) := d;
end proc:
```

This procedure converts a list, as a conventional printed representation of a commutator such as  $[a, b]$ , into a commutator.

```
> list2commutator := proc(a::list)
    if nops(a) = 2 then
        a[1] &c a[2];
    else
        a
    end if;
end proc:
```

This procedure replaces a list of two elements by their commutator.

```
> list2com := proc(a)
    if type(a, list) then
        list2commutator(a)
    elif type(a, {numeric,symbol}) then
        a
    else
        map(procname, a)
    end if;
```

**end proc:**

This procedure truncates undesired terms according to a specified order.

```
> truncate := proc(c)
  if type(c, {'+', '*'}) then
    map(procname, c);
  elif type(c, constant) then
    c;
  elif type(c, '&*') then
    if nops(c) < Order then c else 0; end if;
  elif type(c, name) then
    c;
  else
    c;
  end if;
end proc;
```

This procedure converts a product  $\langle j | k \rangle$  of bra  $\langle j |$  and ket  $| k \rangle$  into a [Kronecker delta function](#), for which  $\delta_{j,k} = 1$  if  $j = k$  or  $\delta_{j,k} = 0$  otherwise.

```
> `convert/Krondelta` := proc(a)
  local a1,a2,b1,b2;
  if type(a,function) and op(0,a)=braket2 then
    a1 := op(1,a);
    a2 := op(2,a);
    if type(a1, function) and op(0,a1)=bra then
      b1 := op(1,a1);
    end if;
    if type(a2, function) and op(0,a2)=ket then
      b2 := op(1,a2);
    end if;
    if assigned(b1) and assigned(b2) then
      return Krondelta(b1,b2);
    else
      return a;
    end if;
  elif type(a, constant) or type(a, name) then
    a
  else
    map(procname, a)
  end if;
end proc;
```

This procedure evaluates a Kronecker delta function  $\delta_{j,k}$  according to the relative symbolic values of  $j$  and  $k$ .

```

> Krondelta := proc(a,b)
  local c;
  c := b-a;
  if type(c,integer) then
    if c=0 then
      1
    else
      0
    end if;
  else
    'procname'(args);
  end if;
end proc:

```

This procedure alters the effect of the evaluation of the Kronecker delta function on bra  $\langle j |$  and ket  $| k \rangle$ .

```

> `simplify/Krondelta` := proc(a)
  local a1,a2,ia,r;
  if type(a,function) and op(0,a) = Krondelta then
    a1 := op(1,a);
    a2 := op(2,a);
    if type(a2,name) or type(a2,constant) then
      return a;
    elif type(a2,`+`) then
      ia := indets(a2, name);
      if nops(ia) = 1 then
        ia := op(1,ia);
      else
        return a;
      end if;
      r := solve(a1=a2, ia);
      return Krondelta(r,ia);
    end if;
  elif type(a, constant) or type(a, name) then
    a;
  else
    map(procname, a);
  end if;
end proc:

```

This procedure prints a Kronecker delta function in a conventional manner.

```

> `print/Krondelta` := proc(a,b)
  delta[a,b]
end proc:

```



## 1.242 application to canonical linear harmonic oscillator

> # no restart here!

The physical state of a system, of which an index is denoted  $n$ , is represented in a dual space of complex vectors according to quantities *ket*, denoted  $|n\rangle$ , and *bra*, denoted  $\langle n|$ ; such a ket or bra is supposed to carry, in an abstract sense, complete information about that physical state. An observable property of a system is represented by an operator, such as  $A$ , that acts on a ket, represented as  $A|n\rangle$ , to yield another ket. An inner product  $\langle m|n\rangle$  of a bra and a ket is in general a complex number, and  $\langle m|n\rangle = \langle n|m\rangle^*$

in which  $*$  implies a complex conjugate. Two kets are orthogonal if an inner product of one ket with a bra corresponding to the other equal zero, so  $\langle m|n\rangle = 0$ , hence with  $|n\rangle$  orthogonal to  $\langle m|$ ; a ket is normalised if the corresponding inner product equal unity, so  $\langle n|n\rangle = 1$ . An outer product  $|m\rangle\langle n|$  acts as an operator, such as in  $(|m\rangle\langle n|)|l\rangle$  that evaluates to  $|m\rangle(\langle n|l\rangle)$  in which the inner product, according to the content between parentheses, is simply a number or a quantity that evaluates to a number; an outer product acting on a ket hence produces another ket, just like an operator. These operators are linear, in the sense that  $A(|m\rangle + |n\rangle) = A|m\rangle + A|n\rangle$ .

We postulate operators for creation and destruction that can act on states of particles, represented as ket or bra with vectorial sense, of various types, such as fermions with half-integer intrinsic angular momentum or bosons with integer intrinsic angular momentum, but their properties differ for these two types. We design and form procedures to implement these properties. We first specify in a list the names of operators on bosons that fail to commute according to multiplication.

> Operators := [a,b,N,p,q];

*Operators := [a, b, N, p, q]*

(10.2.1)

According to Dirac's formalism, for a canonical linear harmonic oscillator we proceed to define two operators, one for *destruction*,  $a$ , and another for *creation*,  $b$ , accordingly implemented with two additional procedures, for specific application to the canonical linear harmonic oscillator. The first procedure, of name  $a$ , implements an operation on a state of which a *ket* or  $|>$  is named as argument of this procedure; also known as a *lowering* operator, this particular operator is Dirac's operator  $a$  for destruction, such that its operation on a ket of a particular state decreases a population of that state to which it is applied by one unit and increases accordingly the population of an adjacent state of one unit less, with a normalising factor  $\sqrt{n}$  as follows.

$a|n\rangle = \sqrt{n}|n-1\rangle$  with a scalar multiplicand  $\sqrt{n}$  for  $n > 0$ ,  
and a special case  $a|0\rangle = 0$ .

```
> a := proc(x)
  local n;
  if type(x, 'ket') then
    n := op(1,x);
    if n = 0 then 0 else
      sqrt(n)*ket(n-1);
    end if;
  elif type(x, {'*', '+', '^'}) then
    map(procname, x);
  else x;
  end if;
end proc;
```

Another procedure has as name  $b$ , replacing  $a$  with suffixed superscript *dagger*, like  $a^\dagger$ , that is unprintable here, and implements its operation on a state of which a *ket* or  $|>$  is named as argument of this procedure; this particular quantity is Dirac's operator for creation, such that its operation increases a population of a particular state to which it is applied, as the argument of the procedure, by one unit and decreases accordingly the population of an adjacent state of one unit greater, with its normalising factor  $\sqrt{n+1}$ , also known as a raising operator,

$$b |n> = \sqrt{n+1} |n+1>, \text{ with a scalar multiplicand } \sqrt{n+1}.$$

```
> b := proc(x)
  local n;
  if type(x, 'ket') then
    n := op(1,x) + 1;
    sqrt(n)*ket(n);
  elif type(x, {'*', '+', '^'}) then
    map(procname, x);
  else x;
  end if;
end proc;
```

We test both operators  $a$  and  $b$ .

```
> `a |n>` = a &@ ket(n);
```

$$a |n> = \sqrt{n} \text{ ket}(n-1) \quad (10.2.2)$$

```
> `b |n>` = b &@ ket(n);
```

$$b |n> = \sqrt{n+1} \text{ ket}(n+1) \quad (10.2.3)$$

Being satisfied that these operators work as designed, we next test the commutation property, by operating consecutively with first  $a$ ,

```
> `a |n>` = a &@ ket(n);
```

$$a |n> = \sqrt{n} \text{ ket}(n-1) \quad (10.2.4)$$

then on that result with  $b$ ,

```
> `b a |n>` = b &@ rhs(%);
```

$$b a |n> = n \text{ ket}(n) \quad (10.2.5)$$

then in the reverse order,

```
> `b |n>` = b &@ ket(n);
```

$$b |n> = \sqrt{n+1} \text{ ket}(n+1) \quad (10.2.6)$$

```
> `a b |n>` = factor(a &@ rhs(%));
```

$$a b |n> = (n+1) \text{ ket}(n) \quad (10.2.7)$$

and find the difference between the results.

```
> factor(rhs(%%) - rhs(%));
```

$$-\text{ket}(n) \quad (10.2.8)$$

The products, in one or other order, of these creation and destruction operators, as defined and implemented above, clearly fail to commute, and thereby become suitable for the purpose of quantum-

mechanical operations according to the fundamental postulate of quantum mechanics. The effect of the preceding five commands is to prove that

$$b a - a b = -1 .$$

in which form operations on appropriate kets are implicit.

Auxiliary operator  $N$  that is defined as  $b a$  is called also a number operator because its operation on a state with  $ket\ n$ , with  $\&*$  as operator between  $b$  and  $a$ ,

$$\begin{aligned} > N := b \&* a; \\ N &:= b \&* a \end{aligned} \quad (10.2.9)$$

$$\begin{aligned} > `N | n >` = N \&@ ket(n); \\ N | n > &= n ket(n) \end{aligned} \quad (10.2.10)$$

returns that state with factor  $n$ ; so  $b a | n > = N | n > = n | n >$ . This relation has the form of an eigenvalue equation, with linear operator  $N$ , eigenvector  $| n >$  and eigenvalue  $n$ ; the eigenvalues of this operator are non-negative integers. Repeated use of  $b$ , or analogously  $a$ , yields these results.

$$\begin{aligned} > `b | n >` = b \&@ ket(n); \\ b | n > &= \sqrt{n+1} ket(n+1) \end{aligned} \quad (10.2.11)$$

Here  $\%$  denotes the preceding output.

$$\begin{aligned} > `b b | n >` = b \&@ rhs(%); \\ b b | n > &= \sqrt{n+1} \sqrt{n+2} ket(n+2) \end{aligned} \quad (10.2.12)$$

$$\begin{aligned} > `b b b | n >` = b \&@ rhs(%); \\ b b b | n > &= \sqrt{n+1} \sqrt{n+2} \sqrt{n+3} ket(n+3) \end{aligned} \quad (10.2.13)$$

$$\begin{aligned} > `a | n >` = a \&@ ket(n); \\ a | n > &= \sqrt{n} ket(n-1) \end{aligned} \quad (10.2.14)$$

$$\begin{aligned} > `a a | n >` = a \&@ rhs(%); \\ a a | n > &= \sqrt{n} \sqrt{n-1} ket(n-2) \end{aligned} \quad (10.2.15)$$

$$\begin{aligned} > `a a a | n >` = a \&@ rhs(%); \\ a a a | n > &= \sqrt{n} \sqrt{n-1} \sqrt{n-2} ket(n-3) \end{aligned} \quad (10.2.16)$$

In raising to a power an operator that is a non-commuting quantity, we must use  $\&^$  rather than  $^$ , just as in forming a product in which multiplicands are non-commuting operators we must use  $\&*$  rather than  $*$ .

We hence obtain the same result directly by operating on  $| n >$  with operator  $b$  cubed;

$$\begin{aligned} > `b^3 | n >` = b\&^3 \&@ ket(n); \\ b^3 | n > &= \sqrt{n+1} \sqrt{n+2} \sqrt{n+3} ket(n+3) \end{aligned} \quad (10.2.17)$$

$$\begin{aligned} > `a^3 | n >` = a\&^3 \&@ ket(n); \\ a^3 | n > &= \sqrt{n} \sqrt{n-1} \sqrt{n-2} ket(n-3) \end{aligned} \quad (10.2.18)$$

The preceding results are general, resulting from merely the definitions of  $a$  and  $b$  as operators for destruction and creation, or equivalently for lowering and raising.

One approach to obtain the eigenvalues corresponding to energy associated with hamiltonian operator  $H$  applies operator  $N$  as follows. For state  $| n >$  that yields eigenvalue  $N | n > = n ket(n)$  as

above, with a normalised state such that  $\langle n | n \rangle = 1$ , it follows that

$$n = \langle n | N | n \rangle = \langle n | b a | n \rangle = \langle a n | a n \rangle \geq 0,$$

in which  $\langle n | N | n \rangle$  denotes a bracket quantity as evaluated below, so that the eigenvalues of  $N$  are non-negative and that there must exist a smallest eigenvalue  $n_0$ . According to the latter relation, we define of

operator  $a$  a norm as  $\|a | n \rangle\|^2 = \langle n | b a | n \rangle = n$  and  $\|b | n \rangle\|^2 = \langle n | a b | n \rangle = n + 1$ . Applying

$$N b | n \rangle = b a b | n \rangle = b (b a + 1) | n \rangle = (n + 1) b | n \rangle,$$

analogously,  $N a | n \rangle = (n - 1) a | n \rangle$ .

$$\langle n | a | n \rangle = 0, \quad \langle n | a^2 | n \rangle = 0, \quad \langle n | a^3 | n \rangle = 0, \quad \dots$$

$$\|a | n \rangle\|^2 = n \quad (10.2.19)$$

$$\langle n | b | n \rangle = 0, \quad \langle n | b^2 | n \rangle = 0, \quad \langle n | b^3 | n \rangle = 0, \quad \dots$$

$$\|b | n \rangle\|^2 = n + 1 \quad (10.2.20)$$

Operating repeatedly with  $a$ , as above, yields states in a sequence with eigenvalues  $(n - 1), (n - 2), \dots$  until a least eigenvalue  $n_0$ , for which  $a | n_0 \rangle = 0$ . As  $N | n_0 \rangle = b a | n_0 \rangle = 0$ , state  $| n_0 \rangle$  has eigenvalue 0; the eigenvalues of  $N$  are 0, 1, 2, ... Operation of operator  $a$  on a bra is equivalent to operation of  $b$  on a ket:  $\langle n | a = \langle b n |$ , as applied above. After we split the hamiltonian, below, we find the energy eigenvalues of the hamiltonian of the oscillator.

For our application on the canonical linear harmonic oscillator as a boson with zero intrinsic angular momentum, we must relate the creation and destruction operators, defined above, to the mechanical variables coordinate and momentum. We assume that a hamiltonian divided by a characteristic energy can be factored into complex multiplicands: one such multiplicand becomes an operator for creation, named  $a^\dagger$  or  $b$  below; the other becomes an operator for destruction, named  $a$ . The operation of first  $a$  and then  $b$  on a ket, operating from right to left, must yield the energy relative to a particular state, but the intermediate result with only  $a$  is found to be the decreased population of that state by one unit, as shown above; the second and separate application of  $b$  must hence increase the population by one unit, so as to leave the resulting ket to be identical with the initial ket. According to that assumption, of two operators  $a$  for destruction and  $b$  for creation from the hamiltonian, their product  $b a$  operating on a ket of a particular state clearly yields the energy of that state divided by the characteristic energy; that product  $b a$  that contains implicit division by a characteristic energy causes its operation on a ket pertaining to a state to yield a dimensionless quantity, a number denoting the energy of that state in terms of that characteristic energy. We express the hamiltonian as

$$H = \frac{p^2}{2\mu} + \frac{1}{2} k_e q^2.$$

Force coefficient  $k_e$  for a canonical linear harmonic oscillator we express in terms of angular frequency

$\omega_0$ , as  $\omega_0 = \sqrt{\frac{k_e}{\mu}}$ , or circular frequency  $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k_e}{\mu}}$ . We rewrite accordingly the hamiltonian as

$$H = \frac{p^2}{2\mu} + \frac{4\pi^2 \nu_0^2 \mu q^2}{2\mu},$$

applying the fact that

$$k_e = 4\pi^2 \nu_0^2 \mu,$$

and retaining product  $2 \mu$  in the denominator. To eliminate the dimensions from this hamiltonian formula that has the dimension of energy, we divide the entire formula by a characteristic energy,  $h v_0 =$

$$\frac{h}{2 \pi} \sqrt{\frac{k_e}{\mu}}.$$

$$\frac{H}{h v_0} = \frac{\frac{p^2}{2 \mu} + \frac{4 \pi^2 v_0^2 \mu^2 q^2}{2 \mu}}{h v_0}$$

```
> H/(h*nu[0]) = (p^2/(2*mu)+4*Pi^2*nu[0]^2*mu^2*q^2/(2*mu))/(h*nu[0]);
```

$$\frac{H}{h v_0} = \frac{\frac{p^2}{2 \mu} + 2 \pi^2 v_0^2 \mu q^2}{h v_0} \quad (10.2.21)$$

We then factor the resulting expression over the complex domain, to yield, with  $I = \sqrt{-1}$ ,

```
> H/(h*nu[0]) = PolynomialTools[Split](numer(rhs(%)), p)/denom(rhs(%));
```

$$\frac{H}{h v_0} = \frac{2 \left( \mu q v_0 \pi - \frac{\text{RootOf}(\_Z^2 + 1) p}{2} \right) \left( \mu q v_0 \pi + \frac{\text{RootOf}(\_Z^2 + 1) p}{2} \right)}{\mu h v_0} \quad (10.2.22)$$

```
> H/(h*nu[0]) = convert(rhs(%), radical);
```

$$\frac{H}{h v_0} = \frac{2 \left( \mu q v_0 \pi - \frac{I p}{2} \right) \left( \mu q v_0 \pi + \frac{I p}{2} \right)}{\mu h v_0} \quad (10.2.23)$$

so

$$\frac{H}{h v_0} = - \frac{(p I + 2 \mu v_0 q \pi) (p I - 2 \mu v_0 q \pi)}{2 h \mu v_0}.$$

We separate the multiplicands in the numerator, and take the square root of the denominator,  $2 \mu h v_0$ , as  $\sqrt{2 \mu h v_0}$ ; we apportion this quantity equally to each factor of the numerator, yielding these results for the two factors,

```
> f1 := 2*(op(2, rhs(%))/(sqrt(denom(rhs(%)))));
```

$$f1 := \frac{\left( \mu q v_0 \pi - \frac{I p}{2} \right) \sqrt{2}}{\sqrt{\mu h v_0}} \quad (10.2.24)$$

```
> f2 := 2*op(3, 2*rhs(%))/(sqrt(denom(rhs(%))));
```

$$(10.2.25)$$

$$f2 := \frac{\left(\mu q v_0 \pi + \frac{I p}{2}\right) \sqrt{2}}{\sqrt{\mu h v_0}} \quad (10.2.25)$$

which are evidently mutually complex conjugate. We define  $b$  as the quantity of the two above that contains a minus sign, and  $a$  as the other quantity. To avoid problems with infinite recursion of names, we use ``p``, ``q``, ``a`` and ``b`` to exhibit the properties of these quantities without affecting the corresponding operators.

```
> `b` := select(has, {f1, f2}, -1/2*I);
```

$$b := \left\{ \frac{\left(\mu q v_0 \pi - \frac{I p}{2}\right) \sqrt{2}}{\sqrt{\mu h v_0}} \right\} \quad (10.2.26)$$

```
> `a` := select(has, {f1, f2}, +1/2*I);
```

$$a := \left\{ \frac{\left(\mu q v_0 \pi + \frac{I p}{2}\right) \sqrt{2}}{\sqrt{\mu h v_0}} \right\} \quad (10.2.27)$$

With destruction operator  $a$  and creation operator  $b$  defined in terms of momentum  $p$  and coordinate  $q$  in appropriate combinations, we proceed to perform calculations of expectation values and matrix elements of a canonical linear harmonic oscillator as in preceding treatments with matrix mechanics and wave mechanics.

Taking  $a$  and  $b$  to be expressible according to the particular formulae presented in the text above as factors of the hamiltonian of the canonical harmonic oscillator divided by  $h v_0$ , we solve for the general coordinate,  $q$ , and general momentum,  $p$ , variables,

```
> sol := solve({a = 1/2*(`p`*I+2*Pi*mu*`q`*nu[0])*2^(1/2)/(mu*h*nu[0])^(1/2),
               b = 1/2*(2*Pi*mu*`q`*nu[0]-I*`p`)*2^(1/2)/(mu*h*nu[0])^(1/2)}, {`p`, `q`});
```

$$sol := \left\{ p = -\frac{I}{2} \sqrt{\mu h v_0} (a - b) \sqrt{2}, q = \frac{\sqrt{\mu h v_0} (a + b) \sqrt{2}}{4 \pi \mu v_0} \right\} \quad (10.2.28)$$

which we implement with general coordinate  $q$  as defined in terms of creation  $b$  and destruction  $a$  operators,

```
> q := subs(sol, `q`);
```

$$q := \frac{\sqrt{\mu h v_0} (a + b) \sqrt{2}}{4 \pi \mu v_0} \quad (10.2.29)$$

and general momentum  $p$  as a conjugate quantity defined in terms of creation and destruction operators as

```
> p := subs(sol, `p`);
```

(10.2.30)

$$p := -\frac{I}{2} \sqrt{\mu h v_0} (a - b) \sqrt{2} \quad (10.2.30)$$

When we solve for  $a$  and  $b$  in those two relations for  $p$  and  $q$ ,

```
> sol2 := simplify(expand(subs(pp=`p`, qq=`q`, solve({pp=p, qq=q},
{a, b}))), symbolic);
```

$$sol2 := \left\{ a = \frac{(Ip + 2\pi\mu q v_0) \sqrt{2}}{2\sqrt{\mu} \sqrt{h} \sqrt{v_0}}, b = -\frac{(-2\pi\mu q v_0 + Ip) \sqrt{2}}{2\sqrt{\mu} \sqrt{h} \sqrt{v_0}} \right\} \quad (10.2.31)$$

we find that  $a$  and  $b$  are precisely complex conjugates of each other, as above. The product of these two quantities,

```
> subs(sol2, a);
```

$$\frac{(Ip + 2\pi\mu q v_0) \sqrt{2}}{2\sqrt{\mu} \sqrt{h} \sqrt{v_0}} \quad (10.2.32)$$

```
> subs(sol2, b);
```

$$-\frac{(-2\pi\mu q v_0 + Ip) \sqrt{2}}{2\sqrt{\mu} \sqrt{h} \sqrt{v_0}} \quad (10.2.33)$$

```
> subs(sol2, `(a)*`(b)) = expand(subs(sol2, a*b));
```

$$\left( \frac{(Ip + 2\pi\mu q v_0) \sqrt{2}}{2\sqrt{\mu} \sqrt{h} \sqrt{v_0}} \right) \left( -\frac{(-2\pi\mu q v_0 + Ip) \sqrt{2}}{2\sqrt{\mu} \sqrt{h} \sqrt{v_0}} \right) = \frac{2\mu v_0 \pi^2 q^2}{h} + \frac{p^2}{2\mu h v_0} \quad (10.2.34)$$

is precisely  $\frac{H}{h v_0}$ , which we recall from above,

```
> H/(h*nu[0]) = expand((`p`^2/(2*mu) + 4*Pi^2*nu[0]^2*mu^2*`q`
^2/(2*mu))/(h*nu[0]));
```

$$\frac{H}{h v_0} = \frac{2\mu v_0 \pi^2 q^2}{h} + \frac{p^2}{2\mu h v_0} \quad (10.2.35)$$

```
> is(rhs(%) = rhs(%));
```

*true* (10.2.36)

demonstrating the correctness and consistency of the derivation.

To find the energies of this system of a canonical linear harmonic oscillator, we recall the hamiltonian,

$$H = \frac{p^2}{2\mu} + \frac{k_e q^2}{2},$$

in which we replace  $k_e$  with its equivalent involving  $v_0$  and  $\mu$ .

```
> k[e] := 4*Pi^2*nu[0]^2*mu;
```

$$k_e := 4 \pi^2 v_0^2 \mu \quad (10.2.37)$$

and express that hamiltonian in terms of creation and destruction operators through the above assignments of  $p$  and  $q$ .

$$\begin{aligned} & > \text{H} := 1/(2*\mu)*p\&^2 + 1/2*k[e]*q\&^2; \\ H &:= - \frac{\hbar v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} \\ & + \frac{v_0 \hbar (a \&* a + a \&* b + b \&* a + b \&* b)}{4} \end{aligned} \quad (10.2.38)$$

The operation of a hamiltonian as operator within a bracket, or combination of *bra* and *ket*, of the same state yields the energy of that state, hence as an expectation value;

$$\begin{aligned} & > \text{`< n | H | n >`} = \text{factor}(\text{expand}(\text{braket3}(n, H, n))); \\ & \text{< n | H | n >} = \frac{\hbar v_0 (1 + 2n)}{2} \end{aligned} \quad (10.2.39)$$

$$\begin{aligned} & > \text{`< n-1 | H | n-1 >`} = \text{braket3}(n-1, H, n-1); \\ & \text{< n-1 | H | n-1 >} = \frac{\hbar v_0 (-1 + 2n)}{2} \end{aligned} \quad (10.2.40)$$

$$\begin{aligned} & > \text{`< n+1 | H | n+1 >`} = \text{braket3}(n+1, H, n+1); \\ & \text{< n+1 | H | n+1 >} = \frac{\hbar v_0 (3 + 2n)}{2} \end{aligned} \quad (10.2.41)$$

we alternatively apply this hamiltonian operator directly on a ket,  $|n\rangle$ ,

$$\begin{aligned} & > \text{`H |n>`} = \text{factor}(H \&@ \text{ket}(n)); \\ & H|n\rangle = \frac{\hbar v_0 \text{ket}(n) (1 + 2n)}{2} \end{aligned} \quad (10.2.42)$$

which confirms that states  $|n\rangle$  are eigenstates of the hamiltonian operator, just as for  $H \psi_n = E_n \psi_n$  in wave mechanics.  $N|n\rangle = n|n\rangle$  differs from  $\frac{H}{\hbar v_0} |n\rangle = (n + \frac{1}{2}) |n\rangle$ ; the difference is  $\frac{1}{2} |n\rangle$ , as we show here.

We apply these formulae for  $p$  and  $q$  to evaluate quantities known as expectation values and matrix elements of momentum and coordinate, respectively, just like the usage in the preceding sections on matrix mechanics, section 1.22, and on wave mechanics, section 1.23; the connexions to matrix mechanics and wave mechanics appear in this equality for  $q$ ,

$$\begin{aligned} q_{n,n} &= \text{< n | q | n >} = \int_{-\infty}^{\infty} \psi_n q \psi_n dq \\ q_{n,m} &= \text{< m | q | n >} = \int_{-\infty}^{\infty} \psi_m q \psi_n dq \end{aligned}$$

and similarly for expectation values or matrix elements of other quantities. We form matrix elements



for a particular state, hence expectation values, first for quantities  $q$  and  $p$  to the first power with their corresponding results of operations on  $|n\rangle$  for comparison,

$$> \text{'q' | n>} = \text{factor(q \& ket(n));}$$

$$q |n\rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) + \sqrt{n+1} \text{ket}(n+1))}{4 \pi \mu v_0} \quad (10.2.43)$$

$$> \text{'< n | q | n >'} = \text{braket3(n, q, n);}$$

$$\langle n | q | n \rangle = 0 \quad (10.2.44)$$

$$> \text{'p' | n>} = \text{factor(p \& ket(n));}$$

$$p |n\rangle = -\frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1)) \quad (10.2.45)$$

$$> \text{'< n | p | n >'} = \text{braket3(n, p, n);}$$

$$\langle n | p | n \rangle = 0 \quad (10.2.46)$$

and then of  $q$  and  $p$  to the second power.

$$> \text{'q^2' * '| n>'} = \text{factor(q\&^2 \& ket(n));}$$

$$q^2 |n\rangle \quad (10.2.47)$$

$$= \frac{h (\sqrt{n} \sqrt{n-1} \text{ket}(n-2) + 2n \text{ket}(n) + \text{ket}(n) + \sqrt{n+1} \sqrt{n+2} \text{ket}(n+2))}{8 \mu v_0 \pi^2}$$

$$> \text{'< n | ' * 'q^2' * '| n >'} = \text{braket3(n, q\&^2, n);}$$

$$\langle n | q^2 | n \rangle = \frac{h (1 + 2n)}{8 \mu v_0 \pi^2} \quad (10.2.48)$$

$$> \text{'p^2' * '| n>'} = \text{factor(p\&^2 \& ket(n));}$$

$$p^2 |n\rangle = \quad (10.2.49)$$

$$-\frac{1}{2} (\mu h v_0 (\sqrt{n} \sqrt{n-1} \text{ket}(n-2) - 2n \text{ket}(n) - \text{ket}(n) + \sqrt{n+1} \sqrt{n+2} \text{ket}(n+2)))$$

$$> \text{'< n | ' * 'p^2' * '| n >'} = \text{braket3(n, p\&^2, n);}$$

$$\langle n | p^2 | n \rangle = \frac{\mu h v_0 (1 + 2n)}{2} \quad (10.2.50)$$

The expectation value of kinetic energy is  $\langle \frac{p^2}{2\mu} \rangle$ ,

$$> \text{'< n | ' * 'p^2' * '| n >' / (2*mu)} = \text{braket3(n, p\&^2, n) / (2*mu);}$$

$$\frac{\langle n | p^2 | n \rangle}{2\mu} = \frac{h v_0 (1 + 2n)}{4} \quad (10.2.51)$$

The expectation value of potential energy is  $\langle \frac{1}{2} k_e q^2 \rangle = \langle \frac{1}{2} q^2 (4 \pi^2 \mu v_0^2) \rangle$ , for which purpose we replace  $k_e$  with its equivalent involving  $v_0$  and  $\mu$ .

```
> 1/2 * k[e] * `

```

$$2 \pi^2 v_0^2 \mu \langle n | q^2 | n \rangle = \frac{h v_0 (1 + 2 n)}{4} \quad (10.2.52)$$

The result shows that  $\langle \text{potential energy} \rangle = \langle \text{kinetic energy} \rangle$ , i.e. the expectation values of these quantities in any state defined with quantum number  $n$  of this canonical linear harmonic oscillator are equal, in accordance with the *virial theorem* in quantum mechanics. This theorem states that, for a potential energy that depends on distance according to  $r^n$ , the expectation value of kinetic energy, which is expressed as  $\langle \frac{p^2}{2m} \rangle$ , equals  $\frac{n}{2}$  times the expectation value of potential energy, expressed as  $\langle V \rangle$ .

In the case of the canonical linear harmonic oscillator, the potential energy has the form  $\sim q^2$ , which means that  $n=2$  and so  $\langle \frac{p^2}{2m} \rangle = \langle V \rangle$ , and the total energy =  $\langle \frac{p^2}{2m} \rangle + \langle V \rangle$ , as derived above. In contrast, for the H atom, the potential energy has the form  $\frac{1}{r}$ , which means that  $n = -1$  and  $\langle \frac{p^2}{2m} \rangle = -\frac{1}{2} \langle V \rangle$ , so that the total energy =  $\frac{1}{2} \langle V \rangle$ , i.e. the total energy is half the potential energy.

For an important derivation we apply our quantities defined above as follows. The variance of quantity  $x$  that is defined as  $\sigma_x^2$  equals the difference of expectation values of  $\langle x^2 \rangle$  and  $\langle x \rangle^2$ , so

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2;$$

the square root of the variance is the standard deviation  $\sigma_x$ . In terms of Dirac's approach, an expectation value  $\langle x \rangle$  is simply  $\langle n | x | n \rangle$ . For quantity  $q$  as an operator, we have therefore

```
> `

$$\langle n | q^2 | n \rangle = \frac{h (1 + 2 n)}{8 \mu v_0 \pi^2} \quad (10.2.53)$$


```

```
> `

$$\langle n | q | n \rangle^2 = 0 \quad (10.2.54)$$


```

```
> sigma['q'] := sqrt(rhs(%%) - rhs(%));
```

$$\sigma_q := \frac{\sqrt{2} \sqrt{\frac{h (1 + 2 n)}{\mu v_0}}}{4 \pi} \quad (10.2.55)$$

For quantity  $p$  we have correspondingly

```
> `

```

-----

$$\langle n | p^2 | n \rangle = \frac{\mu h v_0 (1 + 2n)}{2} \quad (10.2.56)$$

$$\begin{aligned} &> \langle n | p | n \rangle^2 = \text{braket3}(n, p, n)^2; \\ &\quad \langle n | p | n \rangle^2 = 0 \end{aligned} \quad (10.2.57)$$

$$\begin{aligned} &> \text{sigma['p']} := \sqrt{\text{rhs}(\%) - \text{rhs}(\%)}; \\ &\quad \sigma_p := \frac{\sqrt{2} \sqrt{\mu h v_0 (1 + 2n)}}{2} \end{aligned} \quad (10.2.58)$$

The product of these two quantities  $\sigma_p \sigma_q$  is thus

$$\begin{aligned} &> \text{'sigma'['p']} * \text{'sigma'['q']} = \text{simplify}(\text{sigma['p']} * \text{sigma['q']}) \\ &\quad \text{assuming positive;} \\ &\quad \sigma_p \sigma_q = \frac{2 h n + h}{4 \pi} \end{aligned} \quad (10.2.59)$$

The latter result, which is expressible as

$$\sigma_p \sigma_q = \frac{1}{2} \left( n + \frac{1}{2} \right) \frac{h}{2 \pi},$$

has thus its minimum value for  $n = 0$ . This formula becomes thus

$$\sigma_p \sigma_q \geq \frac{1}{2} \frac{h}{2 \pi}$$

or

$$\Delta p \Delta q \geq \frac{1}{2} \frac{h}{2 \pi},$$

which is known as Heisenberg's *principle of indeterminacy* and which has general applicability, not merely to a canonical linear harmonic oscillator: any couple of non-commuting and self-adjoint operators, such as  $p$  and  $q$ , that represent observable quantities are subject to this constraint, such that the minimum product of their uncertainties, such as  $\sigma_p$  and  $\sigma_q$  or  $\Delta p$  and  $\Delta q$ , is  $\frac{1}{2} \frac{h}{2 \pi}$ . The distinction

between indeterminacy and uncertainty implies that there is a fundamental limit to the accuracy of a simultaneous determination of two such non-commuting quantities, independent of the uncertainty of any particular observer or measurement. Conversely, the addend  $\frac{1}{2}$  of  $n$ , implying a residual energy,

for the energy in  $E_n = \left( n + \frac{1}{2} \right) h v_0$  might be considered to be present as a result of indeterminacy.

A product of complementary variables energy  $E$  and time  $t$  has the dimensions of Planck's constant  $h$ , like a product of  $p$  and  $q$ ; a corresponding relation  $\Delta E \Delta t \geq \frac{1}{2} \frac{h}{2 \pi}$  exists, but differs from the product

of uncertainties of  $p$  and  $q$  because only energy  $E$  has a legitimate uncertainty. Under this condition,  $\Delta t$  is regarded as an evolutionary interval, rather than as an uncertainty, during which a system might evolve from one state to another. The latter inequality is useful in specifying a relation between a mean lifetime  $\Delta t$  of, typically, an excited state and its energy width. The significance of these relations is that calculations according to quantum-mechanical algorithms are subject to indeterminacy, and

consequently any system to which these calculations are applied.

As an alternative formulation, for two hermitian operators  $A$  and  $B$ , with commutator  $[A, B] = AB - BA$ , a relation for indeterminacy due to Robertson is expressible as

$$\sigma_A \sigma_B = \frac{1}{2} | \langle [A, B] \rangle |$$

in which the right side of the equality denotes half an absolute value of an expectation value of that commutator. Other relations involving such commutators, expressed according to definition as

$$[A, B] \equiv AB - BA,$$

and anti-commutators, expressed according to definition as

$$\{A, B\} \equiv AB + BA,$$

are known.

We test the evaluation of commutator  $p q - q p$ , employing commutator operator **&c**, recalling the derivations of  $p$  and  $q$  in terms of  $a$  and  $b$ , as generated above.

```
> pcq := p &c q;
```

$$pcq := \frac{-\frac{1}{2} h (a \&* b - (b \&* a))}{\pi} \quad (10.2.60)$$

We generally express such a commutator as  $[p, q]$  that has significance identical to  $p q - q p$ , but resembles a list comprising two items; we input that commutator as a list,

```
> pcq := [p, q];
```

$$pcq := \left[ -\frac{1}{2} \sqrt{\mu h v_0} (a - b) \sqrt{2}, \frac{\sqrt{\mu h v_0} (a + b) \sqrt{2}}{4 \pi \mu v_0} \right] \quad (10.2.61)$$

which hence becomes expressed in terms of  $a$  and  $b$ . We convert that list into a commutator with

```
> pcqn := list2com(pcq);
```

$$pcqn := \frac{-\frac{1}{2} h (a \&* b - (b \&* a))}{\pi} \quad (10.2.62)$$

which yields the same result as above. To obtain an elegant result for this commutator  $p q - q p$  according to the fundamental postulate of quantum mechanics

$$p q - q p = -\frac{i h}{2 \pi},$$

we apply it to a quantity  $ket(n)$ , employing operator **&@** for this purpose.

```
> pcqn := pcq &@ ket(n);
```

$$pcqn := \frac{-\frac{1}{2} h ket(n)}{\pi} \quad (10.2.63)$$

```
> pcqn := simplify(pcq &@ ket(n), symbolic);
```

$$pcqn := \frac{-\frac{1}{2} h ket(n)}{\pi} \quad (10.2.64)$$

> `(p q - q p)`\*`|n>` = %;

$$(p q - q p) |n\rangle = \frac{-\frac{1}{2} \hbar \text{ket}(n)}{\pi} \quad (10.2.65)$$

as expected from the above formula. The anti-commutator of  $p$  and  $q$  is

> `( &\*` (p,q) + `&\*` (q,p)) &@ ket(n);

$$-\frac{1 \hbar \sqrt{n} \sqrt{n-1} \text{ket}(n-2)}{2 \pi} + \frac{1 \hbar \sqrt{n+1} \sqrt{n+2} \text{ket}(n+2)}{2 \pi} \quad (10.2.66)$$

> simplify(%) assuming positive;

$$\frac{-\frac{1}{2} \hbar (\sqrt{n} \sqrt{n-1} \text{ket}(n-2) - \sqrt{n+1} \sqrt{n+2} \text{ket}(n+2))}{\pi} \quad (10.2.67)$$

We examine analogously the commutator of  $a$  and  $b$ ,

> acb := [a, b];

$$acb := [a, b] \quad (10.2.68)$$

> acb := list2com(acb);

$$acb := a \&* b - (b \&* a) \quad (10.2.69)$$

and apply it to a ket of a state,

> acbn := acb &@ ket(n);

$$acbn := \text{ket}(n) \quad (10.2.70)$$

consistent with our test above. The commutator  $a b - b a = 1$ , whereas the anti-commutator  $a b + b a$  is

> factor((`&\*` (a,b) + `&\*` (b,a)) &@ ket(n));

$$\text{ket}(n) (1 + 2 n) \quad (10.2.71)$$

so  $a b + b a = 2 n + 1$ . The difference between the hamiltonian operator and the number operator, each operating on the same ket,  $|n\rangle$ , is

> `H | n >`/(h\*nu[0]) = simplify(H&@ket(n)/(h\*nu[0]));

$$\frac{H | n \rangle}{\hbar \nu_0} = \frac{\text{ket}(n) (1 + 2 n)}{2} \quad (10.2.72)$$

> `N | n >` = N &@ ket(n);

$$N | n \rangle = n \text{ket}(n) \quad (10.2.73)$$

> simplify(rhs(%%) - rhs(%));

$$\frac{\text{ket}(n)}{2} \quad (10.2.74)$$

as derived above. That eigenvalues of number operator  $N$  comprise only non-negative integers is a consequence of the commutation relation  $a b - b a = 1$ . We evaluate also matrix elements of  $q$  between states represented by unequal kets.

> ` $\langle n | q | n+1 \rangle$ ` = `braket3(n, q, n+1);`

$$\langle n | q | n+1 \rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} \sqrt{n+1}}{4 \pi \mu v_0} \quad (10.2.75)$$

When we extract a constant factor  $2 \pi \sqrt{\frac{h}{\mu v_0}}$ ,

> `lhs(%)/sqrt(h/(mu*nu[0]))*2*Pi = simplify(rhs(%)/sqrt(h/(mu*nu[0]))*2*Pi, symbolic);`

$$\frac{2 \langle n | q | n+1 \rangle \pi}{\sqrt{\frac{h}{\mu v_0}}} = \frac{\sqrt{2} \sqrt{n+1}}{2} \quad (10.2.76)$$

we find that the remaining factor is  $\sqrt{\frac{n+1}{2}}$ . We express the matrix element as a bracket in an order opposite that above,

> ` $\langle n+1 | q | n \rangle$ ` = `braket3(n+1, q, n);`

$$\langle n+1 | q | n \rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} \sqrt{n+1}}{4 \pi \mu v_0} \quad (10.2.77)$$

but obtain the same result. Here follow the calculations of some other matrix elements, assuming no value  $n < 0$ .

> ` $\langle n | q | n-1 \rangle$ ` = `braket3(n, q, n-1);`

$$\langle n | q | n-1 \rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} \sqrt{n}}{4 \pi \mu v_0} \quad (10.2.78)$$

> ` $\langle n | q^3 | n+1 \rangle$ ` = `braket3(n, q^3, n+1);`

$$\langle n | q^3 | n+1 \rangle = \frac{3 h \sqrt{\mu h v_0} \sqrt{2} (n+1)^{3/2}}{32 \mu^2 v_0^2 \pi^3} \quad (10.2.79)$$

> ` $\langle n | q^3 | n-1 \rangle$ ` = `braket3(n, q^3, n-1);`

$$\langle n | q^3 | n-1 \rangle = \frac{3 h \sqrt{\mu h v_0} \sqrt{2} n^{3/2}}{32 \mu^2 v_0^2 \pi^3} \quad (10.2.80)$$

> ` $\langle n | q^3 | n+3 \rangle$ ` = `braket3(n, q^3, n+3);`

$$\langle n | q^3 | n+3 \rangle = \frac{h \sqrt{\mu h v_0} \sqrt{2} \sqrt{n+2} \sqrt{n+3} \sqrt{n+1}}{32 \mu^2 v_0^2 \pi^3} \quad (10.2.81)$$

> ` $\langle n | q^2 | n+1 \rangle$ ` = `braket3(n, q^2, n+1);`

(10.2.82)

$$\langle n | q^2 | n+1 \rangle = 0 \quad (10.2.82)$$

$$\begin{aligned} &> \text{'< n | '* 'q^8'* ' | n+2 >'} = \text{braket3(n, q\^8, n+2);} \\ &\langle n | q^8 | n+2 \rangle = \frac{7 h^4 \sqrt{n+2} \sqrt{n+1} (3+2n) (n^2+3n+5)}{1024 \mu^4 v_0^4 \pi^8} \end{aligned} \quad (10.2.83)$$

$$\begin{aligned} &> \text{'< n+1 | p | n >'} = \text{braket3(n+1, p, n);} \\ &\langle n+1 | p | n \rangle = \frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} \sqrt{n+1} \end{aligned} \quad (10.2.84)$$

$$\begin{aligned} &> \text{'< n | p | n-1 >'} = \text{braket3(n, p, n-1);} \\ &\langle n | p | n-1 \rangle = \frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} \sqrt{n} \end{aligned} \quad (10.2.85)$$

$$\begin{aligned} &> \text{'< n | '* 'p^3'* ' | n+1 >'} = \text{braket3(n, p\^3, n+1);} \\ &\langle n | p^3 | n+1 \rangle = -\frac{3I}{4} \mu h v_0 \sqrt{\mu h v_0} \sqrt{2} (n+1)^{3/2} \end{aligned} \quad (10.2.86)$$

$$\begin{aligned} &> \text{'< n | '* 'p^3'* ' | n-1 >'} = \text{braket3(n, p\^3, n-1);} \\ &\langle n | p^3 | n-1 \rangle = \frac{3I}{4} \mu h v_0 \sqrt{\mu h v_0} \sqrt{2} n^{3/2} \end{aligned} \quad (10.2.87)$$

$$\begin{aligned} &> \text{'< n | '* 'p^3'* ' | n+3 >'} = \text{braket3(n, p\^3, n+3);} \\ &\langle n | p^3 | n+3 \rangle = \frac{1}{4} \mu h v_0 \sqrt{\mu h v_0} \sqrt{2} \sqrt{n+2} \sqrt{n+3} \sqrt{n+1} \end{aligned} \quad (10.2.88)$$

$$\begin{aligned} &> \text{'< n | '* 'p^2'* ' | n+1 >'} = \text{braket3(n, p\^2, n+1);} \\ &\langle n | p^2 | n+1 \rangle = 0 \end{aligned} \quad (10.2.89)$$

$$\begin{aligned} &> \text{'< n | '* 'p^8'* ' | n+2 >'} = \text{braket3(n, p\^8, n+2);} \\ &\langle n | p^8 | n+2 \rangle = -\frac{7 (3+2n) \mu^4 \sqrt{n+1} (n^2+3n+5) h^4 v_0^4 \sqrt{n+2}}{4} \end{aligned} \quad (10.2.90)$$

Other observable quantities one calculates analogously.

To work further with symbolic matrix elements, we show the following commands.

$$\begin{aligned} &> \text{'< m | q | n >'} = \text{braket3(m, q, n);} \\ &\langle m | q | n \rangle \end{aligned} \quad (10.2.91)$$

$$\begin{aligned} &= \frac{1}{4 \pi \mu v_0} \left( \sqrt{\mu h v_0} \sqrt{2} \left( \sqrt{n} \text{braket2}(\text{bra}(m), \text{ket}(n-1)) \right. \right. \\ &\quad \left. \left. + \sqrt{n+1} \text{braket2}(\text{bra}(m), \text{ket}(n+1)) \right) \right) \end{aligned}$$

This result is correct, but is displayed with improved meaning as follows.

$$\begin{aligned} &> \text{convert(%, Krondelta);} \\ & \end{aligned} \quad (10.2.92)$$

$$\langle m | q | n \rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \delta_{m, n-1} + \sqrt{n+1} \delta_{m, n+1})}{4 \pi \mu v_0} \quad (10.2.92)$$

For the particular case that  $n = m - 1$ , we find

$$\begin{aligned} &> \text{'< m | q | m-1 >'} = \text{eval(rhs(\%), n=m-1);} \\ &\langle m | q | m-1 \rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} \sqrt{m}}{4 \pi \mu v_0} \end{aligned} \quad (10.2.93)$$

whereas for the case  $n = m + 1$  we find

$$\begin{aligned} &> \text{'< m | q | m+1 >'} = \text{eval(rhs(\%)), n=m+1);} \\ &\langle m | q | m+1 \rangle = \frac{\sqrt{\mu h v_0} \sqrt{2} \sqrt{m+1}}{4 \pi \mu v_0} \end{aligned} \quad (10.2.94)$$

For the case  $n = m$ , we find the same result as above.

$$\begin{aligned} &> \text{'< m | q | m >'} = \text{eval(rhs(\%)), n=m);} \\ &\langle m | q | m \rangle = 0 \end{aligned} \quad (10.2.95)$$

As an important application of the use of commutators, we evaluate commutator  $[H, q]$  between a hamiltonian operator and a coordinate operator.

$$\begin{aligned} &> \text{Hcq := [H, q];} \\ &\text{Hcq := list2com(Hcq);} \\ &\text{Hcq} := \left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} \right. \\ &\quad \left. + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, \frac{\sqrt{\mu h v_0} (a + b) \sqrt{2}}{4 \pi \mu v_0} \right] \\ &\text{Hcq} := -\frac{h \sqrt{\mu h v_0} \sqrt{2} (\&*(a, a, b) - (\&*(a, b, b)) - (\&*(b, a, a)) + \&*(b, b, a))}{8 \pi \mu} \end{aligned} \quad (10.2.96)$$

$$\begin{aligned} &> \text{simplify(Hcq \&@ ket(n));} \\ &-\frac{h \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1))}{4 \pi \mu} \end{aligned} \quad (10.2.97)$$

We multiply the result by  $\frac{i \cdot 2 \pi \mu}{h}$

$$\begin{aligned} &> \text{2*Pi*I*mu/h*;} \\ &-\frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1)) \end{aligned} \quad (10.2.98)$$

We recall  $p | n \rangle$ .



```
> factor(simplify(p &@ ket(n)));
```

$$-\frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1)) \quad (10.2.99)$$

```
> is(% == %%);
```

$$\text{true} \quad (10.2.100)$$

Although we have proved that  $p = \frac{i \cdot 2 \pi \mu}{h} [H, q]$  in the particular case of a canonical linear harmonic oscillator, this relation is general, applicable to any conservative system.

### 1.243 further tests on commutators, ordering and other operations

```
> # no restart here!
```

To illustrate the capabilities of these operators for creation and destruction, we undertake the following tests, first with commutators. In our ensuing work with commutators explicitly, we make use of the following identities, involving three operators A, B and C:

$$\begin{aligned} [A, B] &= -[B, A] \\ [A, A^n] &= 0 \text{ for } n = 1, 2, 3, \dots \\ [A, B C] &= [A, B] C + B [A, C] \\ [A B, C] &= [A, C] B + A [B, C]. \end{aligned}$$

On the basis of the latter results, we expand a square as

$$[A, B^2] = [A, B] B + B [A, B].$$

We evaluate other commutators. The commutator of operators  $a$  and  $b$  is  $[a, b]$ ,

```
> acb := [a, b];
```

$$acb := [a, b] \quad (10.3.1)$$

```
> acb := list2com(acb);
```

$$acb := a \&* b - (b \&* a) \quad (10.3.2)$$

which we apply to  $|n\rangle$ .

```
> simplify(acb &@ ket(n));
```

$$\text{ket}(n) \quad (10.3.3)$$

As  $[a, b] |n\rangle = |n\rangle$ , the commutator of  $a$  and  $b$  is thus unity. We test the other order.

```
> bca := [b, a];
```

$$bca := [b, a] \quad (10.3.4)$$

```
> bca := list2com(bca);
```

$$bca := b \&* a - (a \&* b) \quad (10.3.5)$$

```
> simplify(bca &@ ket(n));
```

$$-\text{ket}(n) \quad (10.3.6)$$

As  $[b, a] |n\rangle = -|n\rangle$ , the commutator of  $b$  and  $a$  is thus negative unity,  $-1$ .

Here are some tests of commutators involving  $H$ . Because  $\&c$  has greater priority than  $*$ , the meaning of  $H \&c 3 * p$  is  $[H, 3] * p$  not  $[H, 3 * p]$ , but  $H \&c (3 * p)$  yields the correct answer. Applying a list notation

to represent the commutator and applying procedure **list2com** yields the correct answer in any case. We first test  $[H, 3p]$ ,

**> l1 := [H, 3\*p];**

$$l1 := \left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, -\frac{3I}{2} \sqrt{\mu h v_0} (a - b) \sqrt{2} \right] \quad (10.3.7)$$

**> l1n := factor(list2com(l1) &@ ket(n));**

$$l1n := \frac{3I}{2} \sqrt{2} (\sqrt{n} \text{ket}(n-1) + \sqrt{n+1} \text{ket}(n+1)) \sqrt{\mu h v_0} v_0 h \quad (10.3.8)$$

for comparison with  $[H, p^* 3]$ .

**> l2 := [H, p\*3];**

$$l2 := \left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, -\frac{3I}{2} \sqrt{\mu h v_0} (a - b) \sqrt{2} \right] \quad (10.3.9)$$

**> l2n := factor(list2com(l2) &@ ket(n));**

$$l2n := \frac{3I}{2} \sqrt{2} (\sqrt{n} \text{ket}(n-1) + \sqrt{n+1} \text{ket}(n+1)) \sqrt{\mu h v_0} v_0 h \quad (10.3.10)$$

**> is(l1n = l2n);**

*true* (10.3.11)

As the first commutator with  $H$ , we apply  $[H, q]$  to act on  $|n\rangle$ ,

**> [H, q];**

$$\left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, \frac{\sqrt{\mu h v_0} (a + b) \sqrt{2}}{4 \pi \mu v_0} \right] \quad (10.3.12)$$

**> list2com(%);**

$$-\frac{h \sqrt{\mu h v_0} \sqrt{2} (\&*(a, a, b) - (\&*(a, b, b)) - (\&*(b, a, a)) + \&*(b, b, a))}{8 \pi \mu} \quad (10.3.13)$$

**> simplify(% &@ ket(n));**

$$-\frac{h \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1))}{4 \pi \mu} \quad (10.3.14)$$

for comparison with  $-i p |n\rangle$ ,

**> simplify(p &@ ket(n));**

$$-\frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1)) \quad (10.3.15)$$

by calculating the ratio.

**> simplify(%/%, symbolic);**

$$\frac{-\frac{1}{2} h}{\pi \mu} \quad (10.3.16)$$

Between the latter expressions there is hence a factor  $-\frac{i h}{2 \pi \mu}$ , which indicates that

$$[H, q] |n\rangle = \frac{h}{2 \pi \mu} (-i p) |n\rangle,$$

as derived above.

Here is the corresponding commutator  $[H, p]$ ,

**> [H, p];**

$$\left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} \right. \\ \left. + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, -\frac{1}{2} \sqrt{\mu h v_0} (a - b) \sqrt{2} \right] \quad (10.3.17)$$

**> list2com(%);**

$$\frac{1 h v_0 \sqrt{\mu h v_0} \sqrt{2} (\&*(a, a, b))}{4} + \frac{1 h v_0 \sqrt{\mu h v_0} \sqrt{2} (\&*(a, b, b))}{4} \\ - \frac{1 h v_0 \sqrt{\mu h v_0} \sqrt{2} (\&*(b, a, a))}{4} - \frac{1 h v_0 \sqrt{\mu h v_0} \sqrt{2} (\&*(b, b, a))}{4} \quad (10.3.18)$$

**> factor(simplify(% &@ ket(n)));**

$$\frac{1}{2} h v_0 \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) + \sqrt{n+1} \text{ket}(n+1)) \quad (10.3.19)$$

which we compare with  $i q |n\rangle$ ,

**> simplify((I \* q) &@ ket(n));**

$$\frac{\frac{1}{4} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) + \sqrt{n+1} \text{ket}(n+1))}{\pi \mu v_0} \quad (10.3.20)$$

through a ratio.

**> simplify(%/%, symbolic);**

$$2 h v_0^2 \pi \mu \quad (10.3.21)$$

Here the factor between the expressions is  $2 \pi \mu h v_0^2$ , which indicates that

$$[H, p] |n\rangle = 2 \pi \mu h v_0^2 (i q) |n\rangle.$$

Some further examples of commutators follow.

**> Hca := [H, a];**

$$Hca := \left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, a \right] \quad (10.3.22)$$

**> Hca := list2com(Hca);**

$$Hca := \frac{h v_0 (\&*(b, a, a))}{2} - \frac{h v_0 (\&*(a, a, b))}{2} \quad (10.3.23)$$

**> Hcan := Hca &@ ket(n);**

$$Hcan := -h v_0 \sqrt{n} \text{ket}(n-1) \quad (10.3.24)$$

**> a &@ ket(n);**

$$\sqrt{n} \text{ket}(n-1) \quad (10.3.25)$$

**> Hcan/%;**

$$-h v_0 \quad (10.3.26)$$

Here the factor is  $-h v_0$ , which indicates that  $[H, a] |n\rangle = -h v_0 a |n\rangle$ , which is appropriate because  $H$  has dimensions of energy. For  $[H, b]$ ,

**> Hcb := [H, b];**

$$Hcb := \left[ -\frac{h v_0 (a \&* a - (a \&* b) - (b \&* a) + b \&* b)}{4} + \frac{v_0 h (a \&* a + a \&* b + b \&* a + b \&* b)}{4}, b \right] \quad (10.3.27)$$

**> Hcb := list2com(Hcb);**

$$Hcb := \frac{h v_0 (\&*(a, b, b))}{2} - \frac{h v_0 (\&*(b, b, a))}{2} \quad (10.3.28)$$

**> Hcbn := Hcb &@ ket(n);**

$$Hcbn := h v_0 \sqrt{n+1} \text{ket}(n+1) \quad (10.3.29)$$

**> b &@ ket(n);**

$$\sqrt{n+1} \text{ket}(n+1) \quad (10.3.30)$$

**> Hcbn/%;**

$$(10.3.31)$$

$$h v_0 \quad (10.3.31)$$

the factor is just  $h v_0$ , which indicates that  $[H, b] |n\rangle = h v_0 b |n\rangle$ . We test the product of operators  $N$  and  $a$ ,

$$\begin{aligned} &> \text{Npa} := N \&* a; \\ &Npa := \&*(b, a, a) \end{aligned} \quad (10.3.32)$$

$$\begin{aligned} &> \text{collect}(\text{Npa} \& \text{ket}(n), \text{ket}); \\ &(n^{3/2} - \sqrt{n}) \text{ket}(n-1) \end{aligned} \quad (10.3.33)$$

and  $N$  and  $b$ .

$$\begin{aligned} &> \text{Npb} := N \&* b; \\ &Npb := \&*(b, a, b) \end{aligned} \quad (10.3.34)$$

$$\begin{aligned} &> \text{Npb} \& \text{ket}(n); \\ &(n+1)^{3/2} \text{ket}(n+1) \end{aligned} \quad (10.3.35)$$

When we operate on a bra or  $\langle |$  with  $a$  on the right, we obtain no result directly,

$$\begin{aligned} &> \langle n | \&* a = \text{bra}(n) \& a; \\ &\langle n | a = \text{bra}(n) a \end{aligned} \quad (10.3.36)$$

but when we complete the bracket with  $|n+1\rangle$  we obtain

$$\begin{aligned} &> \langle n | a | n+1 \rangle = \text{braket3}(n, a, n+1); \\ &\langle n | a | n+1 \rangle = \sqrt{n+1} \end{aligned} \quad (10.3.37)$$

which implies that  $\langle n | a = \langle n+1 | \sqrt{n+1}$  because  $\langle n | a | n+1 \rangle = \langle n+1 | \sqrt{n+1} | n+1 \rangle = \sqrt{n+1} \langle n+1 | n+1 \rangle = \sqrt{n+1}$ . Analogously for  $b$ , we obtain

$$\begin{aligned} &> \text{braket3}(n, b, n-1); \\ &\sqrt{n} \end{aligned} \quad (10.3.38)$$

which implies that  $\langle n | b = \langle n-1 | \sqrt{n}$ . Operating with  $a$  on a bra hence yields a result that corresponds to operation with  $b$  on the same ket, and vice versa.

Operation with  $\frac{p}{\mu}$  on a ket of a state yields

$$\begin{aligned} &> \text{pn} := \text{factor}((1/\mu * p) \& \text{ket}(n)); \\ &pn := \frac{-\frac{1}{2} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) - \sqrt{n+1} \text{ket}(n+1))}{\mu} \end{aligned} \quad (10.3.39)$$

to which we apply a hamiltonian operator.

$$\begin{aligned} &> \text{simplify}(\text{collect}(\text{factor}(\text{simplify}(H \& \text{pn})), [\text{ket}, h, \text{nu}[0]])); \\ &\frac{1}{2} \sqrt{2} h \left( \text{ket}(n+1) \left( \frac{3}{2} + n \right) \sqrt{n+1} + \frac{\text{ket}(n-1) (\sqrt{n} - 2 n^{3/2})}{2} \right) v_0 \sqrt{\mu h v_0} \end{aligned} \quad (10.3.40)$$

As that result is complicated, we form a bracket of the former result with  $H$ .

**> r1 := brak3(pn, H, pn);**

$$r1 := \frac{3 h v_0}{8} \quad (10.3.41)$$

We make an analogous calculation with  $q$ .

**> qn := simplify(collect(simplify(I\*mu\*nu[0]\*q &@ ket(n)), ket));**

$$qn := \frac{\frac{I}{4} \sqrt{\mu h v_0} \sqrt{2} (\sqrt{n} \text{ket}(n-1) + \sqrt{n+1} \text{ket}(n+1))}{\pi} \quad (10.3.42)$$

**> r2 := brak3(qn, H, qn);**

$$r2 := \frac{h v_0}{4} \quad (10.3.43)$$

We test  $\frac{p}{\mu} + i \mu v_0 q$  and then form  $\langle \frac{p}{\mu} + i \mu v_0 q | H | \frac{p}{\mu} + i \mu v_0 q \rangle$ .

**> ppq := expand(simplify(((1/mu\*p) + (I\*mu\*nu[0]\*q)) &@ ket(n), symbolic));**

$$ppq := \frac{I \sqrt{h} \sqrt{2} \sqrt{v_0} \sqrt{n+1} \text{ket}(n+1)}{2 \sqrt{\mu}} + \frac{I \sqrt{h} \sqrt{\mu} \sqrt{2} \sqrt{v_0} \sqrt{n+1} \text{ket}(n+1)}{4 \pi} - \frac{I \sqrt{h} \sqrt{2} \sqrt{v_0} \sqrt{n} \text{ket}(n-1)}{2 \sqrt{\mu}} + \frac{I \sqrt{h} \sqrt{\mu} \sqrt{2} \sqrt{v_0} \sqrt{n} \text{ket}(n-1)}{4 \pi} \quad (10.3.44)$$

**> collect(ppq, ket);**

$$\left( -\frac{I \sqrt{h} \sqrt{2} \sqrt{v_0} \sqrt{n}}{2 \sqrt{\mu}} + \frac{I \sqrt{h} \sqrt{\mu} \sqrt{2} \sqrt{v_0} \sqrt{n}}{4 \pi} \right) \text{ket}(n-1) + \left( \frac{I \sqrt{h} \sqrt{2} \sqrt{v_0} \sqrt{n+1}}{2 \sqrt{\mu}} + \frac{I \sqrt{h} \sqrt{\mu} \sqrt{2} \sqrt{v_0} \sqrt{n+1}}{4 \pi} \right) \text{ket}(n+1) \quad (10.3.45)$$

**> collect(brak3(ppq, H, ppq), ket);**

$$\frac{h v_0}{4} \quad (10.3.46)$$

We test analogously the action of  $\frac{p}{\mu} - i \mu v_0 q$  on a state.

**> 1/2\*I\*(b-a)\*2^(1/2)\*(mu\*nu[0]\*h)^(1/2);**

$$\frac{I}{2} (b-a) \sqrt{2} \sqrt{\mu h v_0} \quad (10.3.47)$$

```
> pmq := (p/mu) - (I*mu*nu[0]*q);
```

$$pmq := -\frac{I\sqrt{\mu h v_0} (a-b)\sqrt{2}}{2\mu} - \frac{I\sqrt{\mu h v_0} (a+b)\sqrt{2}}{4\pi} \quad (10.3.48)$$

```
> simplify(collect(simplify(pmq &@ ket(n), symbolic), ket));
```

$$\frac{\frac{I}{2}\sqrt{h}\left(ket(n+1)\left(\pi-\frac{\mu}{2}\right)\sqrt{n+1}-\left(\pi+\frac{\mu}{2}\right)\sqrt{n}ket(n-1)\right)\sqrt{2}\sqrt{v_0}}{\sqrt{\mu}\pi} \quad (10.3.49)$$

```
> collect(braket3(%, H, %), ket);
```

$$\frac{3 h v_0}{8} \quad (10.3.50)$$

Expressions  $\left(\frac{p}{\mu} + i\mu v_0 q\right)|n\rangle$  and  $\left(\frac{p}{\mu} - i\mu v_0 q\right)|n\rangle$  are thus eigenfunctions of hamiltonian operator  $H$  with the corresponding eigenvalues, which is a reason to define  $p$  and  $q$  in terms of  $a$  and  $b$  as in section 1.242.

To test the ordering of operators, for two new operators  $a$  and  $b$  without their former significance,

```
> a, b := 'a', 'b':
```

```
Operators := [a,b]:
```

we define their commutator to be  $[a, b] = -i h$ .

```
> [a,b] = def_c(a,b,-I*h);
```

$$[a, b] = -Ih \quad (10.3.51)$$

We test two expressions with  $a$  and  $b$ .

```
> ja := a&*b&*a&*b&*a;
```

$$ja := \&*(a, b, a, b, a) \quad (10.3.52)$$

```
> jb := (a + b)&^4;
```

$$\begin{aligned} jb := & \&*(a, a, a, a) + \&*(a, a, a, b) + \&*(a, a, b, a) + \&*(a, a, b, b) + \&*(a, b, a, a) \\ & + \&*(a, b, a, b) + \&*(a, b, b, a) + \&*(a, b, b, b) + \&*(b, a, a, a) + \&*(b, a, a, b) \\ & + \&*(b, a, b, a) + \&*(b, a, b, b) + \&*(b, b, a, a) + \&*(b, b, a, b) + \&*(b, b, b, a) \\ & + \&*(b, b, b, b) \end{aligned} \quad (10.3.53)$$

We specify the order to have all  $b$  before  $a$ .

```
> deforder(b,a);
```

$$2 \quad (10.3.54)$$

```
> ordering(ja);
```

$$\&*(b, b, a, a, a) + 3 Ih (\&*(b, a, a)) - h^2 a \quad (10.3.55)$$

```
> ordering(jb);
```

$$6 Ih (a \&*a) + 12 Ih (b \&*a) + 6 Ih (b \&*b) + 6 (\&*(b, b, a, a)) + 4 (\&*(b, b, b, a)) \quad (10.3.56)$$





$$\begin{aligned}
& - \frac{Ih(\&^*(a, a, a, a, a, a, a, a, a, a))}{403200} + \frac{Ih(\&^*(a, a, a, a, a, a, a, a, a, a, a))}{3326400} \\
& - \frac{Ih(\&^*(a, a, a, a, a, a, a, a, a, a, a, a))}{43545600} + \frac{Ih(\&^*(a, a, a, a, a, a, a, a, a))}{630} \\
& - \frac{Ih(\&^*(a, a, a, a, a, a, a, a, a))}{5760} - \frac{(\&^*(a, a, a, a, a, a, b))}{60} - \frac{(\&^*(a, a, a, a, b))}{3} \\
& + 3 Ih a - \frac{Ih(\&^*(a, a, a, a, a, a))}{144} + \frac{Ih(\&^*(a, a, a, a, a))}{20} \\
& - \frac{Ih(\&^*(a, a, a, a))}{8} + \frac{2 Ih(\&^*(a, a, a))}{3} - \frac{Ih(a \&^* a)}{2} \\
& + \frac{Ih(\&^*(a, a))}{5792623828992000} + 2 Ih \\
& - \frac{(\&^*(a, a, a, a, a, a, a, a, a, a, a, a, a, a, a, a, b))}{653837184000} \\
& - \frac{(\&^*(a, a, a, a, a, a, a, a, a, a, a, a, a, a, a, a, a, b))}{177843714048000} \\
& - \frac{(\&^*(a, a, a, a, a, a, a, a, a, a, a, a, a, a, b))}{3113510400} - \frac{(\&^*(a, a, a, a, a, a, a, a, a, a, a, b))}{181440} \\
& - \frac{(\&^*(a, a, a, a, a, a, a, a, a, a, a, b))}{19958400} - \frac{(\&^*(a, a, a, a, a, a, a, b))}{2520}
\end{aligned}$$

Are these numerical coefficients related to Euler or Bernoulli numbers?

**> seq(euler(2\*i), i=1..12);**

$$-1, 5, -61, 1385, -50521, 2702765, -199360981, 19391512145, -2404879675441, \quad (10.3.62) \\
370371188237525, -69348874393137901, 15514534163557086905$$

**> seq(euler(2\*i)/(2\*i)!, i=1..12);**

$$\begin{aligned}
& -\frac{1}{2}, \frac{5}{24}, -\frac{61}{720}, \frac{277}{8064}, -\frac{50521}{3628800}, \frac{540553}{95800320}, -\frac{199360981}{87178291200}, \frac{3878302429}{4184557977600}, \quad (10.3.63) \\
& -\frac{2404879675441}{6402373705728000}, \frac{14814847529501}{97316080327065600}, -\frac{69348874393137901}{1124000727777607680000}, \\
& \frac{238685140977801337}{9545360026665222144000}
\end{aligned}$$

**> seq(bernoulli(2\*i)/(2\*i), i=1..12);**

$$\begin{aligned}
& \frac{1}{12}, -\frac{1}{120}, \frac{1}{252}, -\frac{1}{240}, \frac{1}{132}, -\frac{691}{32760}, \frac{1}{12}, -\frac{3617}{8160}, \frac{43867}{14364}, -\frac{174611}{6600}, \frac{77683}{276}, \quad (10.3.64) \\
& -\frac{236364091}{65520}
\end{aligned}$$

```
> seq(bernoulli(2*i)/(2*i-2), i=2..12);
```

$$-\frac{1}{60}, \frac{1}{168}, -\frac{1}{180}, \frac{5}{528}, -\frac{691}{27300}, \frac{7}{72}, -\frac{3617}{7140}, \frac{43867}{12768}, -\frac{174611}{5940}, \frac{854513}{2760},$$

$$-\frac{236364091}{60060}$$
(10.3.65)

### *x1.21 example, asymptotic solution in wave mechanics*

> restart:

We revisit the canonical linear harmonic oscillator according to wave mechanics. For this purpose we first recall Schroedinger's equation in a simplified form,

```
> Schr_eq := - diff(f(x),x$2) + x^2*f(x) = E*f(x);
```

$$Schr\_eq := -\frac{d^2}{dx^2} f(x) + x^2 f(x) = E f(x)$$
(11.1)

in which  $f(x)$  represents a reduced displacement coordinate incorporating factors for mass and force coefficient as well as Planck's constant, and the potential energy is simply expressed as  $V(x) = x^2$ . We consider the solution under conditions of large  $x$ , such that the right side  $E f(x)$  is negligible with respect to  $x^2 f(x)$

```
> asymp_eq := subs(E*f(x)=0, Schr_eq);
```

$$asymp\_eq := -\frac{d^2}{dx^2} f(x) + x^2 f(x) = 0$$
(11.2)

Because of the symmetry of the potential energy in its reduced form, such that  $V(x)$  is the same for a value  $-x$  as for  $+x$ , we expect to find solutions of even or odd form. For the even solutions the initial conditions for the solution of the differential equation are

```
> ics := D(f)(0)=0, f(0)=1;
```

$$ics := D(f)(0) = 0, f(0) = 1$$
(11.3)

for which we obtain this solution.

```
> sole := dsolve({asymp_eq,ics});
```

$$sole := f(x) = \begin{cases} \frac{\Gamma\left(\frac{3}{4}\right) \sqrt{-x} \left( \sqrt{2} \operatorname{BesselI}\left(\frac{1}{4}, \frac{x^2}{2}\right) \pi + 2 \operatorname{BesselK}\left(\frac{1}{4}, \frac{x^2}{2}\right) \right)}{2 \pi} & x < 0 \\ 1 & x = 0 \\ \frac{\Gamma\left(\frac{3}{4}\right) \sqrt{x} \left( \sqrt{2} \operatorname{BesselI}\left(\frac{1}{4}, \frac{x^2}{2}\right) \pi + 2 \operatorname{BesselK}\left(\frac{1}{4}, \frac{x^2}{2}\right) \right)}{2 \pi} & 0 < x \end{cases}$$
(11.4)

```
> op(6, rhs(sole));
```

(11.5)

$$\frac{\Gamma\left(\frac{3}{4}\right) \sqrt{x} \left( \sqrt{2} \operatorname{BesselI}\left(\frac{1}{4}, \frac{x^2}{2}\right) \pi + 2 \operatorname{BesselK}\left(\frac{1}{4}, \frac{x^2}{2}\right) \right)}{2 \pi} \quad (11.5)$$

The asymptotic solution at large  $x$  thus becomes

**> solea := asympt(op(6, rhs(sole)), x);**

$$\text{solea} := \left( \frac{\Gamma\left(\frac{3}{4}\right) \sqrt{2} \sqrt{\frac{1}{x}}}{2 \sqrt{\pi}} + \frac{3 \Gamma\left(\frac{3}{4}\right) \sqrt{2} \left(\frac{1}{x}\right)^{5/2}}{32 \sqrt{\pi}} + \frac{105 \Gamma\left(\frac{3}{4}\right) \sqrt{2} \left(\frac{1}{x}\right)^{9/2}}{1024 \sqrt{\pi}} \right. \\ \left. + O\left(\left(\frac{1}{x}\right)^{13/2}\right) \right) \sqrt{e^{x^2}} \quad (11.6)$$

### e1.24 exercise

For conjugate coordinate  $q$  and momentum  $p$ , subject to a commutator  $[p/\mu, q] = \frac{i\mu}{\hbar}$ , and their hamiltonian  $H(q, p)$ , evaluate these four commutators in application to the canonical linear harmonic oscillator; test whether the first two are related to each other, and likewise the second two. For these calculations, define the procedures in section 1.241; then execute commands in section 1.242 down to definitions of  $a$  and  $b$ , and copy the assignments to define  $p$  and  $q$  from the latter section. For the fifth commutator, generate any required relations from section 1.242.

- i)  $[q, p^2]$ ,
- ii)  $[p^2, q]$ ,
- iii)  $[q^2, p]$ , and
- iv)  $[p, q^2]$ .

### e1.25 exercise

Evaluate these commutators for the canonical linear harmonic oscillator; generate any required relations from section 1.242.

- i)  $[H, p]$ ,
- ii)  $[N, a]$ ,
- iii)  $[N, b]$ .

Prove the following result.

$$|n\rangle = b^n |0\rangle$$

### e1.26 exercise

Applying the definition of the commutator between  $a$  and  $b$ , evaluate  $b a |n\rangle$ .

### e1.27 exercise

Find representations of  $a, b, p$  and  $q$  as matrices; show that  $b$  and  $a$  are not hermitian but are adjoint of one another, whereas that  $p$  and  $q$  are hermitian.

### e1.28 exercise

Derive the indeterminacy relation of Heisenberg for a canonical linear harmonic oscillator,

- i) according to wave mechanics, and

ii) according to matrix mechanics using Robertson's relation.

### e1.29 exercise

For a single particle in one dimension in a pure eigenstate of energy, expectation value  $\langle k | \frac{p_x^2}{2m} | k \rangle$   

$$= \frac{1}{2} \langle k | x \left( \frac{d}{dx} V(x) \right) | k \rangle.$$

Derive this relation using commutators

$$[p_x, H] = -i \frac{h}{2\pi} \frac{\partial}{\partial x} V \quad \text{and} \quad [x, H] = \frac{h^2}{4\pi^2 m} \frac{\partial}{\partial x},$$

and the relation

$$\langle k | H x p_x | k \rangle = \sum_{k' \neq k} \langle k | H | k' \rangle \langle k' | x p_x | k \rangle = E_k \langle k | x p_x | k \rangle.$$

Maple is unnecessary for this exercise.

### 1.25 significance of these results

#### > restart:

What do these results signify? The matrix mechanics of Heisenberg, Born and Jordan and the wave mechanics of Schroedinger that together constitute *pioneer quantum mechanics* are both non-relativistic in that these formulations take no account of the variation of mass with velocity or momentum. That these approaches to quantum mechanics are equivalent was demonstrated first formally by Eckert, then in progressively greater sophistication by Pauli, Schroedinger, Dirac and von Neumann. There is required in matrix mechanics neither amplitude function nor other operand of a matrix because multiplication of one matrix by another can intrinsically conform to the fundamental postulate of quantum mechanics, whereas wave mechanics requires an operand for its differential operators; that operand, called an amplitude function or wave function, or an orbital in a particular case of a solution of Schroedinger's temporally independent equation for an atom or molecule having only one electron, is hence an artefact of that particular approach and its particular representation -- either coordinate or momentum, and is not an observable physical quantity. Such an amplitude function has an algebraic form depending on variables as coordinates or momenta, depending thus on the representation. For Dirac's operators for creation and destruction, an operand is equally required, but these operands are abstract vectors, having directly no internal intrinsic algebraic or geometric form.

As mentioned in the overview, formulations of quantum mechanics include the following [adapted and extended from D. F. Styer et alii, *American Journal of Physics*. 70 (3) 288 - 297, 2002].

- matrix mechanics, of Heisenberg, 1925, with Born and Jordan
- symbolic method developed by Pauli, 1926, developed by Green, 1965
- wave mechanics, of Schroedinger, 1926
- path integral, of Wiener, 1926, developed by Feynman, 1948
- second quantization with Dirac's operators for creation and destruction, 1927
- density matrix, of von Neumann, 1927
- variational formulation, distinct from variational method, of Jordan and Klein, 1927
- pilot wave, of de Broglie, 1927, and Bohm, 1952
- relativistic wave mechanics, of Dirac, 1928

- phase space, of Wigner, 1932
- octonionic quantum mechanics, Jordan, 1933
- quaternionic quantum mechanics, of Birkhoff and von Neumann, 1936, developed by Adler and others
- Hamilton-Jacobi formulation, developed by Leacock and Padgett, 1983

Of these methods, the most practical for most chemical purposes such as quantum-chemical calculations involving spatial coordinates of particles is wave mechanics in the coordinate representation, either directly with amplitude functions or indirectly with density functionals (Kohn and Sham, 1965), but other methods might be more efficient for particular purposes; for calculations involving intrinsic angular momenta of electrons or nuclei, matrix mechanics is practical.

According to matrix mechanics, dynamical variables such as coordinates relative to some axes, components of momentum and energy of a particle appear explicitly in the equations of motion of the system without their being subject to multiplication or differentiation by an amplitude function, which is just the structure of the classical equations; for this reason one expects a resemblance between the classical and quantum formalisms closer than in Schroedinger's theory. The principal formal distinction is that the quantum-dynamical variables are not subject to the commutative law of multiplication. To represent as a matrix such a non-commutative dynamical variable is convenient; such a matrix maintains the connotation of an operator, as a matrix might operate on a vector to rotate it for instance. Such a matrix scheme provides an especially flexible representation, as a choice of the rows and columns of a matrix can be implemented in ways of arbitrarily large number, each of equal validity. This formal resemblance between quantum matrix mechanics and classical dynamics enabled Heisenberg in 1925 to discover the first formulation of quantum theory.

For the canonical linear harmonic oscillator, the quantization of energies in matrix mechanics arises naturally because, even for a matrix of infinite order, its rows and columns are counted or numbered with integers; the discrete states of the oscillator are numbered with the same integers. The differences between two elements of the diagonal energy matrix become the differences of energy between two states that might be observable in a spectral transition, and the square of the corresponding matrix element of the coordinate matrix between two states determines the intensity of that spectral transition in absorption or emission according to electric dipole type. In the case of wave mechanics, the requirement to have quadratically integrable amplitude functions of spatial variables for bound states imposes integer or half-integer labels on those states, i.e. quantum numbers. For Dirac's operators, the nature of the ket or bra on which these operators operate is abstract, but, from a point of view of a change of population, again an integer as a label of such a bra or ket is appropriate; the definition of the creation and destruction operators involves integer increments or decrements that eventually yield integer values of a quantum number for the states of discrete energy. Treatments of this canonical linear harmonic oscillator according to classical and quantum mechanics differ in that classical mechanics yields no residual energy,  $\frac{1}{2} h \nu_0$ , that directly appears in each quantum-mechanical treatment.

Apart from other mathematical quantities that naturally fail to commute, such as quaternions or octonions upon which quantum mechanics in another variant has been constructed as discussed in section 1.84, one can devise further approaches to quantum mechanics that conform to the commutation formula but that require neither matrices nor amplitude functions; such an instance, explained in section 1.24, involves Dirac's operators for creation and destruction that has also a non-relativistic context. For this reason, all three methods presented here yield identical results for the observable properties of a canonical linear harmonic oscillator, including the frequencies of transitions and their intensities according to an electric-dipolar transition moment independent of time.

Although a matrix can act as an operator, for instance to operate on a vector to rotate that vector, in

the particular calculation of an harmonic oscillator according to matrix mechanics above, the matrices appear to operate on no explicit vector. For the canonical linear harmonic oscillator, we deduced a formulation of the elements of the coordinate matrix that yielded, eventually, an energy matrix that was diagonal; in other cases in which such a fortuitous deduction is inapplicable, an explicit diagonalization of the energy matrix is necessary, as practised for the anharmonic oscillator in section 1.47 for instance.

In wave mechanics the operators, such as  $\frac{\partial}{\partial q}$  or  $\frac{\partial}{\partial p}$ , must operate on an explicit function of coordinates or momentum variables according to the representation, such as  $\psi(q)$  or  $\chi(p)$ , respectively, that might be interpreted as vectors, because Schroedinger's equation independent of time, as  $H\psi = E\psi$ , resembles an equation containing eigenvalue  $E$  and eigenvector  $\psi$ ; the algebraic forms of the latter functions are derived explicitly. Although Dirac's operators  $a$  and  $a^\dagger$  for destruction and creation, represented in the calculations above as  $a$  and  $b$ , must operate explicitly on a state vector, ket  $|n\rangle$  or bra  $\langle n|$ , the explicit form or nature of those state vectors never arises. Also, whereas with matrix mechanics and wave mechanics, we must calculate matrix elements for transitions between specific states, with Dirac's operators we derive directly general formulae, independent of a particular value of  $n$ , but we have no mechanism to incorporate the time factor. In a context of the present calculations, Dirac's approach thus has a further advantage that it produces general results, i.e. for  $\langle n | q | n+1 \rangle$ , independent of a particular numerical value of  $n$ , whereas for both matrix mechanics and wave mechanics we must here evaluate physical quantities for particular numerical values and then deduce a general relation for those results, because Maple is unable to solve directly those general problems.

Here follow the expressions for, for instance, matrix element  $q_{2,1}$  according to the three methods, in terms of mass  $\mu$  and frequency  $\nu_0$ , but it is not obvious how to incorporate the time factor into the Dirac operators.

```
> Q[3,2] := 1/2*1/Pi*(h/mu/nu[0])^(1/2)*exp(2*I*Pi*nu[0]*t); #
matrix mechanics
```

$$Q_{3,2} := \frac{\sqrt{\frac{h}{\mu \nu_0}} e^{2i\pi \nu_0 t}}{2\pi} \quad (18.1)$$

```
> q0[2,1] := 1/2*1/Pi*(h/mu/nu[0])^(1/2); # matrix mechanics
without time factor
```

$$q_{2,1} := \frac{\sqrt{\frac{h}{\mu \nu_0}}}{2\pi} \quad (18.2)$$

```
> Int('psi'(2,q)*q*'psi'(1,q),q = -infinity .. infinity) = 1/2*h^
(1/2)/Pi/mu^(1/2)/nu[0]^(1/2)
*exp(2*I*Pi*nu[0]*t); # wave mechanics
```

$$\int_{-\infty}^{\infty} \psi(2,q) q \psi(1,q) dq = \frac{\sqrt{h} e^{2i\pi \nu_0 t}}{2\pi \sqrt{\mu} \sqrt{\nu_0}} \quad (18.3)$$

```
> Int('psi'(2,q)*q*'psi'(1,q),q = -infinity .. infinity) = 1/2*h^
(1/2)/Pi/mu^(1/2)/nu[0]^(1/2);
```

# wave mechanics without time

factor

$$\int_{-\infty}^{\infty} \psi(2, q) q \psi(1, q) dq = \frac{\sqrt{h}}{2 \pi \sqrt{\mu} \sqrt{v_0}} \quad (18.4)$$

> ` $\langle n+1 | q | n \rangle` := 1/4*2^(1/2)/Pi/mu^(1/2)/nu[0]^(1/2)*h^(1/2)*  
(n+1)^(1/2); # Dirac operators, general$

$$\langle n+1 | q | n \rangle := \frac{\sqrt{2} \sqrt{h} \sqrt{n+1}}{4 \pi \sqrt{\mu} \sqrt{v_0}} \quad (18.5)$$

> ` $\langle 2 | q | 1 \rangle` := eval(` $\langle n+1 | q | n \rangle``, n=1);$$

$$\langle 2 | q | 1 \rangle := \frac{\sqrt{h}}{2 \pi \sqrt{\mu} \sqrt{v_0}} \quad (18.6)$$

Explicitly, the energy of each state is

$$E_n = \langle n | H | n \rangle = \left( n + \frac{1}{2} \right) h v_0,$$

the difference of energy between states of adjacent energies is  $\frac{h \omega_0}{2 \pi} = h v_0$ , the angular frequency of a transition in absorption or emission according to an electric dipole is  $\omega_0$ , or the circular frequency is  $v_0$ ; the matrix element for such a transition, without the time factor, is

$$\langle q_{n, n+1} \rangle = \langle n | q | n+1 \rangle = \sqrt{\frac{n+1}{2}} \frac{\sqrt{\frac{h}{\mu v_0}}}{2 \pi}.$$

The latter matrix element from matrix mechanics or wave mechanics has a further temporal factor,

$e^{2 \pi v_0 t I}$  or  $e^{-2 \pi v_0 t I}$ , that does not arise with Dirac's operators as derived above. We obtain the same result in matrix mechanics on forming the square root of an inner product,

$$|q_{n, n+1}| = (\langle q_{n, n+1} | q_{n, n+1} \rangle)^{\frac{1}{2}},$$

in which  $\langle q_{n, n+1} |$  is the complex conjugate of  $|q_{n, n+1} \rangle$ . Hence,

$$\begin{aligned} |q_{n, n+1}|^2 &= \langle q_{n, n+1} | q_{n, n+1} \rangle \\ &= \sqrt{\frac{n+1}{2}} \frac{\sqrt{\frac{h}{\mu v_0}}}{2 \pi} e^{-2 \pi v_0 t I} \sqrt{\frac{n+1}{2}} \frac{\sqrt{\frac{h}{\mu v_0}}}{2 \pi} e^{2 \pi v_0 t I} \\ &= \left( \frac{\sqrt{n+1}}{2} \frac{\sqrt{\frac{h}{\mu v_0}}}{2 \pi} \right)^2 \end{aligned}$$

or

$$|q_{n,n+1}| = \langle n | q | n+1 \rangle = \sqrt{\frac{n+1}{2}} \frac{\sqrt{\frac{h}{\mu v_0}}}{2\pi}$$

as obtained directly in treatments of wave mechanics, before inclusion of the temporal dependence, and of Dirac's operators.

The technical properties of an acceptable amplitude function  $\psi$ , regarded as a function of coordinates, that it must be finite and continuous and have a single value at any point, as listed at the beginning of section 1.23 are more restrictive than necessary; they are sufficient, but not all necessary and might exclude an admissible eigenvalue. The necessary and sufficient conditions are that  $|\psi|^2$ , regarded as a function of coordinates, be integrable and single-valued; the latter, and weak, conditions are implicit in matrix mechanics, as a finite length of  $\psi^* \psi$  is required.

Having introduced Dirac's bra and ket notation, we proceed to derive de Broglie's relation. As initial point, we take the transformation function  $\langle q | p \rangle$  that connects the coordinate and momentum representations, with  $|p\rangle$  as the basis kets for the latter representation. This transformation must be the solution of a differential equation resulting from the replacement of  $p$  by the corresponding differential

operator  $-i \frac{h}{2\pi} \frac{\partial}{\partial q}$ ; hence  $\langle q | p \rangle \sim e^{\frac{2\pi i p q}{h}}$ . If we replace  $q$  in the exponent by  $q + \frac{n h}{p}$ , for

integer  $n$ , the right side remains unchanged, because  $e^{2\pi i n} = 1$ . Because  $\frac{h}{p}$  has the significance of a

wave length,  $\lambda$ , the desired result is obtained. With this simple derivation, and that for Heisenberg's indeterminacy in section 1.24, we prove that the fundamental postulate of quantum mechanics, namely

$p q - q p = -\frac{i h}{2\pi}$  in one spatial dimension, is a sufficient basis of quantum mechanics; a 'derivation' of

this postulate appears in <http://arxiv.org/pdf/quant-ph/0404009v1>, appendix A, but it seems to involve a circular argument.

Although matrix mechanics and the symbolic method involving Dirac's operators seem elegant, in general the deduction of matrix elements or the relation between Dirac's operators and physical observables is difficult; matrix mechanics finds some application in a treatment of intrinsic angular momenta of electrons or atomic nuclei in systems, for which no explicit formation of an amplitude function in spatial coordinates is practical. Dirac, who considered that matrix mechanics was more fundamental than wave mechanics, found that Schroedinger's approach applied in quantum electrodynamics leads to intractable infinities whereas the approach of Heisenberg, in which the operators contain dependences, is practicable. Despite that reservation, for practical calculations on molecules, particularly in relation to molecular electronic structure, Schroedinger's wave mechanics seems to provide the only practical algorithm within a non-relativistic frame, whether involving orbitals or analogous functions in basis sets or density functionals. For that reason, in either further calculations or consideration of prospective calculations we here adopt generally a wave-mechanical approach.

Although one might expect that a relativistic calculation on the canonical linear harmonic oscillator, for instance according to relativistic wave mechanics that still invokes amplitude or wave functions, might yield an unequal interval of energy between adjacent states because the relativistic mass increases with velocity and hence with momentum or kinetic energy, that interval remains constant although the amplitude functions become strongly modified [formerly at [http://www.elp.uji.es/juan\\_home/research/quantum\\_harmonic\\_oscillator.php](http://www.elp.uji.es/juan_home/research/quantum_harmonic_oscillator.php)].



## 1.26 inter-relations among matrix mechanics, wave mechanics and Dirac operators for a canonical linear harmonic oscillator

> restart:

We relate the three methods to treat a canonical linear harmonic oscillator as a boson. We begin with Schroedinger's equation in one dimension independent of time,

$$H(q) \psi(q) = \left( -\frac{h^2 \left( \frac{\partial^2}{\partial q^2} \right)}{8 \pi^2 \mu} + \frac{k q^2}{2} \right) \psi(q) = E \psi(q)$$

expressed in the same form as before. We make two substitutions,  $k = \mu \nu^2$  and  $q = \sqrt{\frac{h}{\mu \nu}} x$ , so to convert Schroedinger's equation into this form.

$$H(x) \psi(x) = \frac{h \nu \left( -\left( \frac{\partial^2}{\partial x^2} \right) + x^2 \right) \psi(x)}{2} = E \psi(x)$$

The content of the parentheses is expressible as

$$-\left( \frac{\partial^2}{\partial x^2} \right) + x^2 = \left( -\left( \frac{\partial}{\partial x} \right) + x \right) \left( \frac{\partial}{\partial x} + x \right) + \left( \frac{\partial}{\partial x} \right) x - x \left( \frac{\partial}{\partial x} \right)$$

We simplify the latter two terms by considering their action on an arbitrary differentiable function  $f$  of formula  $f(x)$ ,

$$\left( \left( \frac{\partial}{\partial x} \right) x - x \left( \frac{\partial}{\partial x} \right) \right) f(x) = f(x) + x \left( \frac{d}{dx} f(x) \right) - x \left( \frac{d}{dx} f(x) \right) = f(x),$$

which implies that  $\left( \frac{\partial}{\partial x} \right) x - x \left( \frac{\partial}{\partial x} \right) = 1$ . Therefore

$$-\left( \frac{\partial^2}{\partial x^2} \right) + x^2 + 1 = \left( -\left( \frac{\partial}{\partial x} \right) + x \right) \left( \frac{\partial}{\partial x} + x \right) + 1$$

and we rearrange Schroedinger's equation to

$$h \nu \left( \frac{\left( -\left( \frac{\partial}{\partial x} \right) + x \right) \left( \frac{\partial}{\partial x} + x \right)}{\sqrt{2} \sqrt{2}} + \frac{1}{2} \right) \psi(x) = E \psi(x)$$

When we identify  $\frac{-\left( \frac{\partial}{\partial x} \right) + x}{\sqrt{2}}$  with operator  $a^t$ , hereafter expressed as  $b$ , as a creation or raising

operator, and  $\frac{\frac{\partial}{\partial x} + x}{\sqrt{2}}$  with operator  $a$  as a destruction or lowering operator, Schroedinger's equation becomes expressible as

$$h \nu \left( a b + \frac{1}{2} \right) \psi(x) = E \psi(x)$$

With the conjugate operator for momentum as  $p_x = -i \left( \frac{\partial}{\partial x} \right)$ , we evaluate the commutator  $[p_x, x] = -i$ , and

$$a = \frac{x + i p_x}{\sqrt{2}} = \frac{x + \frac{\partial}{\partial x}}{\sqrt{2}}$$

$$b = \frac{x - i p_x}{\sqrt{2}} = \frac{x - \left(\frac{\partial}{\partial x}\right)}{\sqrt{2}}$$

Commutator  $[a, b]$  is then evaluated as

$$[a, b] = \frac{1}{2} [x + i p_x, x - i p_x] = \frac{[x, -i p_x] + [i p_x, x]}{2} = -\frac{i([x, p_x] + [x, p_x])}{2} = 1$$

The hamiltonian operator thereby becomes expressible as

$$H(x) = h \nu \left( a b - \frac{1}{2} \right) = h \nu \left( b a + \frac{1}{2} \right)$$

The commutation relations between the hamiltonian and these other operators become

$$[H(x), a] = -h \nu a \quad \text{and} \quad [H(x), b] = h \nu b.$$

Accordingly, with  $\psi_n(x)$  as an eigenfunction of hamiltonian operator  $H(x)$  such that

$$H(x) \psi_n(x) = E_n \psi_n(x),$$

$$H(x) a \psi_n(x) = (E_n - h \nu) a \psi_n(x)$$

$$H(x) b \psi_n(x) = (E_n + h \nu) b \psi_n(x)$$

which implies that  $a \psi_n(x)$  is an eigenfunction of  $H(x)$  with eigenvalue  $E_n - h \nu$  and  $b \psi_n(x)$  with eigenvalue  $E_n + h \nu$ . The latter properties prove that  $a$  is a lowering operator and  $b$  is a raising operator between the eigenstates, and the difference of energy between the energies of adjacent eigenstates is  $\Delta E = h \nu$ .

For the canonical linear harmonic oscillator in its state  $|0\rangle$  of least energy with amplitude function  $\psi_0(x)$ , or ground state,

$$a |0\rangle = 0,$$

which becomes expressed as this differential equation,

$$x \psi_0(x) + \frac{d}{dx} \psi_0(x) = 0$$

```
> deq := x*psi[0](x) + diff(psi[0](x),x) = 0;
```

$$deq := x \psi_0(x) + \frac{d}{dx} \psi_0(x) = 0 \quad (19.1)$$

The solution of this differential equation is

```
> sol := dsolve(deq, psi[0](x));
```

$$sol := \psi_0(x) = \_C1 e^{-\frac{x^2}{2}} \quad (19.2)$$

The integration constant  $\_C1$  is evaluated from a normalising integral such that  $\int_{-\infty}^{\infty} \psi_0(x)^2 dx = 1$ ,

```
> _C1 := 1/sqrt(int((rhs(sol)/_C1)^2, x=-infinity..infinity));
```

(19.3)

$$_CI := \frac{1}{\pi^{1/4}} \quad (19.3)$$

```
> psi[0](x) := rhs(sol);
```

$$\Psi_0(x) := \frac{e^{-\frac{x^2}{2}}}{\pi^{1/4}} \quad (19.4)$$

which yields directly the amplitude function of simple gaussian form, as found in section 1.23.

We express the creation and destruction operations for the quantum-mechanical canonical harmonic oscillator in matrix form with a submatrix of an infinite matrix as follows,

```
> interface( rtablesiz = 15 );
```

```
> a := Matrix(12,12):
```

```
  for j to 11 do
```

```
    a[j,j+1] := sqrt(j);
```

```
  end do;
```

```
  a := a;
```

$$a := \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{7} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{10} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{11} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (19.5)$$

```
> b := Matrix(12,12):
```

```
  for j to 11 do
```

```
    b[j+1,j] := sqrt(j);
```

```
  end do;
```

```
  b := b;
```

$$b := \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{7} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{10} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{11} & 0 & 0 \end{bmatrix} \quad (19.6)$$

which are consistent with the definitions  $a |n\rangle = \sqrt{n} |n-1\rangle$  and  $b |n\rangle = \sqrt{n+1} |n+1\rangle$ . These operators are analogously converted to differential form for operation on amplitude functions  $\psi(q)$ . These matrices can operate on a column vector to represent a ket as follows, for instance for  $|n\rangle$  with  $n=6$ .

```
> `ket|6>` := <seq(0,j=1..5), 1, seq(0,j=1..5),0>;
```

$$ket|6\rangle := \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (19.7)$$

```
> a.`ket|6>`;
```

$$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \sqrt{5} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (19.8)$$

which, with  $|5\rangle$  defined as

```
> `ket|5>` := <seq(0,j=1..4), 1, seq(0,j=1..6),0>;
```

$$ket|5> := \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (19.9)$$

is equivalent to

```
> sqrt(5)*`ket|5>`;
```

$$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \sqrt{5} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (19.10)$$

Other operations with  $a$  and  $b$  as matrices on kets as vectors proceed analogously.

In section 1.23, we form matrices with elements of form  $\langle n+1 | q | n \rangle$  and  $\langle n+1 | \frac{1}{q} | n \rangle$ ; even though that explanation of the relation between quantities pertaining to matrix mechanics and to wave mechanics might be more appropriate at this point, the practicality of the calculations in that context resulted in their presence there. We here draw, however, attention to this aspect of the inter-relations between these three formalisms -- matrix mechanics, wave mechanics, Dirac operators -- that are formally separate, merely with a common property of conforming to the commutation law; the use of these inter-relations enables the solution of problems that are otherwise less tractable.

### 1.27 canonical harmonic oscillator according to wave mechanics in polar coordinates

**> restart;**

Here we treat the canonical harmonic oscillator, for which the classical restoring force is linearly proportional to the displacement from equilibrium, in two dimensions hence implying two quantum numbers to define a state, specifically in a plane with polar coordinates  $r$  and  $\phi$ , for which the potential energy is proportional to the squared displacement,  $r^2$ , of mass  $\mu$  from the origin; the potential energy is thus independent of angle  $\phi$ . This treatment serves to introduce the concept of *degeneracy*, whereby an energy of a stationary state of the system might pertain to states characterized with quantum numbers in multiple sets.

To begin, we apply this procedure to derive the laplacian operator in polar coordinates.

```
> change_variables := proc(
    # pde1    :: {algebraic, list(algebraic), set(algebraic)},
    pde1     :: anything,
    va1      :: list(name),
    f1       :: list(function),
    va2      :: list(name),
    f2       :: list(function),
```

```

    eq1_2  :: list(equation),
    eqf1_2 :: list(equation), NULL)
# pde1    differential operator such as the Laplacian in
Cartesian coordiantes
#          diff(f(x,y,z),x$2)+diff(f(x,y,z),y$2)+diff(f(x,y,
z),z$2)
# va1     list of old indepentdent variables  such as    [x,y,z]
# f1      list of old functions  such as    [f(x,y,z)]
# va2     list of new indepentdent variables  such as    [r,t,p]
# va2     list of new functions  such as    [g(r,t,p)]
# eq1_2   list of equations expressing old variables in terms of
new variables
#          such as [x=r*sin(t)*cos(p),y=r*sin(t)*sin(p),z=r*
cos(t)]
# eqf1_2  list of equations expressing the old functions in terms
of the new functions
#          such as [f(x,y,z)=g(r,t,p)]
local n,J,i,g,j,J1,pde,id1,d,a,v,ss,df1,df2;
n := nops(va1);
J := Matrix(n);
for i to n do
    g := subs(eq1_2,va1[i]);
    for j to n do
        J[i,j] := diff(g,va2[j]);
    end do;
end do;
J1 := 1/J;
pde := subs(diff=df1,pde1);
pde := subs(eqf1_2,pde);
id1 := indets(pde,df1(anything,name));
for d in id1 do
    a := op(1,d);
    v := op(2,d);
    member(v,va1,'j');
    ss := add(df2(a,va2[i])*J1[i,j],i=1..n);
# Use the chain rule
    pde := subs(d=ss,pde);
end do;
pde := subs(eq1_2,pde);
pde := eval(pde,df2=diff);
pde := simplify(pde);
pde := expand(pde);

```

```
pde;
end proc;
```

Here is a list of cartesian or rectangular coordinates in two spatial dimensions and a name of an arbitrary function of those coordinates.

```
> val := [x,y];
```

$$val := [x, y] \quad (20.1)$$

```
> f1 := [f(x,y)];
```

$$f1 := [f(x, y)] \quad (20.2)$$

Here is a laplacian in cartesian coordinates in two dimensions,

```
> val := [x,y]:
> f1 := [f(x,y)]:
> pde1 := add(diff(f1[1],val[i]$2),i=1..2);
```

$$pde1 := \frac{\partial^2}{\partial x^2} f(x, y) + \frac{\partial^2}{\partial y^2} f(x, y) \quad (20.3)$$

which we transform to cylindrical coordinates.

```
> va2 := [r,phi];
```

$$va2 := [r, \phi] \quad (20.4)$$

```
> f2 := [g(r,phi)];
```

$$f2 := [g(r, \phi)] \quad (20.5)$$

```
> eq1_2 := [x=r*cos(phi),y=r*sin(phi)];
```

$$eq1\_2 := [x = r \cos(\phi), y = r \sin(\phi)] \quad (20.6)$$

```
> eqf1_2 := [f1[1]=f2[1]]:
```

Applying the procedure above to change the variables yields

```
> pde2 := change_variables(pde1,val,f1,va2,f2,eq1_2,eqf1_2);
```

$$pde2 := \frac{\partial^2}{\partial r^2} g(r, \phi) + \frac{\frac{\partial}{\partial r} g(r, \phi)}{r} + \frac{\frac{\partial^2}{\partial \phi^2} g(r, \phi)}{r^2} \quad (20.7)$$

We replace formal function g by  $\psi$ .

```
> pde3 := subs(g=psi, pde2);
```

$$pde3 := \frac{\partial^2}{\partial r^2} \psi(r, \phi) + \frac{\frac{\partial}{\partial r} \psi(r, \phi)}{r} + \frac{\frac{\partial^2}{\partial \phi^2} \psi(r, \phi)}{r^2} \quad (20.8)$$

We define the function for potential energy,  $V = \frac{1}{2} k_e r^2$ , which depends on only  $r$ , not  $\phi$ , and in which we replace force coefficient  $k_e$  by  $\mu \omega^2$  in which  $\omega$  is a characteristic radial frequency of the system,

```
> V := 1/2*mu*omega^2*r^2;
```



$$V := \frac{\mu \omega^2 r^2}{2} \quad (20.9)$$

generate Schroedinger's partial-differential equation in polar coordinates,

$$\begin{aligned} &> \text{Seq} := -\hbar b^2 / (2 \mu) * \text{pde3} + V * \psi(r, \phi) = E * \psi(r, \phi); \\ \text{Seq} &:= -\frac{\hbar b^2 \left( \frac{\partial^2}{\partial r^2} \psi(r, \phi) + \frac{\frac{\partial}{\partial r} \psi(r, \phi)}{r} + \frac{\frac{\partial^2}{\partial \phi^2} \psi(r, \phi)}{r^2} \right)}{2 \mu} + \frac{\mu \omega^2 r^2 \psi(r, \phi)}{2} \\ &= E \psi(r, \phi) \end{aligned} \quad (20.10)$$

and solve it,

$$\begin{aligned} &> \text{solSeq} := \text{pdsolve}(\text{Seq}); \\ \text{solSeq} &:= \psi(r, \phi) = {}_F1(r) {}_F2(\phi) \text{ where } \left[ \left\{ \frac{d^2}{dr^2} {}_F1(r) = \frac{{}_F1(r) {}_c1}{r^2 \hbar b^2} \right. \right. \\ &\quad + \frac{{}_F1(r) \mu^2 \omega^2 r^3 - 2 E {}_F1(r) \mu r - \left( \frac{d}{dr} {}_F1(r) \right) \hbar b^2}{\hbar b^2 r}, \frac{d^2}{d\phi^2} {}_F2(\phi) = \\ &\quad \left. \left. - \frac{{}_F2(\phi) {}_c1}{\hbar b^2} \right\} \right] \end{aligned} \quad (20.11)$$

to obtain a product of two functions, one function of each separate variable. We separate these equations,

$$\begin{aligned} &> \text{if has}(\text{op}(1, \text{op}(1, \text{op}(2, \text{solSeq}))), \phi) \text{ then} \\ &\quad \text{Phieq} := \text{op}(1, \text{op}(1, \text{op}(2, \text{solSeq}))); \\ &\text{else} \\ &\quad \text{Phieq} := \text{op}(2, \text{op}(1, \text{op}(2, \text{solSeq}))); \\ &\text{end if:} \\ &\text{Phieq} := \text{subs}(_F2 = \Phi, {}_c[1] = -{}_c[1], \text{Phieq}); \\ &\quad \text{Phieq} := \frac{d^2}{d\phi^2} \Phi(\phi) = \frac{\Phi(\phi) {}_c1}{\hbar b^2} \end{aligned} \quad (20.12)$$

$$\begin{aligned} &> \text{if has}(\text{op}(1, \text{op}(1, \text{op}(2, \text{solSeq}))), r) \text{ then} \\ &\quad \text{Req} := \text{op}(1, \text{op}(1, \text{op}(2, \text{solSeq}))); \\ &\text{else} \\ &\quad \text{Req} := \text{op}(2, \text{op}(1, \text{op}(2, \text{solSeq}))); \\ &\text{end if:} \\ &\text{Req} := \text{subs}(_F1 = R, \text{Req}); \end{aligned}$$

$$Req := \frac{d^2}{dr^2} R(r) = \frac{R(r) - c_1}{r^2 h b^2} + \frac{R(r) \mu^2 \omega^2 r^3 - 2 E R(r) \mu r - \left( \frac{d}{dr} R(r) \right) h b^2}{h b^2 r} \quad (20.13)$$

and solve the  $\phi$  equation

```
> Phisol := dsolve(Phieq, Phi(phi));
```

$$Phisol := \Phi(\phi) = -C1 e^{\frac{\sqrt{-c_1} \phi}{h b}} + -C2 e^{-\frac{\sqrt{-c_1} \phi}{h b}} \quad (20.14)$$

Although three parameters appear in that solution of the ordinary-differential equation as [constants of integration](#), only two are independent. To introduce the quantum numbers we impose periodicity on the functions of the angular variables and a boundary condition on the distance variable such that the amplitude function must remain finite at an infinite separation. For a suitably [periodic](#) formula, this solution must hence be equivalent to  $\Phi(\phi) = c e^{I m \phi}$  with  $m$  taking values of positive and negative [integer](#) values, which we proceed to form by eliminating the second term.

```
> Phisol := subs(_C2 = 0, Phisol);
```

$$Phisol := \Phi(\phi) = -C1 e^{\frac{\sqrt{-c_1} \phi}{h b}} \quad (20.15)$$

For a function of period  $2\pi$ , the coefficient of  $\phi$  must be an integer, as a boundary condition; we extract that coefficient,

```
> exparg := op([1,1], indets(Phisol, exp(anything)))/phi;
```

$$exparg := \frac{\sqrt{-c_1}}{h b} \quad (20.16)$$

and equate it to integer  $m$  known as the magnetic quantum number because its value distinguishes the various energies, slightly separated, upon the application of a magnetic field to the atom according to a normal Zeeman effect; this splitting is independent of other quantum numbers and equal to  $m B_z \mu_B$ , in which  $B_z$  is the density of magnetic flux parallel to axis  $z$  and  $\mu_B$  denotes the fundamental unit of magnetic dipolar moment, known as the Bohr magneton and equal to  $\frac{e h}{4 \pi m_e}$ .

```
> c1 := solve(exparg = I*m, _c[1]);
```

$$c1 := -m^2 h b^2 \quad (20.17)$$

We implement that result by substitution in the  $\Phi(\phi)$  equation,

```
> Phisol := simplify(subs(_c[1] = c1, Phisol), symbolic)
      assuming m::integer;
```

$$Phisol := \Phi(\phi) = -C1 e^{I m \phi} \quad (20.18)$$

Because Schroedinger's temporally dependent equation has the form of an [eigenvalue](#) equation, or because the corresponding differential equation is homogeneous, any solution  $\psi$  multiplied by [scalar quantity](#)  $c$  to form  $c \psi$  is equally a solution, and the units of  $\psi$  are indeterminate. To impose uniqueness, we apply an interpretation of Born that product  $\psi^* \psi d\tau$  in any volume element  $d\tau$

corresponds to the probability of finding the electron in that volume element, such that the total probability of finding the electron somewhere is unity; hence

$$\int \psi(r, \phi) \psi^*(r, \phi) d\tau = 1,$$

in which the integration is taken over all space. In this case the physical unit of  $\psi$  becomes the unit of area to power  $-\frac{1}{2}$ , or equivalently the unit of length to power  $-1$ . Not only [amplitude](#) function

$\psi(r, \phi)$  but also each spatial component factor  $R(r)$  and  $\Phi(\phi)$  is separately subject to that normalisation. Coefficient  $\_C1$  is accordingly evaluated according to the condition that

$$\int_0^{2\pi} \overline{\Phi(\phi)} \Phi(\phi) d\phi = 1,$$

which makes the unit of  $\Phi$  become the dimensionless unit of the square root of angle, specifically  $\sqrt{rad}$ .

```
> solve(int(subs(I=-I, rhs(Phisol))*rhs(Phisol), phi=0..2*Pi) = 1,
        op(1,rhs(Phisol))) assuming m::real;
```

$$\frac{\sqrt{2}}{2\sqrt{\pi}}, -\frac{\sqrt{2}}{2\sqrt{\pi}} \quad (20.19)$$

```
> _C1:= op(map(abs, {%}));
```

$$\_C1 := \frac{\sqrt{2}}{2\sqrt{\pi}} \quad (20.20)$$

The complete solution of the equation governing  $\Phi(\phi)$  is thus

```
> Phisol := Phisol;
```

$$Phisol := \Phi(\phi) = \frac{\sqrt{2} e^{Im\phi}}{2\sqrt{\pi}} \quad (20.21)$$

We replace  $\_c_1$  in the ordinary-differential equation for  $R(r)$ ,

```
> Req2 := subs(_c[1]=-c1, Req);
```

$$Req2 := \frac{d^2}{dr^2} R(r) = \frac{R(r) m^2}{r^2} + \frac{R(r) \mu^2 \omega^2 r^3 - 2 E R(r) \mu r - \left( \frac{d}{dr} R(r) \right) hb^2}{hb^2 r} \quad (20.22)$$

and solve it.

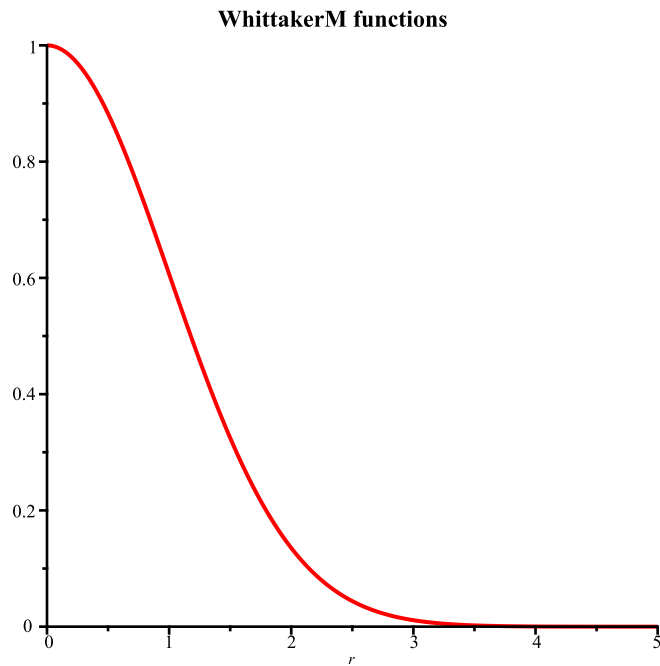
```
> Rsol := dsolve(Req2, R(r));
```

$$Rsol := R(r) = \frac{\_C2 \text{WhittakerM}\left(\frac{E}{2 \omega hb}, \frac{m}{2}, \frac{\mu \omega r^2}{hb}\right)}{r} \quad (20.23)$$

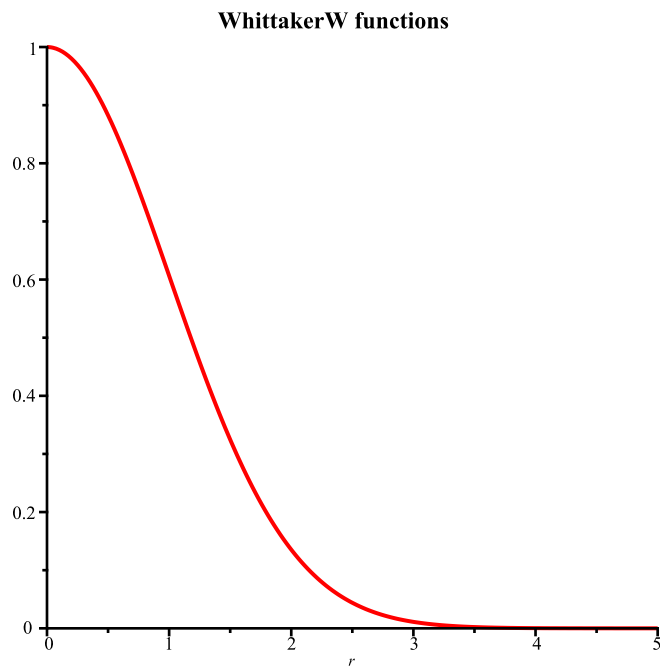
$$+ \frac{\_C3 \text{WhittakerW}\left(\frac{E}{2 \omega hb}, \frac{m}{2}, \frac{\mu \omega r^2}{hb}\right)}{r}$$

We plot both terms containing Whittaker functions separately, using unit values of parameters.

```
> plot(eval(op(1, rhs(Rsol))), [E=1,hb=1,omega=1,m=0,_C2=1,mu=1]), r=
0..5,
      title="WhittakerM functions", titlefont=[TIMES,BOLD,14],
      colour=red);
```



```
> plot(eval(op(2, rhs(Rsol))), [E=1,hb=1,omega=1,m=0,_C3=1, mu=1]),
r=0..5,
      title="WhittakerW functions", titlefont=[TIMES,BOLD,14],
      colour=red);
```



As both Whittaker functions appear to be well behaved, we retain both, but convert them both to Kummer M functions, which pertain to generalized hypergeometric series, as a product with an exponential gaussian function of form  $e^{-r^2}$ .

**> Rsol3 := convert(Rsol, KummerM);**

$$Rsol3 := R(r) = \frac{-C2 \left( \frac{\mu \omega r^2}{hb} \right)^{\frac{m}{2} + \frac{1}{2}} \text{KummerM} \left( \frac{1}{2} + \frac{m}{2} - \frac{E}{2 \omega hb}, m+1, \frac{\mu \omega r^2}{hb} \right)}{r e^{\frac{\mu \omega r^2}{2 hb}}} \quad (20.24)$$

$$+ \frac{1}{r e^{\frac{\mu \omega r^2}{2 hb}}} \left( -C3 \left( \frac{1}{\Gamma \left( \frac{-(m-1) \omega hb - E}{2 hb \omega} \right)} \left( \Gamma(-m) \text{KummerM} \left( \frac{(m+1) \omega hb - E}{2 hb \omega}, m+1, \frac{\mu \omega r^2}{hb} \right) \left( \frac{\mu \omega r^2}{hb} \right)^{\frac{m}{2} + \frac{1}{2}} \right) \right. \right.$$

$$\left. \left. + \frac{\Gamma(m) \text{KummerM} \left( \frac{-(m-1) \omega hb - E}{2 hb \omega}, 1-m, \frac{\mu \omega r^2}{hb} \right)}{\Gamma \left( \frac{(m+1) \omega hb - E}{2 hb \omega} \right) \left( \frac{\mu \omega r^2}{hb} \right)^{\frac{m}{2} - \frac{1}{2}}} \right) \right)$$

As the second term contains both  $\Gamma(-m)$  and  $\Gamma(m)$  of which one must diverge for a positive or negative integer value of  $m$ , we eliminate it, which originated from Whittaker W functions, and retain the first term, which originated from Whittaker M functions.

**> Rsol4 := subs(\_C3=0, Rsol3);**

$$Rsol4 := R(r) = \frac{-C2 \left( \frac{\mu \omega r^2}{hb} \right)^{\frac{m}{2} + \frac{1}{2}} \text{KummerM} \left( \frac{1}{2} + \frac{m}{2} - \frac{E}{2 \omega hb}, m+1, \frac{\mu \omega r^2}{hb} \right)}{r e^{\frac{\mu \omega r^2}{2 hb}}} \quad (20.25)$$

For this Kummer M function to terminate such that the amplitude function is square-integrable, the first argument of this function must be zero or a negative integer, which we call quantum number  $-n$ . We apply this condition to evaluate the energies of the discrete states.

**> En := collect(expand(solve(1/2+1/2\*m-1/2/omega/hb\*E=-n, E)), [hb, omega]);**

**(20.26)**

$$E_n := (2n + 1 + m) \omega \hbar b \quad (20.26)$$

We incorporate that expression for the discrete energies in radial function  $R(r)$  and convert  $m$  to its absolute value.

```
> Rsol5 := subs(E=En, m=abs(m), Rsol4);
```

$$Rsol5 := R(r) = \frac{-C2 \left( \frac{\mu \omega r^2}{\hbar b} \right)^{\frac{|m|}{2} + \frac{1}{2}} \text{KummerM} \left( -n, |m| + 1, \frac{\mu \omega r^2}{\hbar b} \right)}{r e^{\frac{\mu \omega r^2}{2 \hbar b}}} \quad (20.27)$$

In this expression for  $R(r)$ ,  $\_C2$  has the significance of a normalising factor; as that factor depends on both quantum numbers  $n$  and  $m$ , we find specific values for it for  $n$  and  $m$  over a range, rather than trying to find a general expression; in these integrals the integration factor is  $r \, dr \, d\phi$ .

```
> for n from 0 to 6 do
  for m from -4 to 4 do
    N[n,m] := 1/sqrt(simplify(int(simplify(subs(hb=h/(2*Pi),
      subs(I=-I,rhs(Rsol5))*rhs(Rsol5))*r), r=0..infinity)*
2)/_C2^2) assuming positive;
  end do;
end do;
```

For further use of the complete amplitude functions we form  $\psi_{n,m} = N_{n,m} R(r) \Phi(\phi)$ ,

```
> n,m := 'n','m';
psi := (n1,m1) -> simplify(eval(N[n,m]*rhs(Rsol5)/_C2*rhs(Phisol),
[n=n1,m=m1,hb=h/(2*Pi)])) assuming positive;
n,m := n,m
```

$$\psi := (n1, m1) \mapsto \text{simplify} \left( \frac{N_{n,m} \cdot \text{rhs}(Rsol5) \cdot \text{rhs}(Phisol)}{\_C2} \right) \left[ n = n1, m = m1, hb = \frac{h}{2 \cdot \pi} \right] \quad (20.28)$$

```
> psi(n1,m1) := psi(n1,m1);
```

$$\psi(n1, m1) := \frac{1}{r} \left( 2^{\frac{|m1|}{2}} N_{n1, m1} \pi^{\frac{|m1|}{2}} \left( \frac{\mu \omega r^2}{h} \right)^{\frac{|m1|}{2} + \frac{1}{2}} e^{\frac{-\mu \omega \pi r^2 + 1 m1 \phi h}{h}} \text{KummerM} \left( -n1, \right. \right. \quad (20.29)$$

$$\left. \left. |m1| + 1, \frac{2 \mu \omega \pi r^2}{h} \right) \right)$$

and display a few in explicit form.

```
> 'psi'(0,0) = simplify(psi(0,0)) assuming r>0;
```

$$\psi(0, 0) = \frac{\sqrt{\frac{\mu \omega r^2}{h}} e^{-\frac{\mu \omega \pi r^2}{h}}}{r} \quad (20.30)$$

> 'psi'(1,0) = simplify(psi(1,0)) assuming r>0;

$$\psi(1, 0) = \frac{(-2 \mu \omega \pi r^2 + h) \sqrt{\frac{\mu \omega r^2}{h}} e^{-\frac{\mu \omega \pi r^2}{h}}}{r h} \quad (20.31)$$

> 'psi'(0,1) = simplify(psi(0,1)) assuming r>0;

$$\psi(0, 1) = \frac{r \mu \omega \sqrt{\pi} e^{\frac{-\mu \omega \pi r^2 + I \phi h}{h}} \sqrt{2}}{h} \quad (20.32)$$

> 'psi'(0,-1) = simplify(psi(0,-1)) assuming r>0;

$$\psi(0, -1) = \frac{r \mu \omega \sqrt{\pi} e^{\frac{-\mu \omega \pi r^2 - I \phi h}{h}} \sqrt{2}}{h} \quad (20.33)$$

> 'psi'(1,1) = simplify(psi(1,1)) assuming r>0;

$$\psi(1, 1) = \frac{2 r \mu \omega \sqrt{\pi} (-\mu \omega \pi r^2 + h) e^{\frac{-\mu \omega \pi r^2 + I \phi h}{h}}}{h^2} \quad (20.34)$$

> 'psi'(1,-1) = simplify(psi(1,-1)) assuming r>0;

$$\psi(1, -1) = \frac{2 r \mu \omega \sqrt{\pi} (-\mu \omega \pi r^2 + h) e^{\frac{-\mu \omega \pi r^2 - I \phi h}{h}}}{h^2} \quad (20.35)$$

We replace  $m$  in the formula for energy with its absolute value, because the energy can not be less than the zero of the energy scale set by the function for potential energy.

> En := subs(m=abs(m), hb=h/(2\*Pi), (2\*n+1+m)\*omega\*hb);

$$E_n := \frac{(2 n + 1 + |m|) \omega h}{2 \pi} \quad (20.36)$$

This expression implies that, for  $n = m = 0$ , only one state exists and has energy

> En[0,0] := eval(En, [n=0, m=0]);

$$E_{n=0,0} := \frac{\omega h}{2 \pi} \quad (20.37)$$

which corresponds to a residual energy. For  $m \neq 0$ , states with  $+m$  and  $-m$  have the same energy, and the total number of states with the same energy  $E_{n,m}$  equals  $2 n + |m| + 1$  because  $n$  and  $m$  can vary independently; the latter formula hence specifies the degeneracy. As for the canonical linear harmonic oscillator in one dimension, the difference of energy between states of adjacent energies is constant,

equal to  $\frac{h \omega}{2 \pi}$  for radial frequencies or  $h \nu$  for circular frequencies; the number of states is uncountable.

For instance, as the number of states with the same energy equals  $2n + |m| + 1$ , when  $En = 5 \frac{h \omega}{2 \pi}$ , the possible states have  $(n,m) = (2,0)$  or  $(1,\pm 1)$  or  $(0,\pm 2)$ , so five in total.

The average value of a quantity for a particular state is known as its [expectation](#) value, calculated as an integral over the amplitude function for that state. We calculate expectation values of  $r$  for the ground state,

```
> psi(0,0) := psi(0,0);
```

$$\psi(0,0) := \frac{\sqrt{\frac{\mu \omega r^2}{h}} e^{-\frac{\mu \omega r^2}{h}}}{r} \quad (20.38)$$

```
> assume(mu>0,h>0,omega>0);
```

```
> `<r>`[0,0] := simplify(int(int(subs(I=-I,psi(0,0))*r*psi(0,0)*r,
phi=0..2*Pi), r=0..infinity)) assuming positive;
```

$$\langle r \rangle_{0,0} := \frac{\sqrt{h\omega} \sqrt{2}}{8 \sqrt{\omega} \sqrt{\mu}} \quad (20.39)$$

and for a few excited states.

```
> for n from 1 to 3 do
```

```
    `<r>`[n,0] := int(int(subs(I=-I,psi(n,0))*r*psi(n,0)*r, phi=0.
    .2*Pi), r=0..infinity);
```

```
end do;
```

$$\begin{aligned} \langle r \rangle_{1,0} &:= \frac{7 \sqrt{h\omega} \sqrt{2}}{32 \sqrt{\omega} \sqrt{\mu}} \\ \langle r \rangle_{2,0} &:= \frac{145 \sqrt{h\omega} \sqrt{2}}{512 \sqrt{\omega} \sqrt{\mu}} \\ \langle r \rangle_{3,0} &:= \frac{687 \sqrt{h\omega} \sqrt{2}}{2048 \sqrt{\omega} \sqrt{\mu}} \end{aligned} \quad (20.40)$$

```
> n,m := 'n','m':
```

```
for m from -2 to 2 do
```

```
    `<r>`[0,m] := int(int(subs(I=-I,psi(0,m))*r*psi(0,m)*r, phi=0.
    .2*Pi), r=0..infinity);
```

```
end do;
```

$$\langle r \rangle_{0,-2} := \frac{15 \sqrt{h\omega} \sqrt{2}}{64 \sqrt{\omega} \sqrt{\mu}}$$



$$\begin{aligned}
\langle r \rangle_{0,-1} &:= \frac{3 \pi^{5/2} \mu^2 \omega^2 \sqrt{2}}{16 \hbar^2 \left( \frac{\mu \omega \pi}{\hbar} \right)^{5/2}} \\
\langle r \rangle_{0,0} &:= \frac{\mu \omega \pi^{3/2} \sqrt{2}}{8 \hbar \left( \frac{\mu \omega \pi}{\hbar} \right)^{3/2}} \\
\langle r \rangle_{0,1} &:= \frac{3 \pi^{5/2} \mu^2 \omega^2 \sqrt{2}}{16 \hbar^2 \left( \frac{\mu \omega \pi}{\hbar} \right)^{5/2}} \\
\langle r \rangle_{0,2} &:= \frac{15 \sqrt{\hbar} \sqrt{2}}{64 \sqrt{\omega} \sqrt{\mu}}
\end{aligned} \tag{20.41}$$

The expectation value of  $r$  is independent of the sign of quantum number  $m$  but increases gradually with both  $m$  and  $n$ . We calculate likewise the expectation values of  $\langle r^2 \rangle$ .

```

> n,m := 'n','m':
  for n from 0 to 3 do
    `<r^2>`[n,0] := int(int(subs(I=-I,psi(n,0))*r^2*psi(n,0)*r, phi=
0..2*Pi), r=0..infinity);
  end do;

```

$$\begin{aligned}
\langle r^2 \rangle_{0,0} &:= \frac{\hbar}{4 \mu \omega \pi} \\
\langle r^2 \rangle_{1,0} &:= \frac{3 \hbar}{4 \mu \omega \pi} \\
\langle r^2 \rangle_{2,0} &:= \frac{5 \hbar}{4 \mu \omega \pi} \\
\langle r^2 \rangle_{3,0} &:= \frac{7 \hbar}{4 \mu \omega \pi}
\end{aligned} \tag{20.42}$$

```

> n,m := 'n','m':
  for m from -2 to 2 do
    `<r^2>`[0,m] := int(int(subs(I=-I,psi(0,m))*r^2*psi(0,m)*r, phi=
0..2*Pi), r=0..infinity);
  end do;

```

$$\begin{aligned}
\langle r^2 \rangle_{0,-2} &:= \frac{3 \hbar}{4 \mu \omega \pi} \\
\langle r^2 \rangle_{0,-1} &:= \frac{\hbar}{2 \mu \omega \pi}
\end{aligned}$$

$$\begin{aligned}
\langle r^2 \rangle_{0,0} &:= \frac{\hbar}{4 \mu \omega \pi} \\
\langle r^2 \rangle_{0,1} &:= \frac{\hbar}{2 \mu \omega \pi} \\
\langle r^2 \rangle_{0,2} &:= \frac{3 \hbar}{4 \mu \omega \pi}
\end{aligned} \tag{20.43}$$

These results show that  $\langle r^2 \rangle_{0,m}$  increases as  $\frac{(|m| + 1) \hbar}{4 \pi \mu \omega}$ , whereas  $\langle r^2 \rangle_{n,0}$  increases as  $\frac{(2n + 1) \hbar}{4 \pi \mu \omega}$ .

We calculate the variance of  $r$  for a few states as  $\langle r^2 \rangle - \langle r \rangle^2$ .

```

> n,m := 'n','m':
  for n from 0 to 3 do
    n, `variance is `, collect(` $\langle r^2 \rangle$ `[n,0] - (` $\langle r \rangle$ `[n,0])^2, [h,mu,omega]);
    n, `variance is `, evalf(collect(` $\langle r^2 \rangle$ `[n,0] - (` $\langle r \rangle$ `[n,0])^2, [h,mu,omega]));
  end do;

```

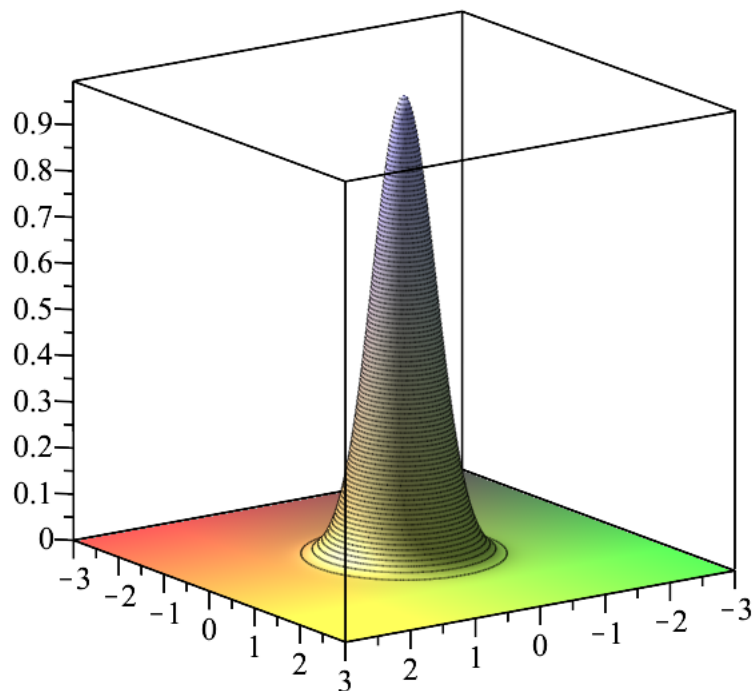
$$\begin{aligned}
0, \text{variance is, } & \frac{\left(-\frac{1}{32} + \frac{1}{4\pi}\right) \hbar}{\omega \mu} \\
0, \text{variance is, } & \frac{0.04832747152 \hbar}{\mu \omega} \\
1, \text{variance is, } & \frac{\left(-\frac{49}{512} + \frac{3}{4\pi}\right) \hbar}{\omega \mu} \\
1, \text{variance is, } & \frac{0.1430292896 \hbar}{\mu \omega} \\
2, \text{variance is, } & \frac{\left(-\frac{21025}{131072} + \frac{5}{4\pi}\right) \hbar}{\omega \mu} \\
2, \text{variance is, } & \frac{0.2374793376 \hbar}{\mu \omega} \\
3, \text{variance is, } & \frac{\left(-\frac{471969}{2097152} + \frac{7}{4\pi}\right) \hbar}{\omega \mu} \\
3, \text{variance is, } & \frac{0.3319899440 \hbar}{\mu \omega}
\end{aligned} \tag{20.44}$$

These values indicate that the variances of  $r$  increase linearly with quantum number  $n$ , with a minimum

variance  $> 0$  for the ground state.

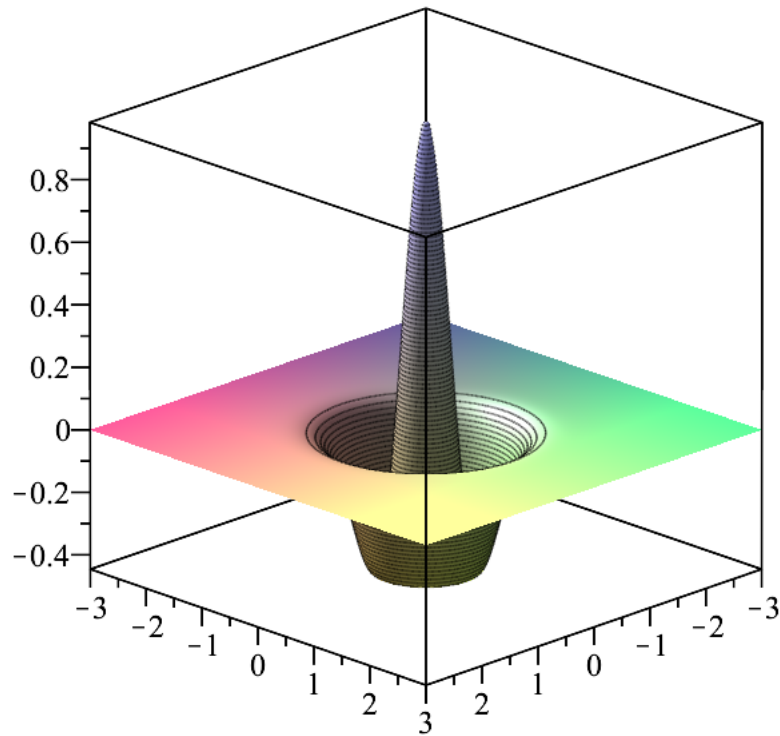
We plot some amplitude functions.

```
> n,m := 'n','m':  
  assume(r>0);  
  p00 := simplify(psi(0,0));  
  p00 := eval(p00, [mu=1,omega=1,h=1]):  
  plot3d(eval(p00, [r=sqrt(x^2+y^2), phi=arctan(y/x)]), x=-3..3, y=  
    -3..3,  
    axes=boxed, title="psi(0,0)", titlefont=[TIMES,BOLD,14],  
    style=patchcontour,  
    contours=100, grid=[100,100], labels=["", "", ""]);  
psi(0,0)
```



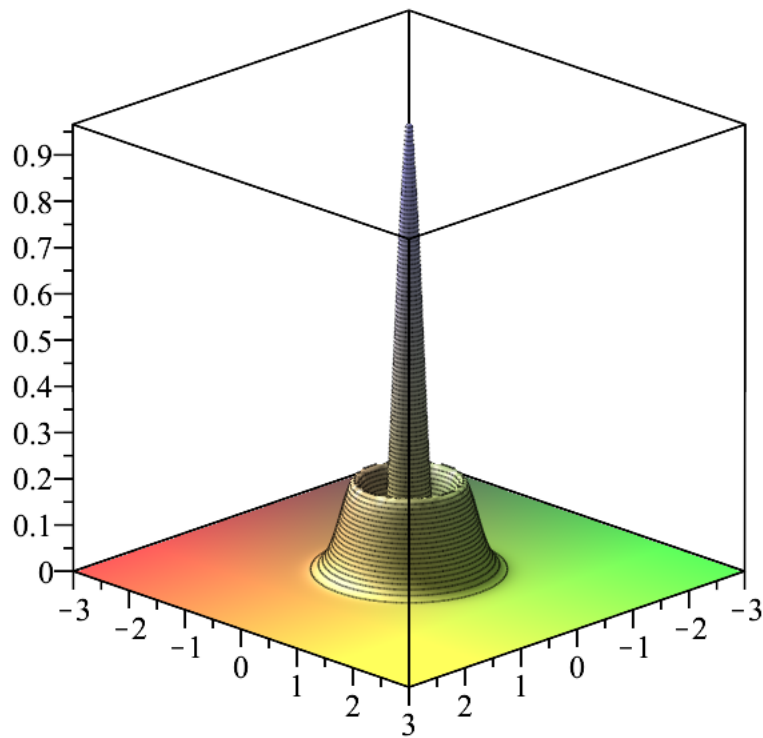
```
> p10 := simplify(psi(1,0));  
  p10 := eval(p10, [mu=1,omega=1,h=1]):  
  plot3d(eval(p10, [r=sqrt(x^2+y^2), phi=arctan(y/x)]), x=-3..3, y=  
    -3..3,  
    axes=boxed, title="psi(1,0)", titlefont=[TIMES,BOLD,14],  
    orientation=[45,70],  
    style=patchcontour, contours=100, grid=[100,100], labels=["",  
    "", ""]);
```

psi(1,0)



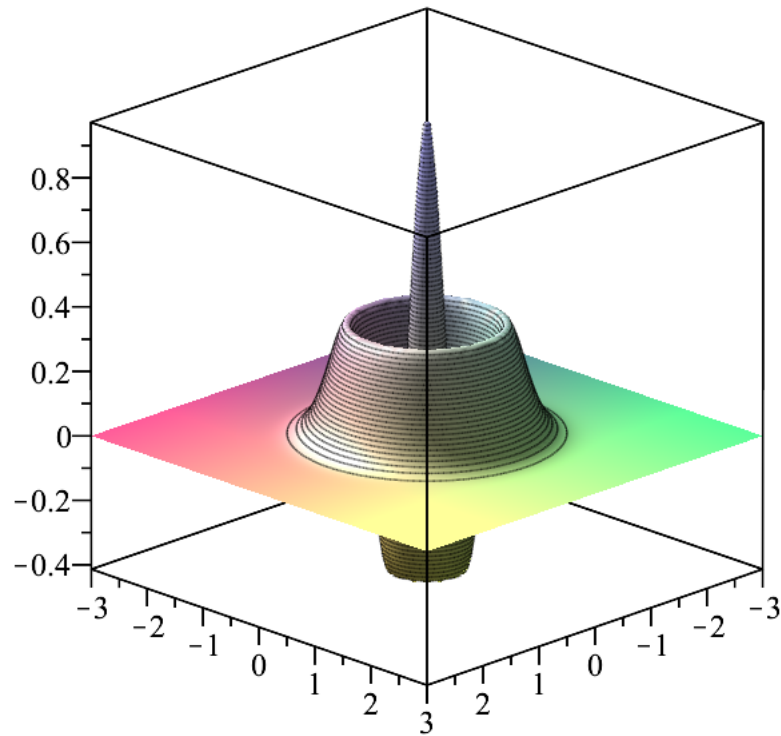
```
> p10 := simplify(subs(I=-I, psi(1,0))*psi(1,0)):
p10 := eval(p10, [mu=1,omega=1,h=1]):
plot3d(eval(p10, [r=sqrt(x^2+y^2), phi=arctan(y/x)]), x=-3..3, y=
-3..3,
      axes=boxed, title="squared psi(1,0)", titlefont=[TIMES,BOLD,
14], labels=["","",""],
      orientation=[45,70], style=patchcontour, contours=100, grid=
[100,100]);
```

squared psi(1,0)



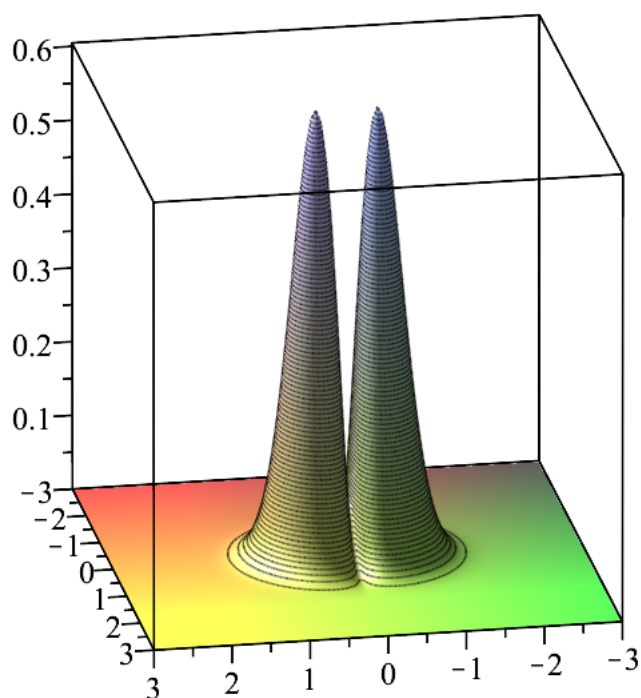
```
> p20 := simplify(psi(2,0)):
p20 := eval(p20, [mu=1,omega=1,h=1]):
plot3d(eval(p20, [r=sqrt(x^2+y^2), phi=arctan(y/x)]), x=-3..3, y=
-3..3,
        axes=boxed, title="psi(2,0)", titlefont=[TIMES,BOLD,14],
labels=["","",""],
        orientation=[45,70], style=patchcontour, contours=100, grid=
[100,100]);
```

psi(2,0)



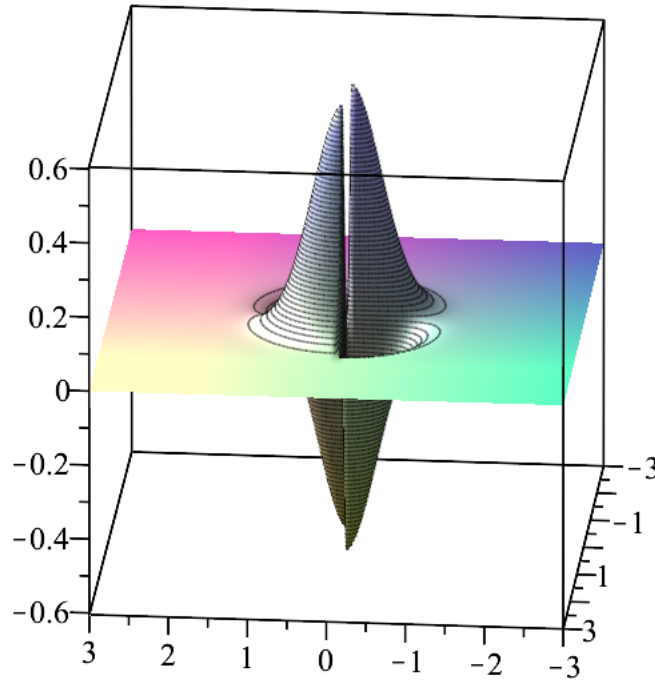
```
> p01r := simplify(Re(psi(0,1))):  
p01r := eval(p01r, [mu=1,omega=1,h=1]):  
plot3d(eval(p01r, [r=sqrt(x^2+y^2), phi=arctan(y/x)]), x=-3..3, y=  
-3..3,  
    axes=boxed, title="real part of psi(0,1)", grid=[80,80],  
    labels=["", "", ""],  
    titlefont=[TIMES,BOLD,14], orientation=[80,70], style=  
patchcontour,  
    contours=100, grid=[100,100]);
```

real part of  $\psi(0,1)$



```
> p01i := simplify(Im(psi(0,1))):  
p01i := eval(p01i, [mu=1,omega=1,h=1]):  
plot3d(eval(p01i, [r=sqrt(x^2+y^2), phi=arctan(y/x)]), x=-3..3, y=  
-3..3,  
    axes=boxed, title="imaginary part of psi(0,1)", grid=[80,80],  
  
    titlefont=[TIMES,BOLD,14], orientation=[95,70], labels=["",  
    "", ""],  
    style=patchcontour, contours=100, grid=[100,100]);
```

imaginary part of psi(0,1)



Other amplitude functions and their squares may be analogously plotted.

We calculate a matrix element of a component of  $r$  in the plane, either  $r \cos(\phi) = x$  or  $r \sin(\phi) = y$ .

```
> seq(int(int(subs(I=-I,psi(0,k))*r*cos(phi)*psi(0,0)*r, phi=0..2*
Pi), r=0..infinity), k=0..3);
```

$$0, \frac{\sqrt{h\sim} \sqrt{2}}{8 \sqrt{\omega\sim} \sqrt{\mu\sim} \sqrt{\pi}}, 0, 0 \quad (20.45)$$

```
> seq(int(int(subs(I=-I,psi(0,k))*r*cos(phi)*psi(0,1)*r, phi=0..2*
Pi), r=0..infinity), k=0..3);
```

$$\frac{\sqrt{h\sim} \sqrt{2}}{8 \sqrt{\omega\sim} \sqrt{\mu\sim} \sqrt{\pi}}, 0, \frac{\sqrt{h\sim}}{4 \sqrt{\mu\sim} \sqrt{\omega\sim} \sqrt{\pi}}, 0 \quad (20.46)$$

These two results imply that non-zero matrix elements occur for only  $\Delta m = \pm 1$ .

```
> seq(int(int(subs(I=-I,psi(k+1,1))*r*cos(phi)*psi(1,0)*r, phi=0..2*
Pi), r=0..infinity), k=0..3);
```

$$\frac{\sqrt{h\sim}}{4 \sqrt{\mu\sim} \sqrt{\omega\sim} \sqrt{\pi}}, 0, 0, 0 \quad (20.47)$$

```
> seq(int(int(subs(I=-I,psi(k,1))*r*cos(phi)*psi(1,0)*r, phi=0..2*
```



Pi), r=0..infinity), k=0..3);

$$-\frac{\sqrt{h}\sqrt{2}}{8\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}}, \frac{\sqrt{h}}{4\sqrt{\mu}\sqrt{\omega}\sqrt{\pi}}, 0, 0 \quad (20.48)$$

> seq(int(int(subs(I=-I,psi(k-1,1))\*r\*cos(phi)\*psi(1,0)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$-\frac{\sqrt{h}\sqrt{2}}{8\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}}, \frac{\sqrt{h}}{4\sqrt{\mu}\sqrt{\omega}\sqrt{\pi}}, 0, 0 \quad (20.49)$$

These three results imply that non-zero matrix elements occur for  $\Delta n = 0$  or  $+1$  when  $\Delta m = +1$ .

> seq(int(int(subs(I=-I,psi(k-1,2))\*r\*cos(phi)\*psi(k,1)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$-\frac{\sqrt{h}\sqrt{2}}{8\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}}, -\frac{\sqrt{h}}{4\sqrt{\mu}\sqrt{\omega}\sqrt{\pi}}, -\frac{\sqrt{h}\sqrt{2}\sqrt{3}}{8\sqrt{\mu}\sqrt{\omega}\sqrt{\pi}}, -\frac{\sqrt{h}\sqrt{2}}{4\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}} \quad (20.50)$$

> seq(int(int(subs(I=-I,psi(k,2))\*r\*cos(phi)\*psi(k,1)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$\frac{\sqrt{h}\sqrt{6}}{8\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}}, \frac{\sqrt{h}\sqrt{2}}{4\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}}, \frac{\sqrt{h}\sqrt{5}\sqrt{2}}{8\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}}, \frac{\sqrt{h}\sqrt{3}}{4\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}} \quad (20.51)$$

> seq(int(int(subs(I=-I,psi(k+1,2))\*r\*cos(phi)\*psi(k,1)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$0, 0, 0, 0 \quad (20.52)$$

> seq(int(int(subs(I=-I,psi(k-1,0))\*r\*cos(phi)\*psi(k,1)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$0, 0, 0, 0 \quad (20.53)$$

> seq(int(int(subs(I=-I,psi(k,0))\*r\*cos(phi)\*psi(k,1)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$\frac{\sqrt{h}}{4\sqrt{\mu}\sqrt{\omega}\sqrt{\pi}}, \frac{\sqrt{h}\sqrt{6}}{8\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}}, \frac{\sqrt{h}\sqrt{2}}{4\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}}, \frac{\sqrt{h}\sqrt{10}}{8\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}} \quad (20.54)$$

> seq(int(int(subs(I=-I,psi(k+1,0))\*r\*cos(phi)\*psi(k,1)\*r, phi=0..2\*Pi), r=0..infinity), k=1..4);

$$-\frac{\sqrt{h}}{4\sqrt{\mu}\sqrt{\omega}\sqrt{\pi}}, -\frac{\sqrt{h}\sqrt{6}}{8\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}}, -\frac{\sqrt{h}\sqrt{2}}{4\sqrt{\omega}\sqrt{\mu}\sqrt{\pi}}, -\frac{\sqrt{h}\sqrt{10}}{8\sqrt{\pi}\sqrt{\omega}\sqrt{\mu}} \quad (20.55)$$

These results indicate that, independent of the values of  $\mu$ ,  $h$ ,  $\omega$ , the only non-zero values of these matrix elements occur for  $\Delta n = 0$  or  $\pm 1$  and  $\Delta m = +1$ , for  $\Delta n = 0$  or  $\pm 1$  and  $\Delta m = -1$ ; these selection rules govern the possible optical transitions of this hypothetical system in absorption or emission.

## 1.28 canonical harmonic oscillator according to wave mechanics in cartesian coordinates in two

## dimensions

> restart;

Schroedinger's temporally independent equation has this form for an isotropic canonical harmonic oscillator in two spatial dimensions, with labels  $x$  and  $y$ .

> Seq := -h^2/(8\*Pi^2\*mu)\*(diff(psi(x,y),x\$2) + diff(psi(x,y),y\$2))  
+ k\*(x^2+y^2)\*psi(x,y)/2 = (Ex(x)+Ey(y))\*psi(x,y);

$$Seq := -\frac{h^2 \left( \frac{\partial^2}{\partial x^2} \Psi(x,y) + \frac{\partial^2}{\partial y^2} \Psi(x,y) \right)}{8 \pi^2 \mu} + \frac{k (x^2 + y^2) \Psi(x,y)}{2} = (Ex(x) + Ey(y)) \Psi(x, \quad (21.1)$$

$y)$

Containing two independent variables, this partial-differential equation is solved,

> sol := pdsolve(Seq, psi(x,y));

$$sol := \Psi(x,y) = \_F1(x) \_F2(y) \text{ where } \left\{ \left\{ \frac{d^2}{dx^2} \_F1(x) = \frac{\_F1(x) \_c1}{h^2} \right. \right. \quad (21.2)$$

$$\left. \left. - \frac{4 \pi^2 \mu \_F1(x) (-k x^2 + 2 Ex(x))}{h^2}, \frac{d^2}{dy^2} \_F2(y) = - \frac{\_F2(y) \_c1}{h^2} \right. \right.$$

$$\left. \left. - \frac{4 \_F2(y) (-k y^2 + 2 Ey(y)) \pi^2 \mu}{h^2} \right\} \right\}$$

on forming a product of two functions, each of a single variable, and each of which is a solution to an ordinary-differential equation.

> op((sol));

$$\Psi(x,y) = \_F1(x) \_F2(y), \left[ \left\{ \frac{d^2}{dx^2} \_F1(x) = \frac{\_F1(x) \_c1}{h^2} - \frac{4 \pi^2 \mu \_F1(x) (-k x^2 + 2 Ex(x))}{h^2}, \right. \right. \quad (21.3)$$

$$\left. \left. \frac{d^2}{dy^2} \_F2(y) = - \frac{\_F2(y) \_c1}{h^2} - \frac{4 \_F2(y) (-k y^2 + 2 Ey(y)) \pi^2 \mu}{h^2} \right\} \right]$$

By a partition of the total energy into contributions from the oscillation in each variable, we make the two ordinary-differential equations entirely parallel and equivalent. At the same time that we separate the two ordinary-differential equations, we eliminate the nominal dependence of the contributions to a particular coordinate,

> dex := subs(Ex(x)=Ex, op(1, op(1, op(2,sol))));

$$dex := \frac{d^2}{dx^2} \_F1(x) = \frac{\_F1(x) \_c1}{h^2} - \frac{4 \pi^2 \mu \_F1(x) (-k x^2 + 2 Ex)}{h^2} \quad (21.4)$$

> dey := subs(Ey(y)=Ey, op(2, op(1, op(2,sol))));

$$dey := \frac{d^2}{dy^2} \_F2(y) = - \frac{\_F2(y) \_c1}{h^2} - \frac{4 \_F2(y) (-k y^2 + 2 Ey) \pi^2 \mu}{h^2} \quad (21.5)$$

and solve the ordinary-differential equations..

**> solx := dsolve(dex, \_F1(x));**

$$\text{solx} := \_F1(x) = \frac{\_C1 \text{ WhittakerM}\left(\frac{8 Ex \pi^2 \mu - \_c1}{8 h \pi \sqrt{k} \sqrt{\mu}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} x^2}{h}\right)}{\sqrt{x}} \quad (21.6)$$

$$+ \frac{\_C2 \text{ WhittakerW}\left(\frac{8 Ex \pi^2 \mu - \_c1}{8 h \pi \sqrt{k} \sqrt{\mu}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} x^2}{h}\right)}{\sqrt{x}}$$

**> soly := dsolve(dey, \_F2(y));**

$$\text{soly} := \_F2(y) = \frac{\_C1 \text{ WhittakerM}\left(\frac{8 Ey \pi^2 \mu + \_c1}{8 h \pi \sqrt{k} \sqrt{\mu}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} y^2}{h}\right)}{\sqrt{y}} \quad (21.7)$$

$$+ \frac{\_C2 \text{ WhittakerW}\left(\frac{8 Ey \pi^2 \mu + \_c1}{8 h \pi \sqrt{k} \sqrt{\mu}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} y^2}{h}\right)}{\sqrt{y}}$$

According to the experience with the canonical linear harmonic oscillator in one spatial dimension, in section 1.23, we eliminate the physically unacceptable Whittaker M functions.

**> \_C1 := 0;**

$$\_C1 := 0 \quad (21.8)$$

**> solx;**

$$\_F1(x) = \frac{\_C2 \text{ WhittakerW}\left(\frac{8 Ex \pi^2 \mu - \_c1}{8 h \pi \sqrt{k} \sqrt{\mu}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} x^2}{h}\right)}{\sqrt{x}} \quad (21.9)$$

**> soly;**

$$\_F2(y) = \frac{\_C2 \text{ WhittakerW}\left(\frac{8 Ey \pi^2 \mu + \_c1}{8 h \pi \sqrt{k} \sqrt{\mu}}, \frac{1}{4}, \frac{2 \pi \sqrt{k} \sqrt{\mu} y^2}{h}\right)}{\sqrt{y}} \quad (21.10)$$

We convert the Whittaker W functions to Hermite H functions, according to traditional practice with the linear oscillator.

**> solx := convert(solx, HermiteH);**

$$\text{solx} := \_F1(x) = \left( \_C2 \text{ HermiteH}\left(\frac{8 Ex \pi^2 \mu - 6 h \pi \sqrt{k} \sqrt{\mu} - \_c1}{4 h \pi \sqrt{k} \sqrt{\mu}}\right) + 1, \right. \quad (21.11)$$

$$\sqrt{2} \sqrt{\frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h}} \left( \frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h} \right)^{1/4} \left( \frac{8 E x \pi^2 \mu - 4 h \pi \sqrt{k} \sqrt{\mu} - c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} - \frac{3}{4} \frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h} \right)$$

**> soly := convert(soly, HermiteH);**

$$soly := {}_F2(y) = \left( -C2 \operatorname{HermiteH} \left( \frac{8 E y \pi^2 \mu - 6 h \pi \sqrt{k} \sqrt{\mu} + c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} + 1, \right. \right. \quad (21.12)$$

$$\left. \sqrt{2} \sqrt{\frac{\pi \sqrt{k} \sqrt{\mu} y^2}{h}} \left( \frac{\pi \sqrt{k} \sqrt{\mu} y^2}{h} \right)^{1/4} \left( \frac{8 E y \pi^2 \mu - 4 h \pi \sqrt{k} \sqrt{\mu} + c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} - \frac{3}{4} \frac{\pi \sqrt{k} \sqrt{\mu} y^2}{h} \right) \right)$$

To introduce a quantum number as a first argument of the Hermite H functions, we separate the parts of each solution,

**> op(rhs(solx));**

$$\frac{1}{2}, -C2, \frac{1}{\sqrt{x}}, \operatorname{HermiteH} \left( \frac{8 E x \pi^2 \mu - 6 h \pi \sqrt{k} \sqrt{\mu} - c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} + 1, \sqrt{2} \sqrt{\frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h}} \right), \quad (21.13)$$

$$\left( \frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h} \right)^{1/4}, \frac{1}{\frac{8 E x \pi^2 \mu - 4 h \pi \sqrt{k} \sqrt{\mu} - c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} - \frac{3}{4} \frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h}}, \frac{1}{\frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h}}$$

and extract that first argument,

**> Hargx := op(1, op(4, rhs(solx)));**

$$Hargx := \frac{8 E x \pi^2 \mu - 6 h \pi \sqrt{k} \sqrt{\mu} - c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} + 1 \quad (21.14)$$

which we set equal to a quantum number that takes non-negative integer values, and then solve for the contribution to the total energy from that degree of freedom, first for dimension  $x$  with quantum number  $n_x$ ,

**> Ex := solve(Hargx=nx, Ex);**

(21.15)

$$E_x := \frac{4 n_x h \pi \sqrt{k} \sqrt{\mu} + 2 h \pi \sqrt{k} \sqrt{\mu} + \_c_1}{8 \pi^2 \mu} \quad (21.15)$$

**> Hargy := op(1, op(4, rhs(soly)));**

$$Hargy := \frac{8 E_y \pi^2 \mu - 6 h \pi \sqrt{k} \sqrt{\mu} + \_c_1}{4 h \pi \sqrt{k} \sqrt{\mu}} + 1 \quad (21.16)$$

and then for dimension  $y$  with quantum number  $n_y$ .

**> Ey := solve(Hargy=ny, Ey);**

$$E_y := \frac{4 n_y h \pi \sqrt{k} \sqrt{\mu} + 2 h \pi \sqrt{k} \sqrt{\mu} - \_c_1}{8 \pi^2 \mu} \quad (21.17)$$

The total energy is a sum of the two contributions.

**> E := factor(Ex + Ey);**

$$E := \frac{h \sqrt{k} (n_x + 1 + n_y)}{2 \pi \sqrt{\mu}} \quad (21.18)$$

The energy is hence a linear function of quantum numbers  $n_x$  and  $n_y$ , increasing without termination; the difference of energy between states of adjacent energies is  $\frac{h}{2 \pi} \sqrt{\frac{k}{\mu}}$ , which we express alternatively in terms of circular frequency  $\nu$  as  $h \nu$ . In the state of least energy, for which  $n_x = n_y = 0$ , there remains one unit of energy as  $h \nu$ ; there is hence associated with each coordinate  $\frac{1}{2} h \nu$  of residual energy. We recall the normalising factor for each dimension from the case of the linear oscillator in section 1.23, with which we multiply each separate unnormalised amplitude function for a particular coordinate to replace  $\_C2$ ,

**> solxn := sqrt(2^nx/(nx!\*sqrt(Pi)))\*simplify(rhs(solx))/\_C2  
assuming positive;**

**solxn :=** (21.19)

$$\frac{1}{h^{1/4}} \left( \sqrt{\frac{2^{n_x}}{n_x! \sqrt{\pi}}} 2^{\frac{1}{4} - n_x} \text{HermiteH}\left(n_x, \frac{\sqrt{2} x \sqrt{\pi} k^{1/4} \mu^{1/4}}{\sqrt{h}}\right) \pi^{1/4} k^{1/8} \mu^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} x^2}{h}} \right)$$

and test the correctness of the normalisation of the separate functions.

**> seq(simplify(int(simplify(eval(solxn, nx=j)^2), x=-infinity..infinity)), j=0..5) assuming positive;  
1, 1, 1, 1, 1, 1** (21.20)

```
> solyn := sqrt(2^ny/(ny!*sqrt(Pi)))*simplify(rhs(soly))/_C2
    assuming positive;
solyn :=
```

(21.21)

$$\frac{1}{h^{1/4}} \left( \sqrt{\frac{2^{ny}}{ny! \sqrt{\pi}}} 2^{\frac{1}{4} - ny} \text{HermiteH}\left(ny, \frac{\sqrt{2} y \sqrt{\pi} k^{1/4} \mu^{1/4}}{\sqrt{h}}\right) \pi^{1/4} k^{1/8} \mu^{1/8} e^{-\frac{\pi \sqrt{k} \sqrt{\mu} y^2}{h}} \right)$$

```
> seq(simplify(int(simplify(eval(solyn, ny=j)^2), y=-infinity..
    infinity)), j=0..8) assuming positive;
    1, 1, 1, 1, 1, 1, 1, 1, 1
```

(21.22)

According to the solution of Schroedinger's equation as a partial-differential equation, the amplitude function for the system in two dimensions with cartesian coordinates must be a product of the amplitude functions for the separate dimensions.

```
> psi := simplify(solxn*solyn);
```

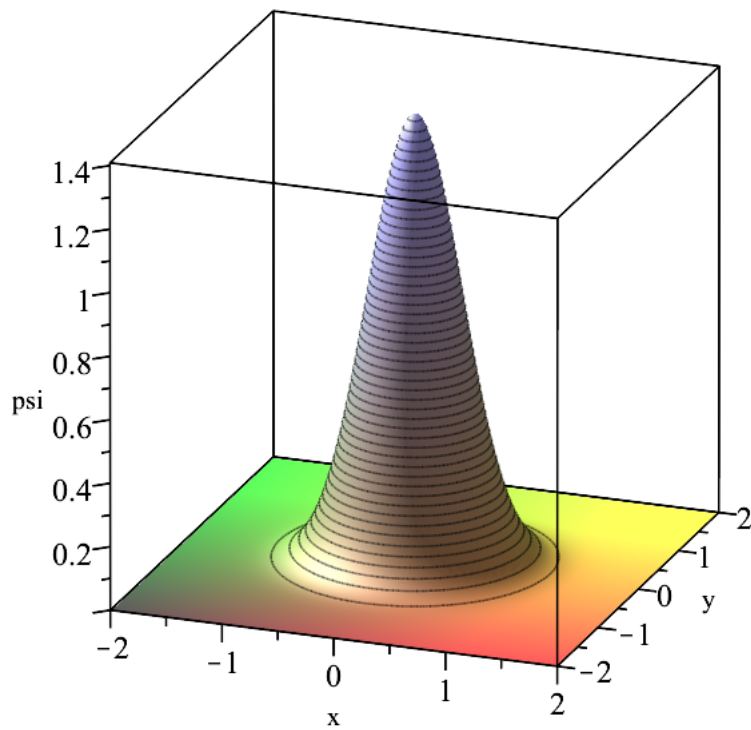
$$\psi := \frac{1}{\sqrt{h}} \left( 2^{\frac{1}{2} - nx - ny} \sqrt{\frac{2^{nx}}{nx!}} \text{HermiteH}\left(nx, \frac{\sqrt{2} x \sqrt{\pi} k^{1/4} \mu^{1/4}}{\sqrt{h}}\right) k^{1/4} \mu^{1/4} e^{-\frac{\sqrt{k} \sqrt{\mu} \pi (x^2 + y^2)}{h}} \sqrt{\frac{2^{ny}}{ny!}} \text{HermiteH}\left(ny, \frac{\sqrt{2} y \sqrt{\pi} k^{1/4} \mu^{1/4}}{\sqrt{h}}\right) \right)$$

(21.23)

We plot these amplitude functions for a few values of quantum numbers  $n_x$  and  $n_y$ .

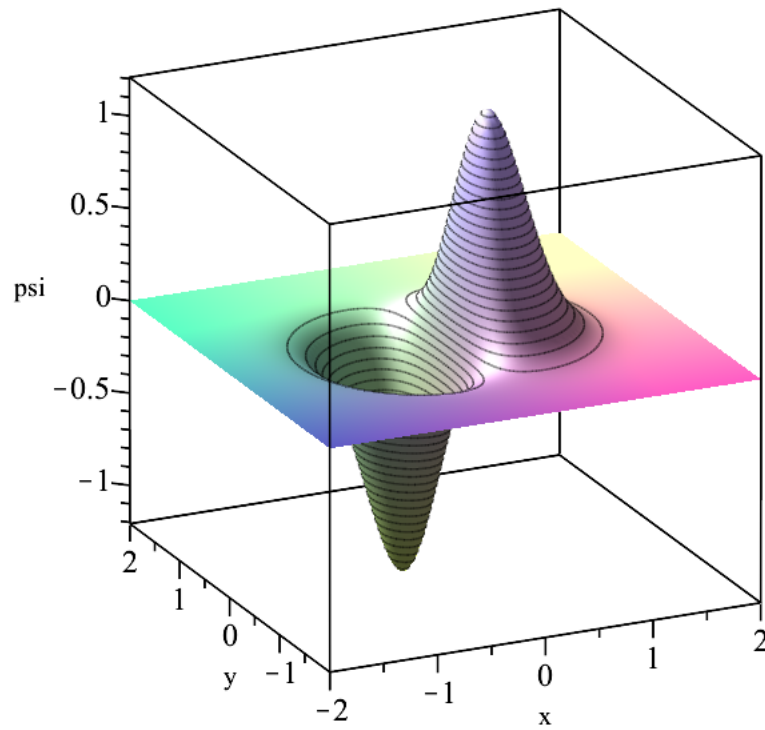
```
> plot3d(simplify(eval(psi, [nx=0, ny=0, h=1,k=1,mu=1])), x=-2..2,
    y=-2..2,
    style=patchcontour, contours=50, title="psi(0,0)", grid=[80,
    80],
    titlefont=[TIMES,BOLD,14], orientation=[-70,70], labels=["x",
    "y","psi"],
    style=patchcontour, axes=boxed);
```

$\psi(0,0)$



```
> plot3d(simplify(eval(psi, [nx=1,ny=0, h=1,k=1,mu=1])), x=-2..2, y=-2..2,  
          style=patchcontour, contours=50, title="psi(1,0)", grid=[80,  
80],  
          titlefont=[TIMES,BOLD,14], orientation=[-115,70], labels=  
["x","y","psi"],  
          style=patchcontour, axes=boxed);
```

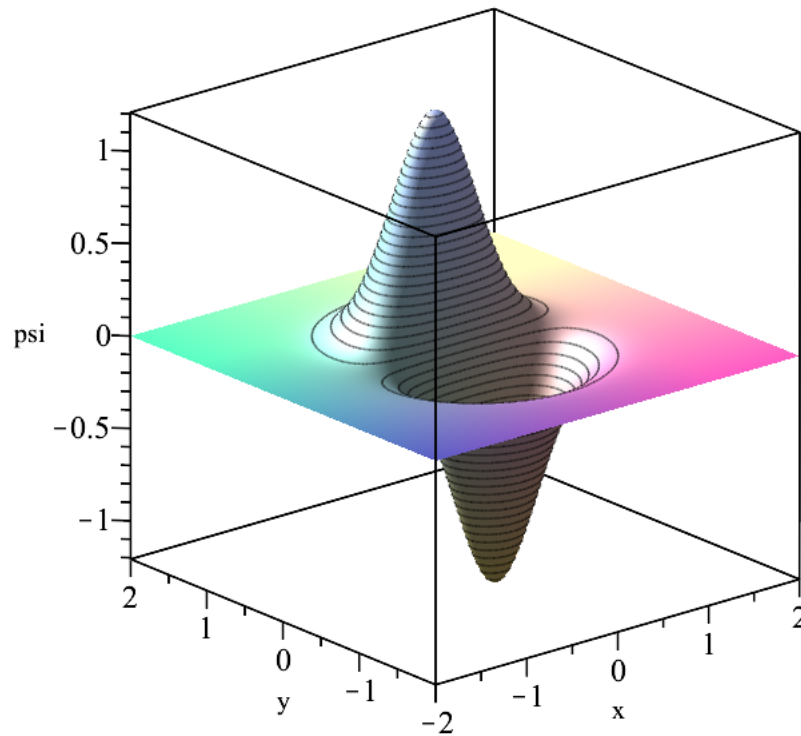
$\psi(1,0)$



```
> plot3d(simplify(eval(psi, [nx=0,ny=1, h=1,k=1,mu=1])), x=-2..2, y=-2..2,  
          style=patchcontour, contours=50, title="psi(0,1)", grid=[80,  
80],  
          titlefont=[TIMES,BOLD,14], orientation=[-130,70], labels=  
["x","y","psi"],  
          style=patchcontour, axes=boxed);
```

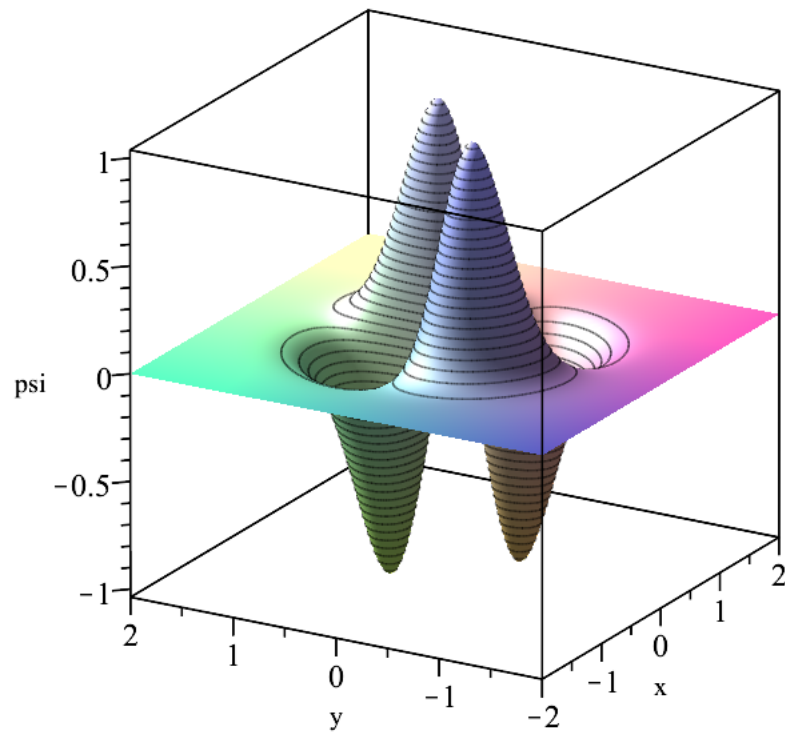


$\psi(0,1)$



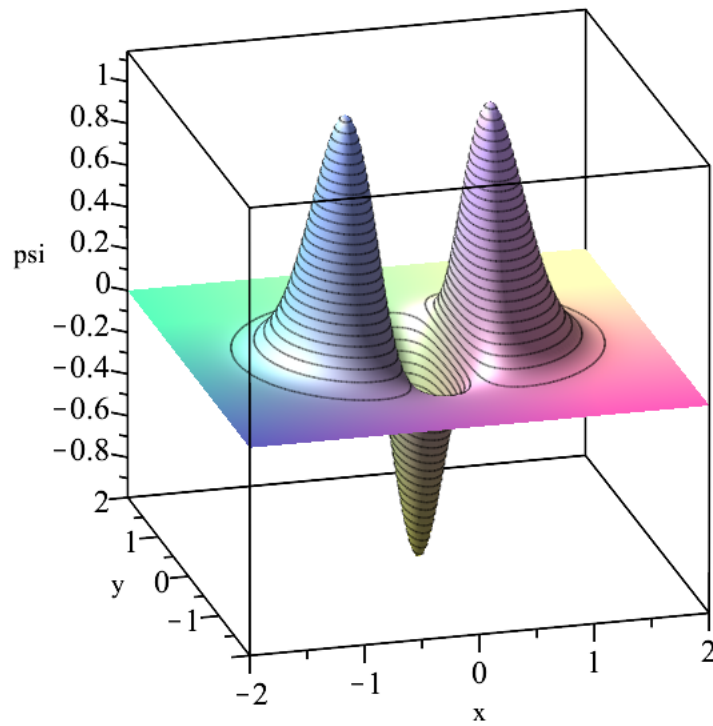
```
> plot3d(simplify(eval(psi, [nx=1,ny=1, h=1,k=1,mu=1])), x=-2..2, y=-2..2,  
          style=patchcontour, contours=50, title="psi(1,1)", grid=[80,  
80],  
          titlefont=[TIMES,BOLD,14], orientation=[-150,70], labels=  
["x","y","psi"],  
          style=patchcontour, grid=[100,100], axes=boxed);
```

$\psi(1,1)$



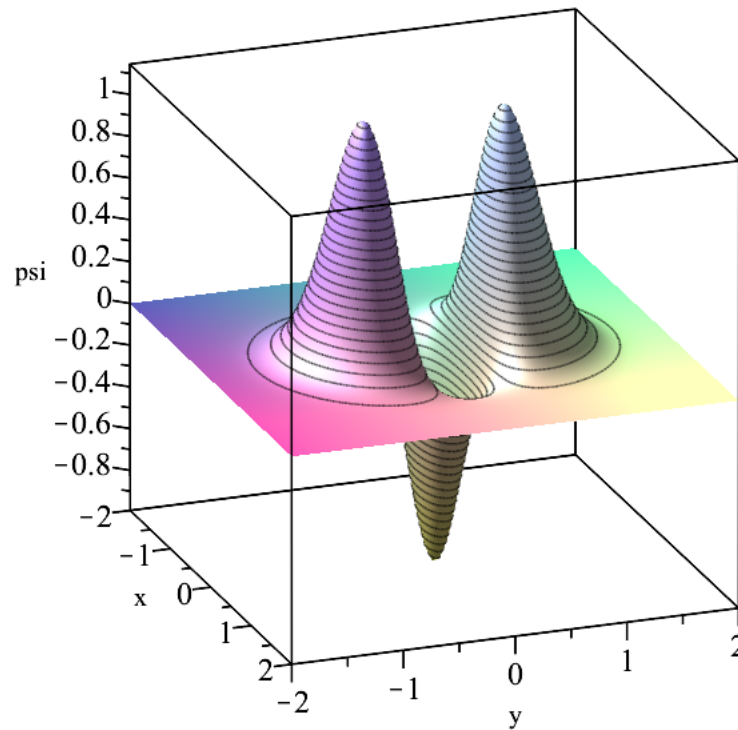
```
> plot3d(simplify(eval(psi, [nx=2,ny=0, h=1,k=1,mu=1])), x=-2..2, y=-2..2,  
          style=patchcontour, contours=50, title="psi(2,0)", grid=[80,  
80],  
          titlefont=[TIMES,BOLD,14], orientation=[-105,70], labels=  
["x","y","psi"],  
          style=patchcontour, grid=[100,100], axes=boxed);
```

$\psi(2,0)$



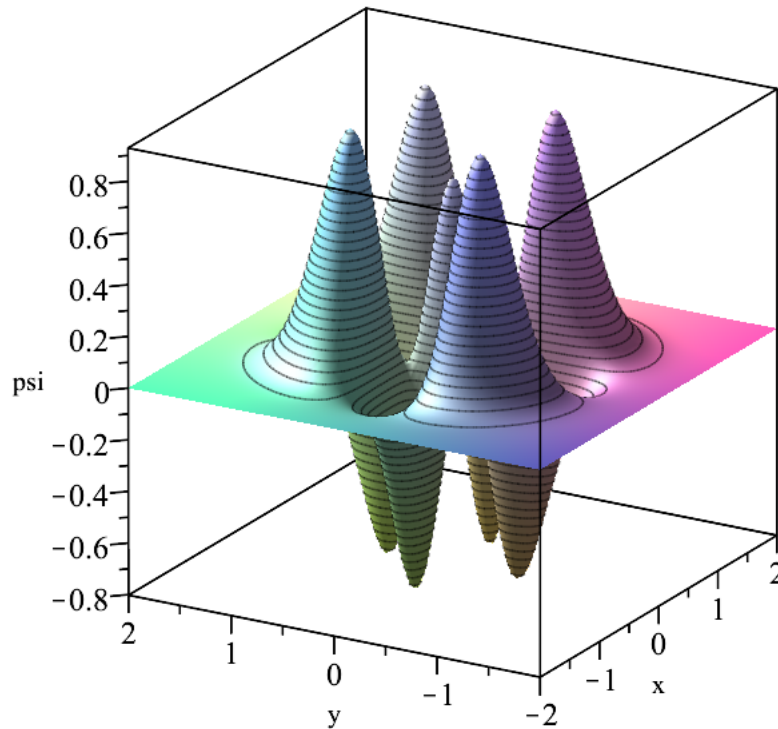
```
> plot3d(simplify(eval(psi, [nx=0,ny=2, h=1,k=1,mu=1])), x=-2..2, y=-2..2,  
         style=patchcontour, contours=50, title="psi(0,2)", grid=  
         [-150,80],  
         titlefont=[TIMES,BOLD,14], orientation=[-20,70], labels=["x",  
         "y","psi"],  
         style=patchcontour, grid=[100,100], axes=boxed);
```

$\psi(0,2)$



```
> plot3d(simplify(eval(psi, [nx=2,ny=2, h=1,k=1,mu=1])), x=-2..2, y=-2..2,  
          style=patchcontour, contours=50, title="psi(2,2)", grid=[80,  
80],  
          titlefont=[TIMES,BOLD,14], orientation=[-150,70], labels=  
["x","y","psi"],  
          style=patchcontour, axes=boxed);
```

psi(2,2)



These plots may be compared with the corresponding plots for the harmonic oscillator in polar coordinates, in section 1.27.

Like the states of that oscillator in polar coordinates, there is a [degeneracy](#) for this oscillator in

cartesian coordinates in that, for each value of total energy, according to  $E = \frac{h^2 k^2}{2 \pi \mu} (n_x + n_y + 1)$ ,

except for the state of least energy for which  $n_x = n_y = 0$ , multiple sets of quantum numbers pertain to the same energy; for instance, for  $n_x + n_y + 1 = 2$ , the sets are  $\{n_x = 1, n_y = 0\}$  and  $\{n_x = 0, n_y = 1\}$ , or for  $n_x + n_y + 1 = 5$ , the sets are  $\{4,0\}$ ,  $\{3,1\}$ ,  $\{2,2\}$ ,  $\{1,3\}$ ,  $\{0,4\}$ , so that the value of  $n_x + n_y + 1$  is also the number of states having the respective energy.

As we can express  $x^2 + y^2 = r^2$  and  $\frac{y}{x} = \tan(\phi)$ , or  $x = r \cos(\phi)$  and  $y = r \sin(\phi)$ , we can express amplitude functions  $\psi_{n,m}(r, \phi)$  in polar coordinates in section 1.27, which are generally complex, in terms of complex linear combinations of  $\psi_{n_x, n_y}(x, y)$  in cartesian coordinates, which are entirely real.

Here are a few examples that follow an obvious pattern.

```
> psi2[0,0] := simplify(eval(psi, [nx=0, ny=0, x=r*cos(theta), y=r*
sin(theta)]));
```

$$\psi_{0,0} := \frac{\sqrt{2} k^{1/4} \mu^{1/4} e^{-\frac{\pi\sqrt{k}\sqrt{\mu} r^2}{h}}}{\sqrt{h}} \quad (21.24)$$

```
> psi2[0,1] := simplify((simplify(eval(psi, [nx=1, ny=0, x=r*cos
(theta), y=r*sin(theta)]))
+ I*simplify(eval(psi, [nx=0, ny=1, x=r*cos(theta),
y=r*sin(theta)])))/sqrt(2));
```

$$\psi_{0,1} := \frac{2\sqrt{k}\sqrt{\mu}\sqrt{\pi} e^{-\frac{\pi\sqrt{k}\sqrt{\mu} r^2}{h}}}{h} r (I \sin(\theta) + \cos(\theta)) \quad (21.25)$$

```
> psi2[0,-1] := simplify((simplify(eval(psi, [nx=1, ny=0, x=r*cos
(theta), y=r*sin(theta)]))
- I*simplify(eval(psi, [nx=0, ny=1, x=r*cos(theta),
y=r*sin(theta)])))/sqrt(2));
```

$$\psi_{0,-1} := -\frac{2\sqrt{k}\sqrt{\mu}\sqrt{\pi} e^{-\frac{\pi\sqrt{k}\sqrt{\mu} r^2}{h}}}{h} r (I \sin(\theta) - \cos(\theta)) \quad (21.26)$$

```
> psi2[1,0] := -simplify((simplify(eval(psi, [nx=2, ny=0, x=r*cos
(theta), y=r*sin(theta)]))
+ simplify(eval(psi, [nx=0, ny=2, x=r*cos(theta), y=
r*sin(theta)])))/sqrt(2));
```

$$\psi_{1,0} := \frac{\sqrt{2} k^{1/4} \mu^{1/4} e^{-\frac{\pi\sqrt{k}\sqrt{\mu} r^2}{h}}}{h^{3/2}} (-2\pi\sqrt{k}\sqrt{\mu} r^2 + h) \quad (21.27)$$

```
> psi2[0,2] := simplify((simplify(eval(psi, [nx=2, ny=0, x=r*cos
(theta), y=r*sin(theta)]))
- simplify(eval(psi, [nx=0, ny=2, x=r*cos(theta), y=
r*sin(theta)]))
+ I*sqrt(2)*simplify(eval(psi, [nx=1, ny=1, x=r*cos
(theta), y=r*sin(theta)])))/2);
```

$$\psi_{0,2} := \frac{4 e^{-\frac{\pi\sqrt{k}\sqrt{\mu} r^2}{h}} \pi k^{3/4} \left( I \sin(\theta) \cos(\theta) + \cos(\theta)^2 - \frac{1}{2} \right) \mu^{3/4} r^2}{h^{3/2}} \quad (21.28)$$

```
> psi2[0,-2] := simplify((simplify(eval(psi, [nx=2, ny=0, x=r*cos
(theta), y=r*sin(theta)]))
- simplify(eval(psi, [nx=0, ny=2, x=r*cos(theta), y=
r*sin(theta)]))
- I*sqrt(2)*simplify(eval(psi, [nx=1, ny=1, x=r*cos
```

**(theta), y=r\*sin(theta)]))/2);**

$$\psi_{0,-2}^2 := - \frac{e^{-\frac{\pi\sqrt{k}\sqrt{\mu}}{h}r^2} \left( I \sin(\theta) \cos(\theta) - \cos(\theta)^2 + \frac{1}{2} \right) \pi k^{3/4} \mu^{3/4} r^2}{h^{3/2}} \quad (21.29)$$

The latter relations between the amplitude functions derived in this section and those derived in section 1.27 demonstrate that we can transform amplitude functions of coordinates in one system to amplitude functions of coordinates in another system for the equivalent function of potential energy.

Some physical models are solvable in multiple systems of coordinates: these models are called *superintegrable*. The best known such models in a euclidean space of three dimensions are the canonical linear harmonic oscillator, as treated in this and preceding sections, and the Kepler-Coulomb problem, such as the hydrogen atom, that have special properties distinct from other spherically symmetric potential energies. In these cases the partial-differential equation governing the physical system is separable into ordinary-differential equations in each spatial variable. The potential

$$V(x, y, z) = \frac{\omega^2}{2} (x^2 + y^2 + z^2)$$

is separable in cartesian, spherical polar, cylindrical polar, cylindrical elliptic, spheroconical, oblate-spheroidal, prolate-spheroidal and ellipsoidal coordinates, even with further terms as in

$$V(x, y, z) = \frac{\omega^2}{2} (x^2 + y^2 + z^2) + \left( \frac{k_1^2 - \frac{1}{4}}{x^2} + \frac{k_2^2 - \frac{1}{4}}{y^2} + \frac{k_3^2 - \frac{1}{4}}{z^2} \right)$$

that is reminiscent of the Davidson function in one dimension, treated in section 1.32. A similar function,

$$V(x, y, z) = \frac{\omega^2}{2} (x^2 + y^2 + 4z^2) + \frac{1}{2} \left( \frac{k_1^2 - \frac{1}{4}}{x^2} + \frac{k_2^2 - \frac{1}{4}}{y^2} \right)$$

is separable in cartesian, cylindrical polar, cylindrical parabolic, cylindrical elliptic and parabolic coordinates. For the Kepler-Coulomb problem, with potential energy,

$$V(r) = - \frac{\alpha}{\sqrt{x^2 + y^2 + z^2}} + \frac{1}{2} \left( \frac{k_1^2 - \frac{1}{4}}{x^2} + \frac{k_2^2 - \frac{1}{4}}{y^2} \right)$$

the function is separable in spherical polar, paraboloidal, prolate spheroidal or ellipsoidal and spheroconical coordinates, as we present in section group 1.5.

### ***e1.210 exercise***

Express amplitude functions  $\psi_{n,m}(r, \phi)$  in polar coordinates, as derived in section 1.27, as linear combinations of  $\psi_{n_x, n_y}(x, y)$  in cartesian coordinates in section 1.28, for the cases of total energy = 3 in

$$\text{unit } \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}.$$

### **1.29 temporally dependent perturbation theory applied to a canonical harmonic oscillator**

**> restart:**

We consider a monochromatic perturbation of finite duration that connects an initially populated ground state to states of greater energy. When evaluated over a finite interval, a sinusoidal signal at a single frequency is no longer monochromatic, but experiences broadening and other effects due to the shape of the pulse. For simplicity we consider eigenstates of a canonical harmonic oscillator. This example was produced by Professor M. Horbatsch and appears here with his kind permission.

```
> Digits := 14:
```

```
with(plots):
```

We define the frequency  $w$  and mass  $m$  of the oscillator as unit quantities,

```
> w := 1;
```

$$w := 1 \quad (23.1)$$

```
> m := 1;
```

$$m := 1 \quad (23.2)$$

and also define  $\hbar = 2 \pi$ .

```
> hbar := 1;
```

$$\hbar := 1 \quad (23.3)$$

The energies are taken to be those of the canonical linear harmonic oscillator, with angular frequency  $w$ .

```
> En := n -> (n+1/2)*hbar*w;
```

$$E_n := n \mapsto \left( n + \frac{1}{2} \right) \cdot \hbar \cdot w \quad (23.4)$$

We invoke the deprecated package of orthogonal functions.

```
> with(orthopoly);
```

$$[G, H, L, P, T, U] \quad (23.5)$$

The normalising factor of the amplitude functions is

```
> An := n -> 1/sqrt(2^n*n!*sqrt(Pi));
```

$$A_n := n \mapsto \frac{1}{\sqrt{2^n \cdot n! \cdot \sqrt{\pi}}} \quad (23.6)$$

and the coefficient of displacement  $x$  is

```
> beta := sqrt(m*w/hbar);
```

$$\beta := 1 \quad (23.7)$$

yielding this amplitude function,

```
> phi := n -> An(n)*exp(-beta^2*x^2/2)*H(n,beta*x);
```

$$\phi := n \mapsto A_n(n) \cdot e^{-\frac{\beta^2 \cdot x^2}{2}} \cdot H(n, \beta \cdot x) \quad (23.8)$$

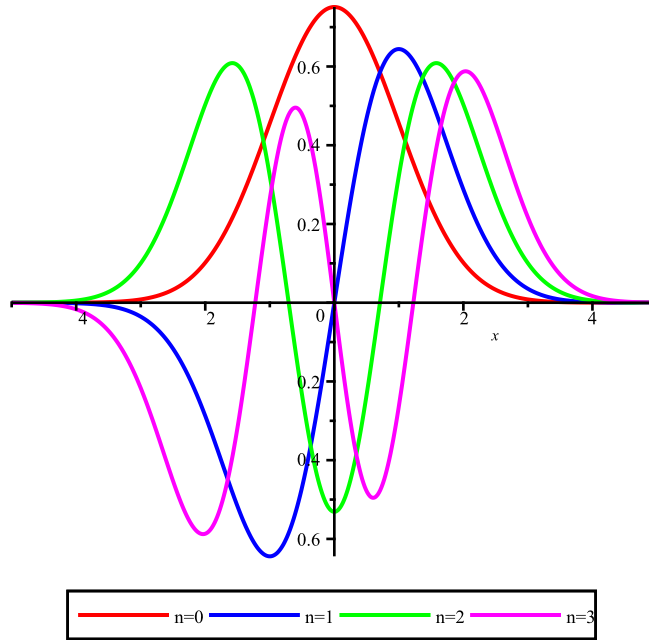
of which we plot four cases.

```
> plot([seq(phi(n), n=0..3)], x=-5..5, colour=[red, blue, green, magenta],
```

```
    numpoints=500, title="amplitude functions of linear harmonic oscillator",
```



**titlefont=[TIMES,BOLD,14], legend=["n=0","n=1","n=2","n=3"]);**  
**amplitude functions of linear harmonic oscillator**



We test the normalisation.

```
> Int(phi(j)^2, x=-infinity..infinity) = seq(int(phi(j)^2, x=-infinity..infinity), j=0..3);
```

$$\int_{-\infty}^{\infty} \frac{\left(e^{-\frac{x^2}{2}}\right)^2 H(j, x)^2}{2^j j! \sqrt{\pi}} dx = (1, 1, 1, 1) \quad (23.9)$$

Without perturbation, the system is defined with  $H_0 |j\rangle = \epsilon_j |j\rangle$ ,  $j = 0, 1, 2, \dots$ , which might be discrete

or continuous. The temporal evolution of eigenstate  $|j\rangle$  of energy conforms to  $|j(t)\rangle = e^{\frac{2\pi i \epsilon_j t}{h}} |\phi_j\rangle$ .

The perturbation is assumed to act during a finite interval,  $0 < t < T$ ; a smallness parameter  $\lambda$  is defined with  $V(t) = \lambda W(t)$  such that  $W(0) = 0$  for  $t \leq 0$  and  $t > T$ . The hamiltonian becomes  $H(t) = H_0 + \lambda W(t)$ . As an initial condition we prepare the system at  $t = 0$  in an eigenstate of  $H_0$ ; after time  $t = T$  when the action of the perturbation is completed, the system is again governed with  $H_0$ . The objective is to find how the quantum ensemble  $|\psi(t > T)\rangle$  is distributed over eigenstates  $|\psi_j\rangle = |j\rangle$ , which involves calculating the fractions that have undergone transitions from  $|\psi_v\rangle$  to  $|\psi_0\rangle$ ,  $|\psi_1\rangle$ ,  $|\psi_2\rangle$ ,  $|\psi_3\rangle$ , ...; from  $|\psi_v\rangle$  to  $|\psi_v\rangle$  corresponds to an elastic channel, whereas for  $\epsilon_j > \epsilon_v$  corresponds to excitation and  $\epsilon_j < \epsilon_v$  corresponds to relaxation or de-excitation. As an initial point we form a matrix representation of the full temporally dependent Schroedinger equation, with  $H = H_0 + \lambda W(t)$ , in terms of the eigenstates of  $H_0$ , which yields exact *coupled-channel* equations. We suppose that the interaction represents a sinusoidally varying homogeneous electric field; the strength parameter  $\lambda$  is unspecified;

the circular frequency of the field is denoted  $\alpha$ .

```
> W := x*sin(alpha*t);
```

$$W := x \sin(\alpha t) \quad (23.10)$$

```
> Wmat := (m,n) -> int(phi(m)*W*phi(n),x=-infinity..infinity);
```

$$Wmat := (m, n) \mapsto \int_{-\infty}^{\infty} \phi(m) \cdot W \cdot \phi(n) \, dx \quad (23.11)$$

```
> Wmat(0,1);
```

$$\frac{\sin(\alpha t) \sqrt{2}}{2} \quad (23.12)$$

```
> Wmat(0,2);
```

$$0 \quad (23.13)$$

```
> Wmat(0,3);
```

$$0 \quad (23.14)$$

The interaction connects states only of opposite parity, as is obvious from the symmetry properties of the integrand. From the calculation it becomes clear also that the interaction connects only neighboring states, which is a special feature of eigenfunctions of the canonical harmonic oscillator. We have two frequencies in our problem -- angular frequency  $\omega = 1$  of the harmonic oscillator and circular frequency  $\alpha$  of the field applied to excite the system. We choose a frequency of the perturbation.

```
> alpha := w*0.999;
```

$$\alpha := 0.999 \quad (23.15)$$

```
> T_field := 2*Pi/alpha;
```

$$T_{field} := 6.2894747819616 \quad (23.16)$$

```
> N_cyc := 3;
```

$$N_{cyc} := 3 \quad (23.17)$$

```
> T := N_cyc*T_field;
```

$$T := 18.868424345885 \quad (23.18)$$

```
> lambda := 0.1;
```

$$\lambda := 0.1 \quad (23.19)$$

Having set the element of the interaction matrix in terms of time  $t$ , we integrate over time  $t$  from 0 to  $s$ , which becomes our symbol for time after integration.

```
> P_0k := k -> 1/hbar^2*abs(lambda*int(exp(I*(En(k)-En(0))*t)*Wmat  
(0,k),t=0..s))^2;
```

$$P_{0k} := k \mapsto \frac{\left| \lambda \cdot \left( \int_0^s e^{i \cdot (E_n(k) - E_n(0)) \cdot t} \cdot Wmat(0, k) \, dt \right) \right|^2}{\hbar^2} \quad (23.20)$$

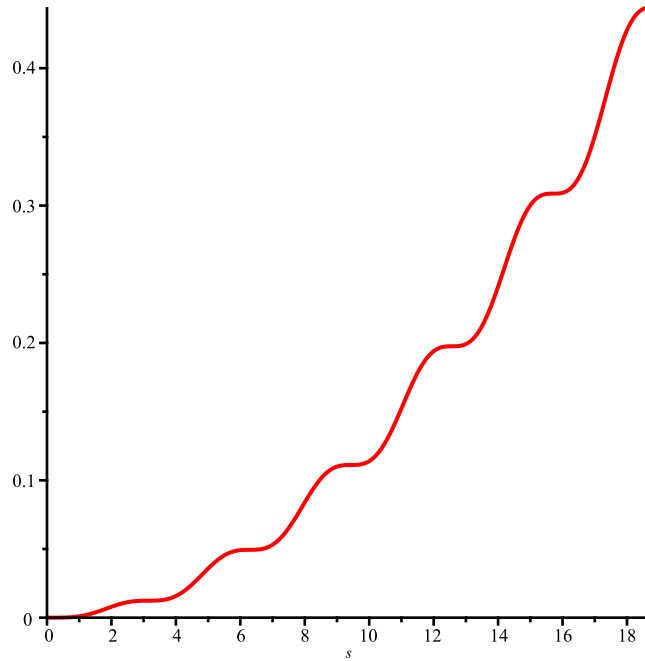
```
> evalf(seq(P_0k(j),j=0..3));
```

$$(23.21)$$

$$0., \left| -35.337652546541 + 35.337652546541 e^{Is} \cos(0.9990000000000000 s) - 35.373025572114 I e^{Is} \sin(0.9990000000000000 s) \right|^2, 0., 0. \quad (23.21)$$

We store the graph for future reference, using `s` as the time parameter.

```
> PL1 := plot(P_0k(1), s=0..T, numpoints=500, colour=red):
plots[display](PL1);
```



How should we interpret this result? We can excite only the neighboring state with  $k=1$  in perturbation theory of first order, but we expect the population of other states to vary as a result of second-order effects. The state, moreover, appears to become not only excited but also de-excited with the same matrix element. At the end of a complete cycle we find a complete return of the population back to the ground state.

Attempt exercise *e1.211* at this point.

The strong excitation results (on resonance) should make us suspicious about the utility of perturbation theory at first order in this problem. After all, the zero-order result for  $c_0(t)$  was used, namely a probability 1 in the original state throughout the interaction. We proceed to some second-order calculations for the population of the levels  $k=0,1,2$ . For this purpose to record the transition probabilities is insufficient -- we must also keep track of the complex amplitudes. To order O1 we have for the only non-vanishing excited-state probability amplitude,

```
> c1_O1 := unapply(-I/hbar*int(exp(I*(En(1)-En(0))*t)*Wmat(0,1), t=
0..s),s);
```

$$c1\_O1 := s \mapsto -I \cdot (-353.37652546541 + 353.37652546541 \cdot e^{Is} \cdot \cos(0.9990000000000000 \cdot s) - 353.73025572114 \cdot I \cdot e^{Is} \cdot \sin(0.9990000000000000 \cdot s)) \quad (23.22)$$

```
> c0_O1 := 1; # This setting is not logical, as it
is the result up to first order.
c0_O1 := 1 \quad (23.23)
```

```
> c2_O2 := unapply(-I/hbar*int(exp(I*(En(2)-En(1))*t)*Wmat(1,2)*
  c1_O1(t),t=0..s),s);
```

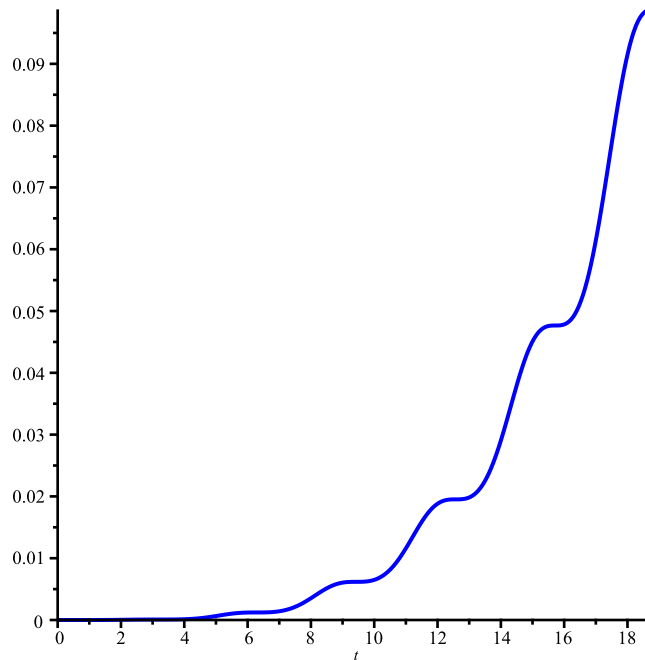
$$c2\_O2 := s \mapsto -I \cdot \left( -88299.937203587 \cdot I + 176599.87440718 \cdot I \cdot e^{I \cdot s} \cdot \cos(0.999000000000000 \cdot s) \right. \quad (23.24)$$

$$+ 176776.65105823 \cdot e^{I \cdot s} \cdot \sin(0.999000000000000 \cdot s) + 88.432563930285 \cdot I \cdot e^{2 \cdot I \cdot s}$$

$$- 88388.369767519 \cdot I \cdot e^{2 \cdot I \cdot s} \cdot \cos(1.998000000000000 \cdot s) - 88388.325529118 \cdot e^{2 \cdot I \cdot s}$$

$$\cdot \sin(1.998000000000000 \cdot s) \Big)$$

```
> PL2 := plot(abs(lambda^2*c2_O2(t))^2, t=0..T, numpoints=500,
  colour=blue):
display(PL2);
```



```
> c0_O2 := unapply(-I/hbar*int(exp(I*(En(0)-En(1))*t)*Wmat(1,0)*
  c1_O1(t), t=0..s), s);
```

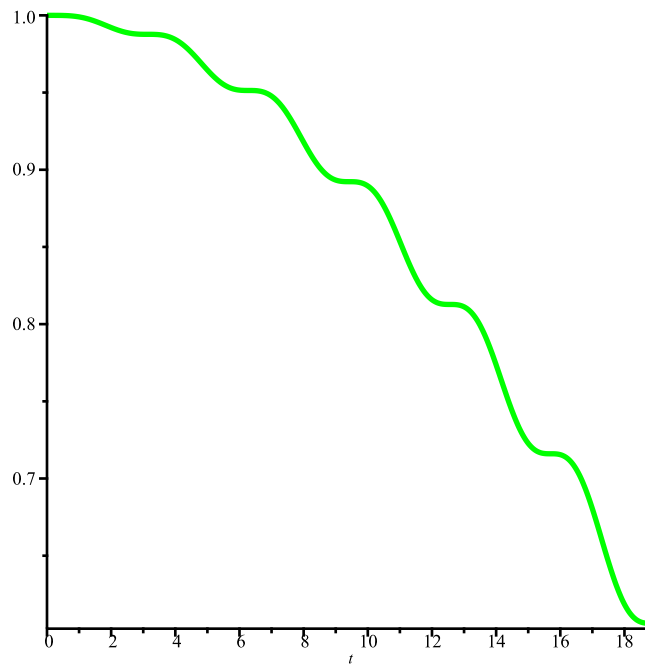
$$c0\_O2 := s \mapsto -I \cdot \left( -124937.50001564 \cdot I + 124874.96875001 \cdot I \cdot e^{-I \cdot s} \cdot \cos(0.999000000000000 \right. \quad (23.25)$$

$$\cdot s) - 124999.96871873 \cdot e^{-I \cdot s} \cdot \sin(0.999000000000000 \cdot s) - 125.06253126564 \cdot s$$

$$+ 62.531265632816 \cdot I \cdot \cos(1.998000000000000 \cdot s) + 62.593859492310$$

$$\cdot \sin(1.998000000000000 \cdot s) \Big)$$

```
> PL3 := plot(abs(1+lambda^2*c0_O2(t))^2,t=0..T, numpoints=500,
  colour=green, thickness=2):
display(PL3);
```



The norm is poorly conserved in the sense that, if we add the second-order probability for  $k=2$  to the first-order probability for  $k=1$ , we have a greater probability than what was removed from unity in the elastic channel; for this reason we refrain from use of the actual probability calculation for the elastic channel, but instead assume that it is unity minus a sum of excitation probabilities. We test the Fourier-transform interpretation of the first-order result.

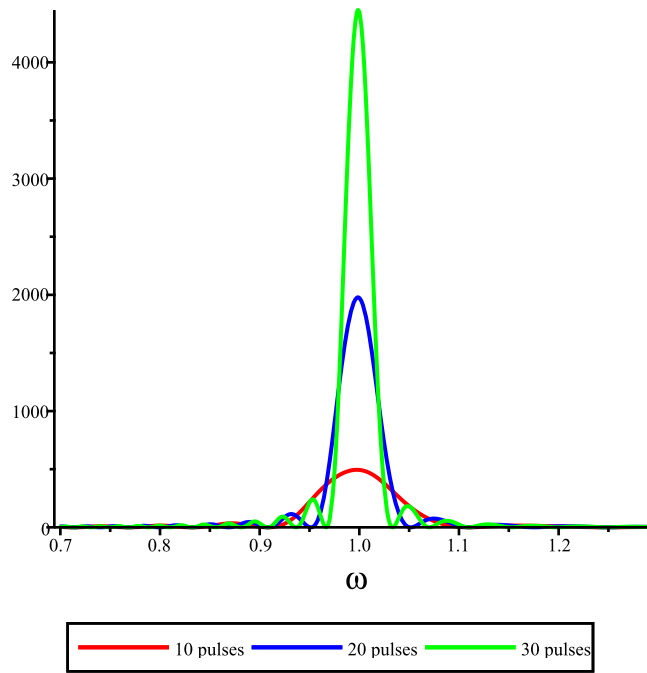
```
> FT := unapply(abs(int(exp(I*omega*t)*Wmat(0,1),t=0..N*2*Pi/omega))
^2, omega,N);
FT := (omega,N) ↦ 500000.000000000
```

(23.26)

$$\cdot \left| \frac{1}{1.000000 \times 10^6 \cdot \omega^2 - 998001.} \left( 1000. \cdot I \cdot e^{6.2831853071796 \cdot I \cdot N \cdot \omega} \cdot \sin\left(\frac{6.2769021218724 \cdot N}{\omega}\right) - 999. \cdot e^{6.2831853071796 \cdot I \cdot N} \cdot \cos\left(\frac{6.2769021218724 \cdot N}{\omega}\right) + 999. \right) \right|$$

We show the frequency spectrum of the pulse for 10, 20 and 30 cycle-length pulses. The pulse shape profile is rectangular, i.e. wave modulation of rectangular profile with sharp onset and termination.

```
> plot([seq(FT(omega,j),j=10..30,10)], omega=0.7*alpha..1.3*alpha,
colour=[red,blue,green],legend=["10 pulses","20 pulses","30
pulses"]);
```



The abrupt onset and termination of the monochromatic pulse, at times 0 and  $N\alpha$  respectively, cause a 'ringing' effect, namely the presence of sidebands around the centre frequency. Note the breadth of the signal for the number of cycles shown. The perturbation is effective within this window, i.e., transitions occur if the transition frequency between initial and final state be within the peak. The consequences are that for a long pulse -- thousands of cycles (or more) -- an effective excitation becomes possible only for small (or negligible) detuning from the resonance frequency.

Attempt exercise *e1.212* at this point.

We proceed to solve the coupled-channel equations. We connect only the levels  $k=0,1,2$ .

$$> \text{Wmat}(0,1); \quad 0.70710678118655 \sin(0.9990000000000000 t) \quad (23.27)$$

$$> \text{Wmat}(1,2); \quad \sin(0.9990000000000000 t) \quad (23.28)$$

$$\begin{aligned} > \text{DE0} := \text{I} * \text{diff}(c0(t), t) = \text{lambda} * \text{add}(c \mid j(t) * \text{Wmat}(0, j) * \exp(\text{I}/\text{hbar} * (\text{En}(j) - \text{En}(0)) * t), j=0..2); \\ \text{DE0} := \text{I} \left( \frac{d}{dt} c0(t) \right) &= 0.070710678118655 c1(t) \sin(0.9990000000000000 t) e^{I t} \end{aligned} \quad (23.29)$$

$$\begin{aligned} > \text{DE1} := \text{I} * \text{diff}(c1(t), t) = \text{lambda} * \text{add}(c \mid j(t) * \text{Wmat}(1, j) * \exp(\text{I}/\text{hbar} * (\text{En}(j) - \text{En}(1)) * t), j=0..2); \\ \text{DE1} := \text{I} \left( \frac{d}{dt} c1(t) \right) &= 0.070710678118655 c0(t) \sin(0.9990000000000000 t) e^{-I t} \\ &+ 0.1 c2(t) \sin(0.9990000000000000 t) e^{I t} \end{aligned} \quad (23.30)$$

$$\begin{aligned} > \text{DE2} := \text{I} * \text{diff}(c2(t), t) = \text{lambda} * \text{add}(c \mid j(t) * \text{Wmat}(2, j) * \exp(\text{I}/\text{hbar} * (\text{En}(j) - \text{En}(2)) * t), j=0..2); \\ & \quad (23.31) \end{aligned}$$

$$DE2 := I \left( \frac{d}{dt} c2(t) \right) = 0.1 c1(t) \sin(0.9990000000000000 t) e^{-It} \quad (23.31)$$

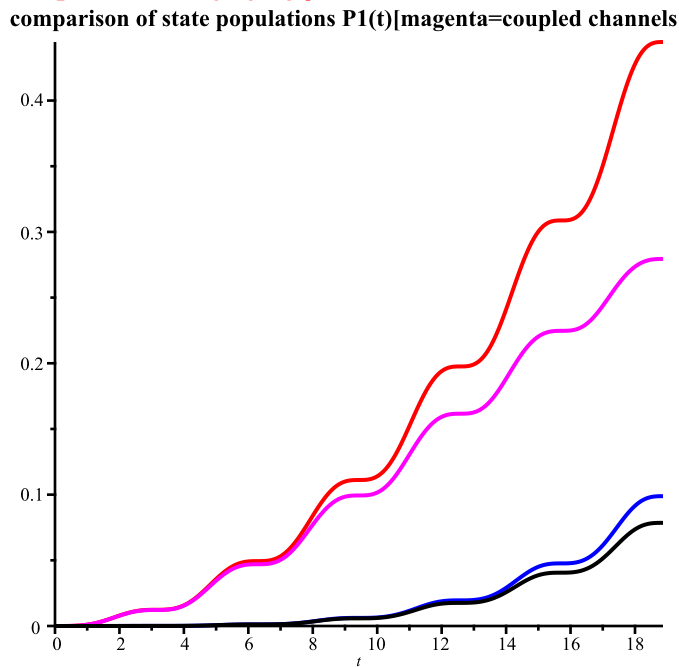
```
> IC := c0(0)=1,c1(0)=0,c2(0)=0;
      IC := c0(0) = 1, c1(0) = 0, c2(0) = 0
```

(23.32)

```
> sol := dsolve({DE0,DE1,DE2,IC},numeric,output=listprocedure);
sol := [t=proc(t) ... end proc, c0(t)=proc(t) ... end proc, c1(t)=proc(t) ... end proc,
      c2(t)=proc(t) ... end proc]
```

(23.33)

```
> C0 := eval(c0(t),sol):
  C1 := eval(c1(t),sol):
  C2 := eval(c2(t),sol):
> PL4 := plot([abs(C1(t))^2,abs(C2(t))^2],t=0..T,colour=[magenta,
  black]):
  display(PL2,PL1,PL4, titlefont=[TIMES,BOLD,14],
    title="comparison of state populations P1(t)[magenta=coupled
  channels; red=TDPT] and P2(t)");
```



The three-channel close-coupling result is not exact as it neglects couplings to state  $k=3$ . Given that the couplings proceed progressively, i.e.,  $k=1$  is populated from  $k=0$ ;  $k=2$  is populated from  $k=1$ , etc. we expect this condition to affect the results at the latest times shown. This feature of step-wise excitation also explains that the discrepancy between the first-order result for  $P1(t)$  overestimates the coupled-channel result by about the level of  $P2(t)$  calculated in temporally dependent perturbation theory at second order. The result at second order for  $P2(t)$  agrees with the coupled-channel calculation at times when the first-order answer for  $P1(t)$  overestimates significantly the corresponding result from the temporally dependent Schroedinger equation.

Attempt exercise *e1.213* at this point.

The philosophy in temporally dependent perturbation theory of order  $n$  is to use the probability

amplitudes in the preceding order for the other levels to obtain the correction at level  $k$  at the order to be computed.

We make a few numerical comparisons.

$$> \text{abs}(C0(T))^2 + \text{abs}(C1(T))^2 + \text{abs}(C2(T))^2; \\ 1.0000001946863 \quad (23.34)$$

$$> \text{evalf}(\text{eval}(P\_0k(1), s=T), \text{abs}(C1(T))^2; \\ 0.44456347397667, 0.27943914125827 \quad (23.35)$$

$$> \text{evalf}(\text{eval}(P\_0k(1), s=T/2), \text{abs}(C1(T/2))^2; \\ 0.11114334153394, 0.099363853239298 \quad (23.36)$$

$$> \text{evalf}(\text{eval}(P\_0k(1), s=T/4), \text{abs}(C1(T/4))^2; \\ 0.029065054692876, 0.028230614447349 \quad (23.37)$$

To what order must we proceed to obtain agreement between the approach from temporally dependent perturbation theory and the integration of the coupled-channel equations not just at the beginning? We try the higher-order result for the excitation of the  $k=1$  state. The scheme is to connect neighboring states:  $0 \rightarrow 1$  occurs at O1,  $1 \rightarrow 2$  and  $1 \rightarrow 0$  at O2. There is no contribution  $0 \rightarrow 1$  at this level because the first-order contribution to coefficient  $c1(t)$  vanishes. We calculate the contribution to  $c1(t)$  at third order.

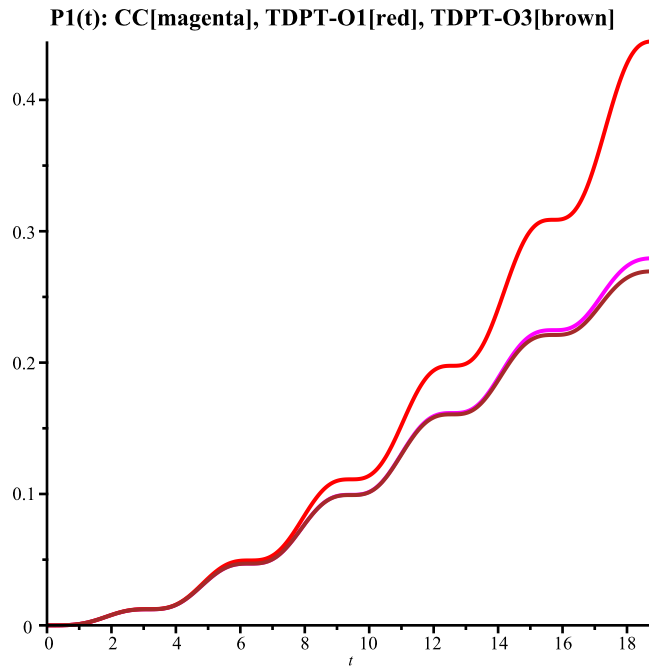
$$> c1\_O3 := \text{unapply}(-I/\hbar * (\text{int}(\exp(I*(En(1)-En(0))*t)*Wmat(0,1)* \\ c0\_O2(t), t=0..s) \\ + \text{int}(\exp(I*(En(1)-En(2))*t)*Wmat(2,1)*c2\_O2(t), t=0..s)), s) \\ ; \\ c1\_O3 := s \mapsto -I \cdot (8.8322056393108 \times 10^7 + 4.4194173829694 \times 10^7 \cdot I \cdot e^{I \cdot s} \quad (23.38)$$

$$\cdot \sin(0.999000000000000 \cdot s) - 4.4150001786136 \times 10^7 \cdot e^{I \cdot s} \cdot \cos(0.999000000000000 \cdot s) \\ - 4.4172054629108 \times 10^7 \cdot I \cdot e^{-I \cdot s} \cdot \sin(0.999000000000000 \cdot s) + 22119.211653533 \cdot e^{I \cdot s} \\ \cdot \cos(2.997000000000000 \cdot s) + 22119.200582860 \cdot I \cdot \sin(1.998000000000000 \cdot s) \\ - 22119.200582863 \cdot I \cdot e^{I \cdot s} \cdot \sin(2.997000000000000 \cdot s) + 44238.401165727 \cdot e^{I \cdot s} \\ \cdot \sin(0.999000000000000 \cdot s) \cdot s + 44194.162764562 \cdot I \cdot e^{I \cdot s} \cdot \cos(0.999000000000000 \cdot s) \cdot s \\ - 66291.244146840 \cdot \cos(1.998000000000000 \cdot s) - 44194.162764555 \cdot I \cdot s \\ - 4.4127882574479 \times 10^7 \cdot e^{-I \cdot s} \cdot \cos(0.999000000000000 \cdot s))$$

$$> c1\_O3(1); \\ -0.006170 + 0.015110 I \quad (23.39)$$

$$> \text{plot}([\text{abs}(C1(t))^2, \text{abs}(\text{lambda} * c1\_O1(t))^2, \text{abs}(\text{lambda} * c1\_O1(t) + \\ \text{lambda}^3 * c1\_O3(t))^2], t=0..T, \\ \text{numpoints}=500, \text{colour}=[\text{magenta}, \text{red}, \text{brown}], \text{titlefont}= \\ [\text{TIMES}, \text{BOLD}, 14], \\ \text{title}="P1(t): \text{CC}[\text{magenta}], \text{TDPT-O1}[\text{red}], \text{TDPT-O3}[\text{brown}]");$$





The result of temporally dependent perturbation theory up to third order follows well the coupled-channel result. At late times the third-order correction overcompensates the large deviation in the first-order result. One can view the scheme of temporally dependent perturbation theory as a scheme of successive approximation that integrates the system of ordinary differential equations (the coupled-channel equations form of the temporally dependent Schrodinger equation) in a scheme of successive approximation.

Attempt exercise *e12a214* at this point.

We proceed with an improved calculation of the probability to remain in the ground state ( $k=0$ ); in this case there is only one contribution, as the connexion is to only state  $k=1$ . We have contributions at order  $\lambda^2$  and  $\lambda^4$  that can be calculated from the known results for  $c1$  at orders  $O1$  and  $O3$ . The  $O2$  result is known already:

$$> \text{c0\_O2}(1);$$

$$-0.049840663966 + 0.013721084528 \text{ I} \quad (23.40)$$

$$> \text{c0\_O4} := \text{unapply}(-\text{I}/\hbar * \text{int}(\exp(\text{I} * (\text{En}(0) - \text{En}(1)) * t) * \text{Wmat}(1, 0) * \text{c1\_O3}(t), t=0..s), s);$$

$$\text{c0\_O4} := s \mapsto -\text{I} \cdot (7.8046894531232 \times 10^9 \cdot \text{I} + 1.5625000001957 \times 10^7 \cdot s - 1.5593749999999 \times 10^{10} \cdot \text{I} \cdot e^{-\text{I} \cdot s} \cdot \cos(0.999000000000000 \cdot s) + 1957.0376069462 \cdot \text{I} \cdot \cos(3.99600000000000 \cdot s) - 7820.3183632840 \cdot \text{I} \cdot e^{-\text{I} \cdot s} \cdot \cos(2.99700000000000 \cdot s) - 7.8125000009785 \times 10^6 \cdot \text{I} \cdot \cos(1.99800000000000 \cdot s) + 1957.0366274484 \cdot \sin(3.99600000000000 \cdot s) - 7.8203203212997 \times 10^6 \cdot \sin(1.99800000000000 \cdot s) - 1.5617179683591 \times 10^7 \cdot e^{-\text{I} \cdot s} \cdot \cos(0.999000000000000 \cdot s) \cdot s - 7.8085898417963 \times 10^6 \cdot \text{I} \cdot e^{-2 \cdot \text{I} \cdot s} - 1.5632812496088 \times 10^7 \cdot \text{I} \cdot e^{-\text{I} \cdot s} \cdot \sin(0.999000000000000 \cdot s) \cdot s + 7.8046874999994 \times 10^9 \cdot \text{I} \cdot e^{-2 \cdot \text{I} \cdot s} \cdot \cos(1.99800000000000 \cdot s) - 7820.3183632841 \cdot \text{I} \cdot s^2 + 7828.1465097939 \cdot \text{I} \cdot s) \quad (23.41)$$

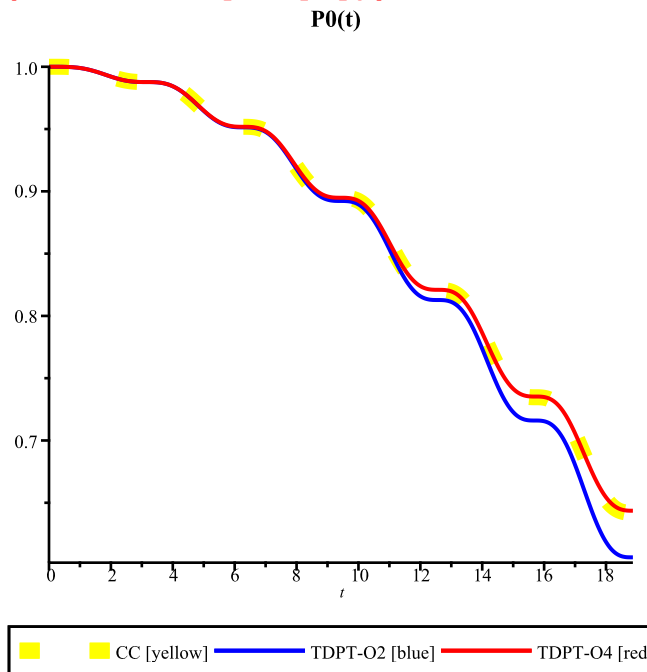
$$\begin{aligned} & \cdot \sin(1.99800000000000 \cdot s) - 7820.3183632843 \cdot s \cdot \cos(1.99800000000000 \cdot s) \\ & + 1.56250000000001 \times 10^{10} \cdot e^{-1 \cdot s} \cdot \sin(0.99900000000000 \cdot s) + 3.8004067538514 \times 10^{-10} \\ & \cdot \sin(2.99700000000000 \cdot s) \cdot e^{-1 \cdot s} - 7.8046835937513 \times 10^9 \cdot e^{-2 \cdot 1 \cdot s} \cdot \sin(1.99800000000000 \\ & \cdot s) \end{aligned}$$

```
> c0_O4(1);
```

$$0.0012 - 0.0005 I$$

(23.42)

```
> plot([abs(C0(t))^2,abs(1+lambda^2*c0_O2(t))^2,abs(1+lambda^2*c0_O2(t)+lambda^4*c0_O4(t))^2],t=0..T,
        numpoints=500, colour=[yellow,blue,red], titlefont=[TIMES,
        BOLD,14], linestyle=[dot,solid,solid],
        thickness=[6,1,1], title="P0(t)", legend=["CC [yellow]",
        "TDPT-O2 [blue]", "TDPT-O4 [red]"]);
```



We observe an impressive agreement between the coupled-channel result and the result from temporally dependent perturbation theory at fourth order for the elastic channel. If the system were to evolve for a greater duration, or for a stronger coupling as  $\lambda$ , we should observe that temporally dependent perturbation theory at high order converges against the close-coupling result with more equations coupled than in the present case. One should bear in mind that the coupling scheme is particularly simple for the harmonic oscillator; for anharmonic potentials direct coupling to more excited states is possible by the time-dependent linear potential.

Attempt exercise *e12.215* at this point.

### *e1.211 exercise, temporally dependent perturbation theory*

Modify the frequency of the perturbation in section 1.29 by choosing  $\alpha$  to be less near the resonance

( $\hbar \omega$  is the energy difference between neighboring levels, i.e., also between  $k = 0$  and  $k = 1$ ). Begin with small deviations from resonance before you choose disparate circular frequencies for the laser pulse to understand better what occurs away from resonance in some work below within section 1.29.

#### ***e1.212 exercise, temporally dependent perturbation theory***

Construct the Fourier transform of pulses containing more cycles. Read on windowing functions in a reference text on discrete (fast) Fourier transforms to learn how they can suppress the ringing effect (e.g., Hamming window function, cf. digital oscilloscopes with FFT function). Realistic laser pulses have pulse shapes with gradual onset and termination.

#### ***e1.213 exercise, temporally dependent perturbation theory***

Extend the close-coupling calculation to include couplings to level  $k = 3$ . At what time do these populations become appreciable? What is the implication for the accuracy of the 3-channel ( $k = 0, 1, 2$ ) close-coupling calculations shown above?

#### ***e1.214 exercise, temporally dependent perturbation theory***

The calculation of  $c1\_O3(t)$  represents the complete pattern of the TDPT scheme for the present problem. Nearest neighbours are connected by the perturbation. One uses the coefficients from the previous approximation (not the complete coefficient, just the contribution from that order), multiplies it with the appropriate coupling matrix and computes the Fourier transform for a fixed transition frequency. The two amplitudes from the lower-lying and higher-lying neighboring energy levels are added coherently to form the overall probability amplitude. Use this pattern to compute the population  $P1(t)$  at the next order for which there is a non-trivial contribution.

#### ***e1.215 exercise, temporally dependent perturbation theory***

Explore what happens to the above results in section 1.29 when the strength parameter  $\lambda$  is increased (e.g., doubled, etc.). Be careful in your interpretation of results. Note when the calculated probability expression exceeds unity and understand what this means. Extend the coupled-channel equations to sufficient matrix dimension to ensure convergence of results against which the TDPT calculations are compared.

### **1.3 two harmonic oscillators in spectrometric context**

#### **1.31 canonical linear harmonic oscillator according to wave mechanics, with spectral parameters**

**> restart:**

In these two sections, we repeat in this section the calculation of the canonical quantum-mechanical linear harmonic oscillator with emphasis on properties in relation to prospective experimental measurement of spectral transitions, and in the next section we perform on an analogous basis a calculation of another quantum-mechanical harmonic oscillator for comparison. In either case, the treatment might serve roughly as a model for that of a diatomic molecule as comprising two atomic centres that are free to oscillate about their equilibrium internuclear distance and to rotate about their centre of mass; with some distribution of populations over accessible vibration-rotational states at a particular temperature, such an hypothetical system would have an associated spectrum in absorption that depends on the properties of the oscillators according to the particular nature of the function for vibrational potential energy.

Here is Schroedinger's radial equation in one dimension and in standard form,

$$H\psi = (T + V)\psi = E\psi$$

Anticipating that we find discrete energies that might bear a numbering according to a vibrational quantum number  $v$ , we specify kinetic energy in a standard form  $\frac{p^2}{2\mu}$  and then replace  $p$  with the

differential operator  $-i \hbar \left( \frac{\partial}{\partial R} \right)$  to obtain our working equation,

$$-\frac{\hbar^2 \left( \frac{d^2}{dR^2} \psi(R) \right)}{8 \pi^2 \mu} + V(R) \psi(R) = E \psi(R)$$

in which  $R$  is the instantaneous distance between two point masses in a system of which the reduced mass of  $\mu = \frac{M_a M_b}{M_a + M_b}$ ; the oscillation of two masses along a line through their centre at  $R_e$  is equivalent to the oscillation of a reduced mass, according to that formula, along a coordinate corresponding to a positive axis. We make a substitution of variable from  $R$  to  $x = \frac{R - R_e}{R_e}$ ; then  $\frac{\partial}{\partial R} x = \frac{1}{R_e}$ .

Schroedinger's equation becomes transformed to

$$-\frac{\hbar^2 \left( \frac{d^2}{dx^2} \psi(x) \right)}{8 \pi^2 \mu R_e^2} + V(x) \psi(x) = E \psi(x).$$

The coefficient of the second derivative is simply  $\frac{\hbar^2}{8 \pi^2 \mu R_e^2}$  that is just a definition of equilibrium

rotational parameter  $B_e$  in wavenumber unit multiplied by  $\hbar c$ . We hence rewrite Schroedinger's equation as

$$\frac{d^2}{dx^2} \psi(x) + \frac{(E - V(x)) \psi(x)}{\hbar c B_e} = 0$$

For the canonical linear harmonic oscillator, we express  $V(x)$  in Dunham's form as  $V(x) = a_0 x^2$  but we

replace  $a_0 = \frac{\omega_e^2}{4 B_e}$  by  $\frac{B_e}{g^2}$  with  $g = \frac{2 B_e}{\omega_e}$ , so obtaining

$$\frac{d^2}{dx^2} \psi(x) + \left( \frac{E}{\hbar c B_e} - \frac{x^2}{g^2} \right) \psi(x) = 0.$$

The two primary spectral parameters are the vibrational parameter  $\omega_e$  related to the interval of energy between adjacent vibrational states and rotational parameter  $B_e$  related to the interval of energy between adjacent rotational states.

On this basis we proceed to solve this differential equation.

```
> with(DEtools):
with(plots):
with(PDEtools, declare):
declare(psi(x), prime=x);
assume(g > 0);
Digits := 16;
```

$\psi(x)$  will now be displayed as  $\psi$

*derivatives with respect to x of functions of one variable will now be displayed with ' (29.1)*

Having set assumptions on the sign of pertinent quantities, we state the resulting differential equation.

```
> V := h*c*B[e]*x^2/g^2;
```

$$V := \frac{h c B_e x^2}{g^2} \quad (29.2)$$

The second derivative of V(x),

```
> Diff('V',x$2) = simplify(diff(V, x$2));
```

$$\frac{\partial^2}{\partial x^2} V = \frac{2 h c B_e}{g^2} \quad (29.3)$$

is independent of x, consistent with the parabolic curve of V(x). We form Schroedinger's temporally independent equation with this function for potential energy.

```
> ode1 := diff(psi(x), x$2) + (E - V)/(h*c*B[e])*psi(x)= 0;
```

$$ode1 := \psi'' + \frac{\left(E - \frac{h c B_e x^2}{g^2}\right) \psi}{h c B_e} = 0 \quad (29.4)$$

What kind is this differential equation?

```
> odeadvisor(ode1);
```

*[[\_2nd\_order, \_with\_linear\_symmetries]] (29.5)*

This differential equation is of second order, and linear because there is no constant term that is not a factor of  $\psi(q)$ . We proceed to solve this equation.

```
> sol1 := dsolve(ode1, psi(x));
```

$$sol1 := \psi = \frac{{}_2C1 \text{ WhittakerM}\left(\frac{g E}{4 h c B_e}, \frac{1}{4}, \frac{x^2}{g}\right)}{\sqrt{x}} + \frac{{}_2C2 \text{ WhittakerW}\left(\frac{g E}{4 h c B_e}, \frac{1}{4}, \frac{x^2}{g}\right)}{\sqrt{x}} \quad (29.6)$$

Is this expression a true solution? We test it.

```
> test := odetest(sol1, ode1);
```

*test := 0 (29.7)*

A zero result of this test proves the correctness of the solution. We try to convert from Whittaker functions to Hermite functions; the latter are more commonly used in quantum mechanics than the former.

```
> psi := convert(rhs(sol1), HermiteH);
```

$$\psi := \frac{{}_2C1 \text{ WhittakerM}\left(\frac{g E}{4 h c B_e}, \frac{1}{4}, \frac{x^2}{g}\right)}{\sqrt{x}} \quad (29.8)$$

$$+ \frac{-C2 \operatorname{HermiteH}\left(\frac{-h c B_e + g_{\sim} E}{2 h c B_e}, \sqrt{\frac{x^2}{g_{\sim}}}\right) \left(\frac{x^2}{g_{\sim}}\right)^{1/4}}{\sqrt{x} 2^{\frac{-h c B_e + g_{\sim} E}{2 h c B_e}} e^{\frac{x^2}{2 g_{\sim}}}}$$

Only a partial conversion occurred. We inquire about WhittakerM functions.

```
> FunctionAdvisor(WhittakerM);
```

# WhittakerM

## describe

WhittakerM = *Whittaker M function*

## definition

$\operatorname{WhittakerM}(a, b, z)$ $= \frac{1}{e^{\frac{z}{2}}} \left( z^{b + \frac{1}{2}} \operatorname{KummerM}\left(\frac{1}{2} - a + b, 1 + 2b, z\right) \right)$	<i>with no restrictions on (a, b, z)</i>
---	--

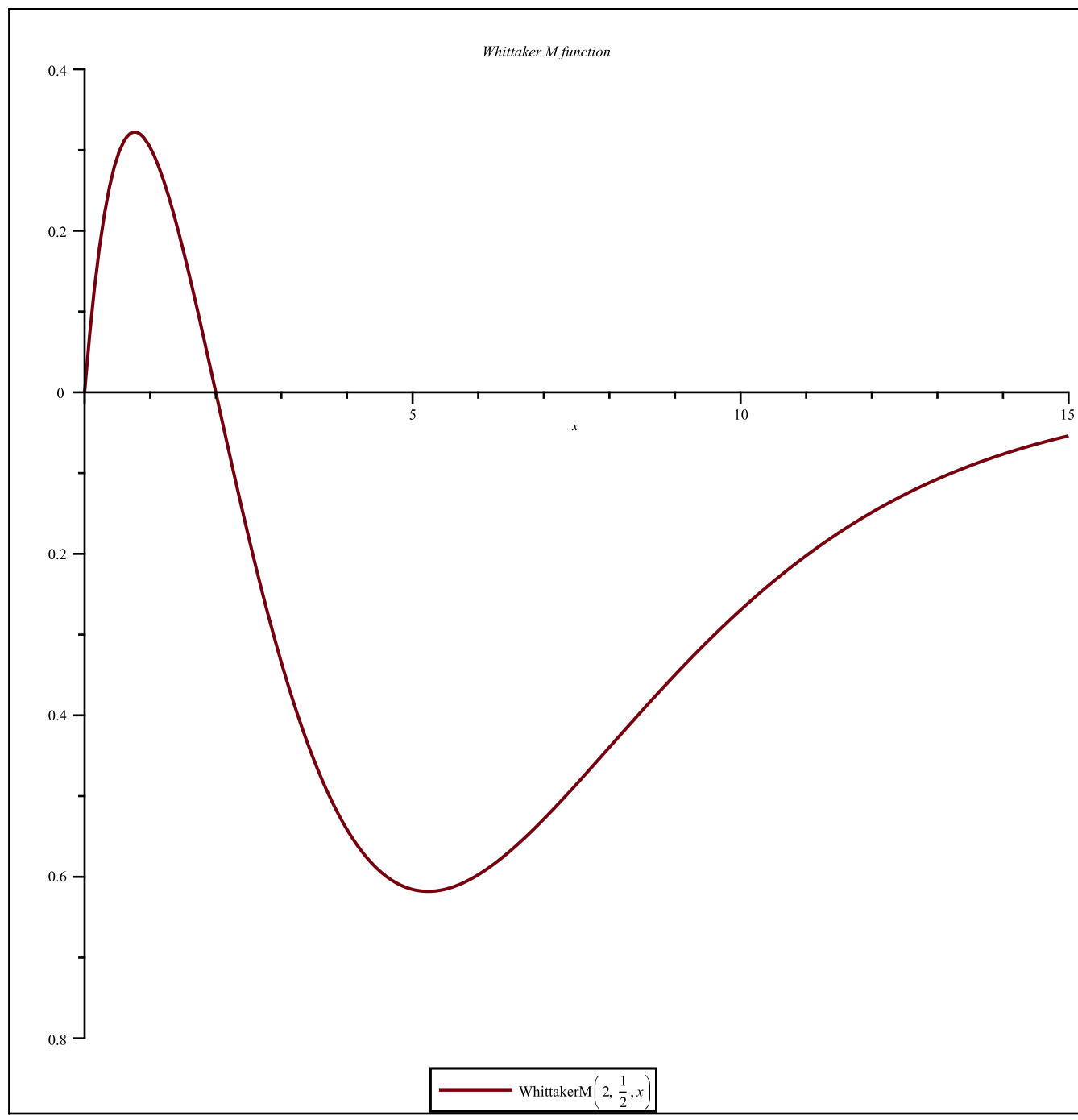
## classify function

<i>Whittaker</i>	<i>IF1</i>
------------------	------------

## periodicity

$\operatorname{WhittakerM}(a, b, z)$	No periodicity
--------------------------------------	----------------

## plot



**special values**

$$\text{WhittakerM}(0, b, z) = \sqrt{z} \text{BesselI}\left(b, \frac{z}{2}\right) \Gamma(b+1) 4^b$$


---

$$\text{WhittakerM}\left(a, a - \frac{3}{2}, z\right) = \frac{z^{a-1} (2a-2-z) e^{-\frac{z}{2}}}{2(a-1)}$$


---

$$\text{WhittakerM}\left(a, a - \frac{1}{2}, z\right) = \frac{z^a}{e^{\frac{z}{2}}}$$


---

$$\text{WhittakerM}\left(a, a + \frac{1}{2}, z\right) = z^{-a} e^{\frac{z}{2}} (-2\Gamma(2a+1, z) a + \Gamma(2a+2) - \Gamma(2a+1, z))$$

## identities

$$\begin{aligned} &\text{WhittakerM}(a, b, z) \\ &= \frac{(-2a+2b+3) \text{WhittakerM}(-2+a, b, z) + (-4+4a-2z) \text{WhittakerM}(-1+a, b, z)}{-1+2a+2b} \end{aligned}$$


---

$$\text{WhittakerM}(a, b, z) = \frac{z^{b+\frac{1}{2}} \text{WhittakerM}(-a, b, -z)}{(-z)^{b+\frac{1}{2}}}$$


---

$$\begin{aligned} &\text{WhittakerM}(a, b, z) \\ &= \frac{(4a-2z+4) \text{WhittakerM}(1+a, b, z) + (-3-2b-2a) \text{WhittakerM}(2+a, b, z)}{1+2a-2b} \end{aligned}$$

## sum form

$\begin{aligned} &\text{WhittakerM}(a, b, z) \\ &= \sum_{k=0}^{\infty} \left( \text{pochhammer}\left(\frac{1}{2} - a + b, \right. \right. \\ &\quad \left. \left. -k\right) z^{b+\frac{1}{2}+k} \right) / \left( e^{\frac{z}{2}} -k! \right. \\ &\quad \left. \text{pochhammer}(2b+1, -k) \right) \end{aligned}$		<p><i>with no restrictions on (a, b, z)</i></p>
--	--	---

## integral form



WhittakerM( $a, b, z$ )

$$= \frac{z^{b + \frac{1}{2}} \Gamma(1 + 2b) \left( \int_0^1 \frac{e^{-zt} (1-t)^{b - \frac{1}{2} + a}}{t^{\frac{1}{2} + a - b}} dt \right)}{\Gamma\left(\frac{1}{2} - a + b\right) \Gamma\left(b + \frac{1}{2} + a\right) e^{\frac{z}{2}}}$$

$$\left( b + \frac{1}{2} + a \right) :: \left( \neg \mathbb{Z}^{(0, -)} \right) \wedge -\frac{1}{2} < \Re(b) - \Re(a) \wedge -\Re(a) - \Re(b) < \frac{1}{2}$$

## differentiation rule

$$\frac{\partial}{\partial z} \text{WhittakerM}(a, b, z) = \left( \frac{1}{2} - \frac{a}{z} \right) \text{WhittakerM}(a, b, z) + \frac{\left( \frac{1}{2} + b + a \right) \text{WhittakerM}(a + 1, b, z)}{z}$$

## DE

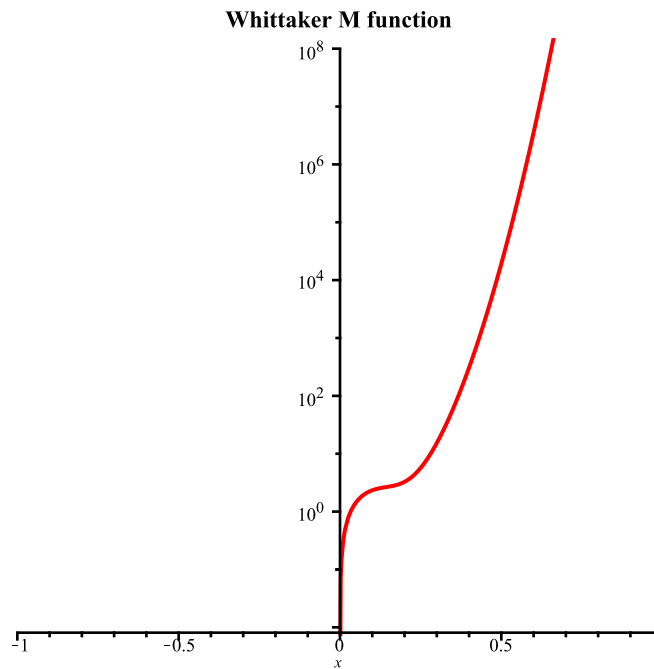
$$f(z) = \text{WhittakerM}(a, b, z) \quad \left| \quad \frac{d^2}{dz^2} f(z) = \frac{(-4az + 4b^2 + z^2 - 1)f(z)}{4z^2} \right.$$

To learn further about WhittakerM functions, we plot them on a logarithmic scale with simple values of constant quantities.

**> op(1,psi);**

$$\frac{{}_C I \text{WhittakerM}\left(\frac{g \sim E}{4 h c B_e}, \frac{1}{4}, \frac{x^2}{g \sim}\right)}{\sqrt{x}} \quad (29.9)$$

**> plots[logplot](eval(op(1,psi)/\_C1,[g=1/100,E=200\*B[e]\*h\*c]), x=-1.  
.1, 0.01..10^8,  
colour=red, titlefont=[TIMES,BOLD,14], title="Whittaker M  
function");**



Because this WhittakerM function in the solution for  $\psi(x)$  clearly diverges as  $x \rightarrow \infty$ , this contribution is unacceptable; we set its coefficient to zero.

```
> psi := subs(_C1=0, psi);
```

$$\psi := \frac{-C2 \operatorname{HermiteH}\left(\frac{-h c B_e + g \sim E}{2 h c B_e}, \sqrt{\frac{x^2}{g \sim}}\right) \left(\frac{x^2}{g \sim}\right)^{1/4}}{\sqrt{x} 2^{\frac{-h c B_e + g \sim E}{2 h c B_e}} e^{\frac{x^2}{2 g \sim}}} \quad (29.10)$$

We inquire about HermiteH functions.

```
> FunctionAdvisor(HermiteH);
```

## HermiteH

### describe

HermiteH = Hermite function

### definition

$$\operatorname{HermiteH}(a, z) = 2^a \sqrt{\pi} \left( \frac{\operatorname{hypergeom}\left(\left[-\frac{a}{2}\right], \left[\frac{1}{2}\right], z^2\right)}{\Gamma\left(\frac{1}{2} - \frac{a}{2}\right)} - \frac{2 z \operatorname{hypergeom}\left(\left[\frac{1}{2} - \frac{a}{2}\right], \left[\frac{3}{2}\right], z^2\right)}{\Gamma\left(-\frac{a}{2}\right)} \right) \quad \left| \quad \begin{aligned} &\left(-\frac{a}{2}\right) :: (\neg \mathbb{Z}^{(0, -)}) \\ &\wedge \left(\frac{1}{2} - \frac{a}{2}\right) :: (\neg \mathbb{Z}^{(0, -)}) \end{aligned} \right.$$

## classify function

*orthogonal\_polynomials*

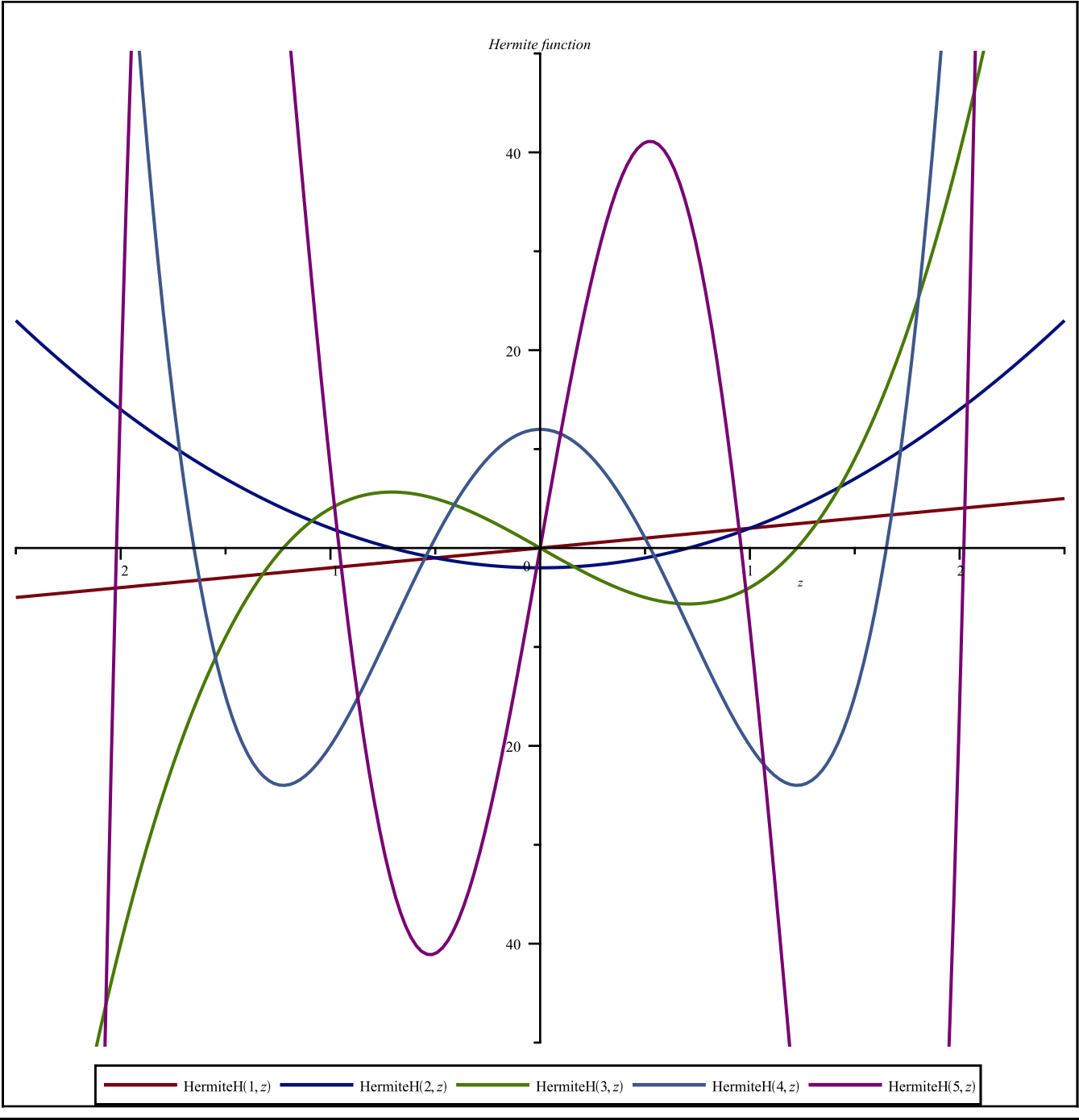
| *1F1*

## periodicity

*HermiteH(a, z)*

| No periodicity

## plot



**singularities**

$HermiteH(a, z)$

$\left| a = \infty + \infty I \vee (a :: (-\mathbb{Z}^{(0,+)}) \wedge z = \infty + \infty I) \right.$

**branch points**

$HermiteH(a, z)$

$\left| \text{No branch points} \right.$

## branch cuts

$$\text{HermiteH}(a, z)$$

| No branch cuts

## special values

$$\text{HermiteH}(0, z) = 1$$

---

$$\text{HermiteH}(1, z) = 2 z$$

---

$$\text{HermiteH}(2, z) = 4 z^2 - 2$$

---

$$\text{HermiteH}(a, 0) = \frac{2^a \sqrt{\pi}}{\Gamma\left(\frac{1}{2} - \frac{a}{2}\right)}$$

## identities

$$\text{HermiteH}(a, z) = 2 z \text{HermiteH}(a - 1, z) + (2 - 2 a) \text{HermiteH}(a - 2, z)$$

---

$$\text{HermiteH}(a, z) = \frac{2 z \text{HermiteH}(a + 1, z) - \text{HermiteH}(a + 2, z)}{2 a + 2}$$

## sum form

$\text{HermiteH}(a, z) = \sum_{k=0}^{\infty} \left( \frac{2^a z^{1+2k} \sqrt{\pi} \text{pochhammer}\left(\frac{1}{2} - \frac{a}{2}, -k\right)}{\text{pochhammer}\left(\frac{3}{2}, -k\right) \Gamma\left(-\frac{a}{2}\right) (-k)!} + \frac{\sqrt{\pi} 2^a \text{pochhammer}\left(-\frac{a}{2}, -k\right) z^{2-k}}{\Gamma\left(\frac{1}{2} - \frac{a}{2}\right) (-k)! \text{pochhammer}\left(\frac{1}{2}, -k\right)} \right)$	$\left(-\frac{a}{2}\right) :: (\neg \mathbb{Z}^{(0,-)}) \wedge \left(\frac{1}{2} - \frac{a}{2}\right) :: (\neg \mathbb{Z}^{(0,-)}) \wedge  z ^2 < 1$
---	--

$\text{HermiteH}(a, z) = \sum_{k=0}^{\infty} \frac{1}{(-k)! \text{pochhammer}\left(\frac{1}{2}, -k\right)} \left( \text{pochhammer}\left(\frac{1}{2} - \frac{a}{2}, -k\right) \frac{a}{2} 2^a \text{pochhammer}\left(-\frac{a}{2}, -k\right) z^{2-k} \right)$	$\left(-\frac{a}{2}\right) :: \mathbb{Z}^{(0,-)} \wedge  z ^2 < 1$
---	--

$\text{HermiteH}(a, z) = \sum_{k=0}^{\infty} \frac{1}{(-k)! \text{pochhammer}\left(\frac{3}{2}, -k\right)} \left( \text{pochhammer}\left(-\frac{a}{2}, \frac{a}{2} - \frac{1}{2}\right) 2^a z \text{pochhammer}\left(\frac{1}{2} - \frac{a}{2}, -k\right) z^{2-k} \right)$	$\left(\frac{1}{2} - \frac{a}{2}\right) :: \mathbb{Z}^{(0,-)} \wedge  z ^2 < 1$
--	---

## series

$$\begin{aligned} \text{series}(\text{HermiteH}(a, z), z, 4) &= \frac{2^a \sqrt{\pi}}{\Gamma\left(\frac{1}{2} - \frac{a}{2}\right)} - 2 \frac{2^a \sqrt{\pi}}{\Gamma\left(-\frac{a}{2}\right)} z - \frac{2^a \sqrt{\pi} a}{\Gamma\left(\frac{1}{2} - \frac{a}{2}\right)} z^2 \\ &\quad - 2 \frac{2^a \sqrt{\pi} \left(\frac{1}{3} - \frac{a}{3}\right)}{\Gamma\left(-\frac{a}{2}\right)} z^3 + O(z^4) \end{aligned}$$

## integral form

$\text{HermiteH}(a, z)$ $= \frac{1}{\sqrt{\pi}} \left( 2 e^{z^2} \left( \int_0^\infty \frac{t^a \cos\left(2 t z - \frac{\pi a}{2}\right)}{e^{-t^2}} dt \right) 2^a \right)$	$-1 < \Re(a)$
---	---------------

$\text{HermiteH}(a, z)$ $= \frac{e^{\frac{3}{2} \pi a} 2^a \left( \int_{-\infty}^\infty \frac{t^a}{e^{(t - iz)^2}} dt \right)}{\sqrt{\pi}}$	$a :: \mathbb{Z}^{(0, +)}$
---	----------------------------

$\text{HermiteH}(a, z)$ $= \frac{e^{z^2} \sqrt{\pi} \left( \int_z^\infty \text{erfc}(-2 - a, t) dt \right)}{2}$	$a :: \mathbb{Z}^{(0, -)}$
---	----------------------------

## differentiation rule

$\frac{\partial}{\partial z} \text{HermiteH}(a, z) = 2 a \text{HermiteH}(a - 1, z)$	
---	--

$\frac{\partial^n}{\partial z^n} \text{HermiteH}(a, z) = \frac{2^n a! \text{HermiteH}(a - n, z)}{(a - n)!}$	
---	--

## DE

$f(z) = \text{HermiteH}(a, z)$	$\frac{d^2}{dz^2} f(z) = 2 \left( \frac{d}{dz} f(z) \right) z - 2 a f(z)$
--------------------------------	---

We try to simplify the form of  $\psi(x)$  by assuming that  $x > 0$ , although such an assumption has no effect on the ultimate validity of the solution.

```
> psi := simplify(psi) assuming x > 0;
```

$$\psi := \frac{{}_C2 \operatorname{HermiteH}\left(\frac{-h c B_e + g_{\sim} E}{2 h c B_e}, \frac{x}{\sqrt{g_{\sim}}}\right) 2^{-\frac{-h c B_e + g_{\sim} E}{2 h c B_e}} e^{-\frac{x^2}{2 g_{\sim}}}}{g_{\sim}^{1/4}} \quad (29.11)$$

We find that the remaining part of  $\psi(x)$  contains an exponential function of  $x^2$ , resembling a gaussian function, with HermiteH functions in  $q$  multiplied by  $\left(\frac{4 \pi^2 k \mu}{h^2}\right)^{\frac{1}{4}}$ . Furthermore, according to the information about special cases of HermiteH functions above for which these functions terminate after terms of finite number, the other argument of HermiteH must be a non-negative integer; we extract this first argument, set it equal to an integer,  $v$ , and solve for  $W$  that yields discrete integers.

```
> coe := op(1, indets(psi, 'specfunc(anything, HermiteH)')[1]);
```

$$coe := \frac{-h c B_e + g_{\sim} E}{2 h c B_e} \quad (29.12)$$

```
> E[v] := solve(coe=v, E);
```

$$E_v := \frac{(2 v + 1) h c B_e}{g_{\sim}} \quad (29.13)$$

We insert this result into our expression for amplitude function  $\psi(x)$ .

```
> psi := simplify(subs(E=E[v], psi));
```

$$\psi := \frac{{}_C2 \operatorname{HermiteH}\left(v, \frac{x}{\sqrt{g_{\sim}}}\right) 2^{-v} e^{-\frac{x^2}{2 g_{\sim}}}}{g_{\sim}^{1/4}} \quad (29.14)$$

We convert this expression for  $\psi$  to a function that we write as  $\psi_n(q)$  but express in *Maple* as a function with arguments integer quantum number  $n$  and displacement variable  $q$ .

```
> psi := unapply(%, (v,x));
```

$$\psi := (v, x) \mapsto \frac{{}_C2 \cdot \operatorname{HermiteH}\left(v, \frac{x}{\sqrt{g_{\sim}}}\right) \cdot 2^{-v} \cdot e^{-\frac{x^2}{2 \cdot g_{\sim}}}}{g_{\sim}^{1/4}} \quad (29.15)$$

We integrate, over all space in one dimension, the first six amplitude functions  $\psi_v(q)$ , which appear purely real with no imaginary part and which are expressed as  $\psi(v, q)$  for which  $v=0..5$ ; we divide by a common factor  ${}_C2^2$  to clarify the remaining expressions.

```
> 'seq'(Int('psi'(v,x)^2/_C2^2, x=-infinity..infinity), v=0..5) =
    seq(simplify(int(psi(v,x)^2/_C2^2, x=-infinity..infinity)), v=0.
    .5);
```

(29.16)



$$\text{seq}\left(\int_{-\infty}^{\infty} \frac{\Psi(v, x)^2}{_C2^2} dx, v=0..5\right) = \left(\sqrt{\pi}, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2}, \frac{3\sqrt{\pi}}{4}, \frac{3\sqrt{\pi}}{2}, \frac{15\sqrt{\pi}}{4}\right) \quad (29.16)$$

By inspection we deduce that these quantities have following form  $\frac{v! \sqrt{\pi}}{2^v}$ .

```
> 'seq'(v!*sqrt(Pi)/2^v, v=0..5) = seq(v!*sqrt(Pi)/2^v, v=0..5);
```

$$\text{seq}\left(\frac{v! \sqrt{\pi}}{2^v}, v=0..5\right) = \left(\sqrt{\pi}, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2}, \frac{3\sqrt{\pi}}{4}, \frac{3\sqrt{\pi}}{2}, \frac{15\sqrt{\pi}}{4}\right) \quad (29.17)$$

For normalisation of these amplitude functions constant  $_C2$  of integration must be set equal to the inverse square root of these quantities.

```
> _C2 := sqrt(2^v/(v!*sqrt(Pi)));
```

$$_C2 := \sqrt{\frac{2^v}{v! \sqrt{\pi}}} \quad (29.18)$$

To incorporate this result we evaluate  $\Psi_v(x)$ .

```
> 'psi[v]'^^(x)^ = eval(psi(v,x));
```

$$\Psi_v(x) = \frac{\sqrt{\frac{2^v}{v! \sqrt{\pi}}} \text{HermiteH}\left(v, \frac{x}{\sqrt{g\sim}}\right) 2^{-v} e^{-\frac{x^2}{2g\sim}}}{g\sim^{1/4}} \quad (29.19)$$

We test the validity of our normalisation over a range greater than that within which we deduced the form of the normalising factor.

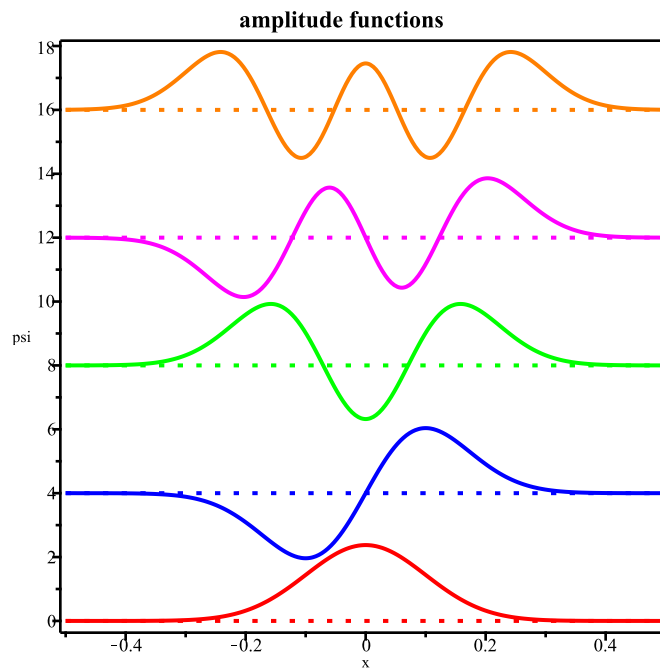
```
> seq(simplify(int(psi(v,x)^2, x=-infinity..infinity)), v=0..10);
```

1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1

(29.20)

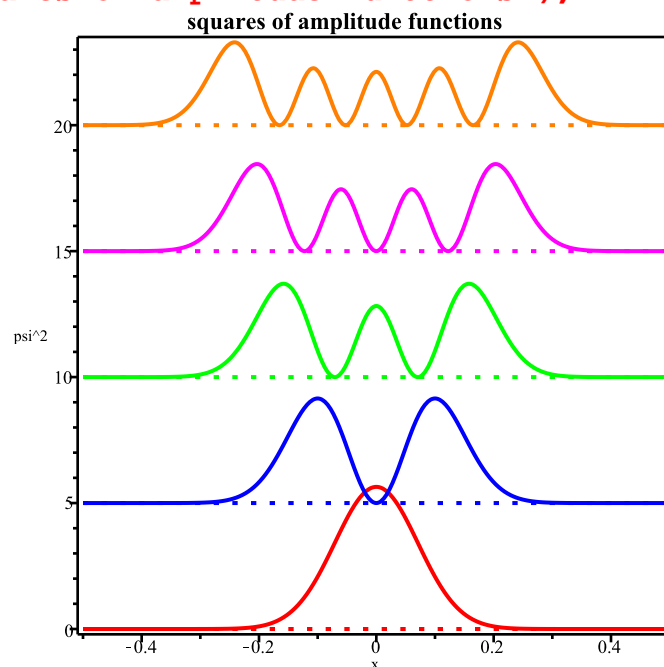
Because these values are all unity we prove that our derivation is correct. We plot  $\Psi_v(x)$  for small values of  $v$ , displacing the functions vertically for clarity.

```
> p1 := plot(4*[0,1,2,3,4], -1/2..1/2, linestyle=[2,2,2,2],
             colour=[red,blue,green,magenta,coral]):
p2 := plot([seq(simplify(eval(psi(v,x)+4*v, [g=1/100])),
               'HermiteH'),
            v=0..4)], x=-1/2..1/2, colour=[red,blue,green,magenta,
            coral]):
display([p1,p2], axes=BOXED, labels=["x","psi"],
        view=[-1/2..1/2,-0.2..18],titlefont=[TIMES,BOLD,14],
        title="amplitude functions");
```



We plot also the squares of these amplitude functions.

```
> p3 := plot(5*[0,1,2,3,4], -1/2..1/2, linestyle=[2,2,2,2,2],
    colour=[red,blue,green,magenta,coral]):
p4 := plot([seq(simplify(eval(psi(v,x)^2+5*v, [g=1/100])),
    'HermiteH'),
    v=0..4)], x=-1/2..1/2, colour=[red,blue,green,magenta,coral]
):
display([p3,p4], axes=BOXED, labels=["x","psi^2"],titlefont=
[TIMES,BOLD,14],
    title="squares of amplitude functions");
```



We test the values of energy according to the fundamental relation

$$\int_{-\infty}^{\infty} \Psi_v(x) H \Psi_v(x) dx = E_v.$$

```
> for v from 0 to 4 do
  Hpsi := - diff(simplify(psi(v,x)), x$2) + v*psi(v,x)/(h*c*B[e]);
  E[v] := h*c*B[e]*int(eval(psi(v,x)*Hpsi, g=1/100),
    x=-infinity..infinity);
end do;
for v from 0 to 4 do
  E[v] := E[v];
end do;
```

$$E_0 := 100 \, h \, c \, B_e$$

$$E_1 := 300 \, h \, c \, B_e$$

$$E_2 := 500 \, h \, c \, B_e$$

$$E_3 := 700 \, h \, c \, B_e$$

$$E_4 := 900 \, h \, c \, B_e \quad (29.21)$$

We equally define the energies directly from the condition as an eigenvalue,  $E_v = \frac{H \Psi_v(x)}{\Psi_v(x)}$

```
> v := 'v':
for v from 0 to 4 do
  Hpsi := - diff(simplify(psi(v,x)), x$2) + v*psi(v,x)/(h*c*B[e]);
  E[v] := simplify(h*c*B[e]*Hpsi/psi(v,x));
end do;
v := 'v':
for v from 0 to 4 do
  E[v] := eval(E[v], g=1/100);
end do;
```

$$E_0 := 100 \, h \, c \, B_e$$

$$E_1 := 300 \, h \, c \, B_e$$

$$E_2 := 500 \, h \, c \, B_e$$

$$E_3 := 700 \, h \, c \, B_e$$

$$E_4 := 900 \, h \, c \, B_e \quad (29.22)$$

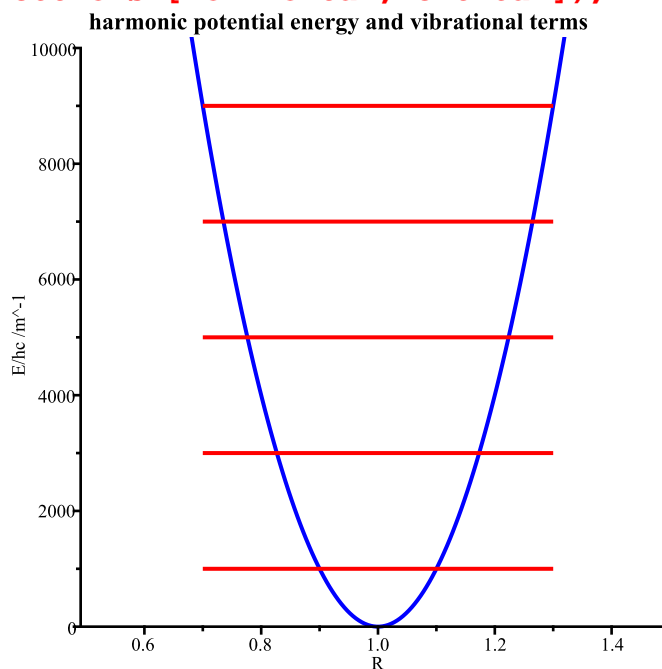
We plot  $V(R)$  and energies  $E_v$  with  $R_e = 1$ ,  $g = \frac{2 \, B_e}{\omega_e} = \frac{1}{100}$  and  $\omega_e = 1000$ .

```
> v := 'v':
```

```

Ev1 := (1+2*v)*h*c*B[e]/g:
VR := eval(eval(V/(h*c), [x=(R-R[e])/R[e], g=1/100]), [R[e]=1,
      B[e]=10]):
p5 := plot(VR, R=1/2..3/2, 0..10000, colour=blue):
p6 := plot([seq(eval(Ev1/(h*c), [B[e]=10, g=1/100]), v=0..4)],
      R=0.7..1.3, colour=red, titlefont=[TIMES,BOLD,14],
      title="harmonic potential energy and vibrational terms"):
plots[display]([p5,p6], labels=["R","E/hc /m^-1"],
      labeldirections=[horizontal,vertical]);

```



We examine the forms of  $\psi_0(x)$ ,

```
> psi[0] = simplify(eval(psi(v,x), v=0), 'HermiteH');
```

$$\psi_0 = \frac{e^{-\frac{x^2}{2g_{\sim}}}}{\pi^{1/4} g_{\sim}^{1/4}} \quad (29.23)$$

$\psi_1(x)$ ,

```
> psi[1] = simplify(eval(psi(v,x), v=1), 'HermiteH');
```

$$\psi_1 = \frac{\sqrt{2} x e^{-\frac{x^2}{2g_{\sim}}}}{\pi^{1/4} g_{\sim}^{3/4}} \quad (29.24)$$

and  $\psi_2(x)$

```
> psi[2] = simplify(eval(psi(v,x), v=2), 'HermiteH');
```

$$\psi_2 = - \frac{\sqrt{2} (-2x^2 + g_{\sim}) e^{-\frac{x^2}{2g_{\sim}}}}{2\pi^{1/4} g_{\sim}^{5/4}} \quad (29.25)$$

Are these amplitude functions orthogonal? We integrate their products over all space in one dimension.

```
> Int('psi(1,x)*psi(0,x)', x=-infinity..infinity)
= int(psi(1,x)*psi(0,x), x=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(1, x) \psi(0, x) dx = 0 \quad (29.26)$$

```
> Int('psi(2,x)*psi(1,x)', x=-infinity..infinity)
= int(psi(2,x)*psi(1,x), x=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(2, x) \psi(1, x) dx = 0 \quad (29.27)$$

```
> Int('psi(2,x)*psi(0,x)', x=-infinity..infinity)
= int(psi(2,x)*psi(0,x), x=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(2, x) \psi(0, x) dx = 0 \quad (29.28)$$

We evaluate a matrix element  $\langle 0 | x | 1 \rangle$ .

```
> Int('psi(1,x)*x*psi(0,x)', x=-infinity..infinity)
= int(eval(psi(v,x),v=1)*x*eval(psi(v,x),v=0), x=-infinity..infinity);
```

$$\int_{-\infty}^{\infty} \psi(1, x) x \psi(0, x) dx = \frac{\sqrt{g_{\sim}} \sqrt{2}}{2} \quad (29.29)$$

```
> `<< 1 | x | 0>` = evalf(eval(rhs(%), g=1/100));
< 1 | x | 0> = 0.07071067811865475 \quad (29.30)
```

The intensity of a spectral transition between pure vibrational states  $v$  and  $v'$  according to an electric dipolar moment is proportional to the square of matrix element  $\langle v' | x | v \rangle$ ; we calculate these matrix elements for transitions from state  $v=0$  to states with  $v'=1 \dots 5$ .

```
> 'seq'(Int(eval('psi'(v,x), v=k)*x*psi(0,x)', x=-infinity..infinity), k=1..5)
= [seq(int(eval(psi(v,x), v=k)*x*eval(psi(v,x),v=0), x=-infinity..infinity), k=1..5)];
```

$$\text{seq}\left(\int_{-\infty}^{\infty} \psi(k, x) x \psi(0, x) dx, k=1 \dots 5\right) = \left[\frac{\sqrt{g_{\sim}} \sqrt{2}}{2}, 0, 0, 0, 0\right] \quad (29.31)$$

We find that a transition with only  $\Delta v = 1$  is possible. We evaluate matrix elements  $\langle v+1 | x | v \rangle$  for  $v$  in  $[0, 5]$ ,

```
> sqrt(g)*[seq(int(eval(psi(v,x), v=k)*x*eval(psi(v,x), v=k+1),
x=-infinity..infinity)/sqrt(g), k=0..5)];
```

$$\sqrt{g} \left[ \frac{\sqrt{2}}{2}, 1, \frac{\sqrt{3}\sqrt{2}}{2}, \sqrt{2}, \frac{\sqrt{2}\sqrt{5}}{2}, \sqrt{3} \right] \quad (29.32)$$

and evaluate them for  $g = \frac{1}{100}$ .

```
> evalf[5](map(eval, %, g=1/100));
```

$$[0.070710, 0.10000, 0.12248, 0.14142, 0.15812, 0.17321] \quad (29.33)$$

By comparison with this sequence,

```
> sqrt(g)*[seq(sqrt((v+1)/2), v=0..5)];
```

$$\sqrt{g} \left[ \frac{\sqrt{2}}{2}, 1, \frac{\sqrt{6}}{2}, \sqrt{2}, \frac{\sqrt{10}}{2}, \sqrt{3} \right] \quad (29.34)$$

we deduce that the matrix elements increase according to  $\sqrt{\frac{v+1}{2}}$ .

We evaluate expectation values  $B_e \langle v | \frac{1}{(1+x)^2} | v \rangle$  that become rotational parameters  $B_v$  for states  $v = 0 \dots 8$ . If an unevaluated integral appear for some value of  $v$ , try another setting of digits in evalf[11], such as 9.

```
> lv := seq(B[e]*evalf[11](Int(eval(psi(v,x), [v=k,g=1/100.])*1/(1+
x)^2*
eval(psi(v,x), [v=k,g=1/100.]), x=-10..10, method=_Gquad)), k=0.
.8);
```

$$lv := 1.0153887504 B_e, 1.0469725780 B_e, 1.0802295218 B_e, 1.1152864696 B_e, \quad (29.35)$$

$$1.1522829718 B_e, 1.1913728232 B_e, 1.2327258844 B_e, 1.2765301854 B_e, 1.3229943647 B_e$$

We fit those values to a polynomial in vibrational quantum number  $v$ ,

```
> pv := CurveFitting[PolynomialInterpolation]([seq(j,j=0..8)], [lv],
v);
```

$$pv := 2.653769841269841 \times 10^{-13} B_e v^8 + 1.021825396825398 \times 10^{-12} B_e v^7 \quad (29.36)$$

$$+ 2.407291666666666 \times 10^{-10} B_e v^6 + 9.149027777777777 \times 10^{-9} B_e v^5$$

$$+ 4.196616145833333 \times 10^{-7} B_e v^4 + 0.00001837904173611111 B_e v^3$$

$$+ 0.0007783385473908730 B_e v^2 + 0.03078668095821429 B_e v + 1.0153887504 B_e$$

```
> B[v] = B[e]*(convert(taylor(pv/B[e], v=-1/2, 6), polynom));
```

$$B_v = B_e \left( 1.015198682961896 + 0.03002191967534784 v + 0.0007513882660529823 \left( v + \frac{1}{2} \right)^2 + 0.00001756199102430555 \left( v + \frac{1}{2} \right)^3 + 3.976884700520834 \times 10^{-7} \left( v \right. \right. \quad (29.37)$$

$$+ \frac{1}{2} \Big)^4 + 8.430347222222221 \times 10^{-9} \left( v + \frac{1}{2} \right)^5 \Big)$$

For  $v = 0 \dots 4$ , these values/ $B_e$  hence increase with increasing vibrational quantum number, in contrast with corresponding values for diatomic molecules that decrease with increasing vibrational quantum number.

We have thus solved the vibrational and rotational energies of this hypothetical system, and also the matrix elements that govern the intensities of vibrational transitions according to  $\Delta v = 1$ .

### 1.32 linear harmonic oscillator according to wave mechanics with Davidson's function and spectral parameters

**> restart:**

**> Digits := 16:**

**with(DEtools): with(plots):**

**with(PDEtools, declare):**

**declare(psi(y), prime=y);**

*$\psi(y)$  will now be displayed as  $\psi$*

*derivatives with respect to y of functions of one variable will now be displayed with ' (30.1)*

We make an analogous calculation on a linear harmonic oscillator according to a distinct function for potential energy. Davidson's function for potential energy (Proc. Roy. Soc. London A135, 459-472, 1932),

$$V(R) = \frac{\kappa}{4} \left( \frac{R}{R_e} - \frac{R_e}{R} \right)^2$$

in which  $\kappa$  has the sense of a force coefficient, we rewrite in convenient spectrometric notation,

$$V(R) = \frac{h c \omega_e^2 \left( \frac{R}{R_e} - \frac{R_e}{R} \right)^2}{16 B_e} = \frac{h c B_e \left( \frac{R}{R_e} - \frac{R_e}{R} \right)^2}{4 g^2}$$

in which appear dimensionless ratio

$$g = \frac{2 B_e}{\omega_e}$$

as the limiting ratio of separations between adjacent rotational lines and between adjacent vibrational states,

$$B_e = \frac{h}{8 \pi^2 c \mu R_e^2} \quad \text{and} \quad \omega_e = \frac{\sqrt{\frac{k_e}{\mu}}}{2 \pi c},$$

both latter quantities of which have unit wavenumber. Schroedinger's equation independent of time for stationary states of an oscillator subject to potential energy becomes

$$-\frac{h \left( \frac{d^2}{dR^2} \psi(R) \right)}{8 \pi^2 \mu} + V(R) \psi(R) = E \psi(R)$$

When we convert the distance variable from  $R$  to dimensionless variable  $y$  such that  $y = \frac{R}{R_e}$  and multiply the first term by  $h c$  in both numerator and denominator, we obtain with the hamiltonian operator on the left side of the equality, so having the form of an eigenvalue equation,

$$H(y) \psi(y) = -\frac{h^2 c \left( \frac{d^2}{dy^2} \psi(y) \right)}{8 \pi^2 h c \mu R_e^2} + \frac{h c B_e \left( y - \frac{1}{y} \right)^2 \psi(y)}{4 g^2} = E \psi(y)$$

or

$$H(y) \psi(y) = -h c B_e \left( \frac{d^2}{dy^2} \psi(y) \right) + \frac{h c B_e \left( y - \frac{1}{y} \right)^2 \psi(y)}{4 g^2} = E \psi(y)$$

and eventually Schroedinger's equation in a simple but exact form.

$$\frac{d^2}{dy^2} \psi(y) + \left( \frac{E}{h c B_e} - \frac{\left( y - \frac{1}{y} \right)^2}{4 g^2} \right) \psi(y) = 0$$

For this function of potential energy,

**> V := (y - 1/y)^2/(4\*g^2);**

$$V := \frac{\left( y - \frac{1}{y} \right)^2}{4 g^2} \quad (30.2)$$

the second derivative depends on  $y$  or  $R$ , like the Morse function but in contrast to  $V(x)$  for the canonical linear harmonic oscillator of which the second derivative is independent of  $x$ .

**> Diff('V', y\$2) = expand(h\*c\*B[e]\*simplify(diff(V, y\$2)));**

$$\frac{\partial^2}{\partial y^2} V = \frac{h c B_e}{2 g^2} + \frac{3 h c B_e}{2 y^4 g^2} \quad (30.3)$$

We enter Schroedinger's equations for subsequent calculations.

**> Seq := diff(psi(y), y\$2) + (E/(h\*c\*B[e]) - V)\*psi(y) = 0;**

$$Seq := \psi'' + \left( \frac{E}{h c B_e} - \frac{\left( y - \frac{1}{y} \right)^2}{4 g^2} \right) \psi = 0 \quad (30.4)$$

What is the kind of this differential equation?

**> odeadvisor(Seq);**

**[[\_2nd\_order, \_with\_linear\_symmetries]]** (30.5)

We solve this differential equation,

**> sol := dsolve(Seq, psi(y));**



$$\begin{aligned}
sol := \psi = & \frac{-CI \operatorname{WhittakerM}\left(\frac{2 E g^2 + h c B_e}{4 h c B_e g}, \frac{\sqrt{g^2 + 1}}{4 g}, \frac{y^2}{2 g}\right)}{\sqrt{y}} \\
& + \frac{-C2 \operatorname{WhittakerW}\left(\frac{2 E g^2 + h c B_e}{4 h c B_e g}, \frac{\sqrt{g^2 + 1}}{4 g}, \frac{y^2}{2 g}\right)}{\sqrt{y}}
\end{aligned} \tag{30.6}$$

and obtain two solutions as a linear combination.

$$\begin{aligned}
& > \text{odetest}(sol, Seq); \\
& 0
\end{aligned} \tag{30.7}$$

According to that assurance, we convert these Whittaker functions into hypergeometric functions. With *Maple* 10, these Whittaker functions contain a product  $\sqrt{g+I} \sqrt{g-I}$  that causes problems in subsequent calculations. We might alternatively convert both Whittaker functions into Laguerre functions, with `sol := convert(sol, LaguerreL)`; in that case the development below is the same except that the first operand of the latter functions must be set equal to a positive integer **v** instead of a negative integer **-v**, and extraction of the content of a list to form **op1** is redundant. Calculations with the solution in terms of hypergeometric functions are quicker than with the solution in terms of LaguerreL functions.

$$\begin{aligned}
& > sol := \text{convert}(sol, \text{hypergeom}); \\
sol := \psi
\end{aligned} \tag{30.8}$$

$$\begin{aligned}
& = \frac{1}{\sqrt{y} e^{\frac{y^2}{4g}}} \left( -CI \left( \frac{y^2}{2g} \right)^{\frac{2g + \sqrt{g^2 + 1}}{4g}} \operatorname{hypergeom} \left( \left[ \frac{1}{4 h c B_e g} \left( \sqrt{g^2 + 1} h c B_e \right. \right. \right. \right. \\
& \quad \left. \left. \left. + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2 \right) \right], \left[ \frac{2 g + \sqrt{g^2 + 1}}{2 g} \right], \frac{y^2}{2 g} \right) \right) \\
& + \frac{1}{\sqrt{y} e^{\frac{y^2}{4g}}} \left( -C2 \left( \Gamma \left( \right. \right. \right.
\end{aligned}$$

$$-\frac{\sqrt{g^2+1}}{2g} \Big) \text{hypergeom} \left( \left[ \frac{\sqrt{g^2+1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \right], \right.$$

$$\left. \left[ \frac{2g + \sqrt{g^2+1}}{2g} \right], \frac{y^2}{2g} \right) \left( \frac{y^2}{2g} \right)^{-\frac{-2g + \sqrt{g^2+1}}{4g} + \frac{\sqrt{g^2+1}}{2g}} \Bigg) /$$

$$\left( \Gamma \left( \frac{-\sqrt{g^2+1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \right) \right)$$

$$\left( \Gamma \left( \frac{\sqrt{g^2+1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} + \frac{-2g + \sqrt{g^2+1}}{4g} \right) \left( \frac{y^2}{2g} \right)^{\frac{-2g + \sqrt{g^2+1}}{4g}} \right) \right)$$

We test whether this converted form is still a solution to the original differential equation.

```
> odetest(sol, Seq);
```

0

(30.9)

These solutions evidently involve confluent hypergeometric functions *hypergeom* with three arguments, of which the first two arguments take typically integer values for physical applications; the third argument embodies the distance variable.

```
> psi[a] := eval(rhs(sol), _C2=0);
```

$\Psi_a :=$

(30.10)

$$\frac{1}{\sqrt{y} e^{\frac{y^2}{4g}}} \left( -C1 \left( \frac{y^2}{2g} \right)^{\frac{2g + \sqrt{g^2 + 1}}{4g}} \text{hypergeom} \left( \left[ \frac{1}{4 h c B_e g} \left( \sqrt{g^2 + 1} h c B_e \right. \right. \right. \right. \right. \\ \left. \left. \left. \left. + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2 \right) \right], \left[ \frac{2g + \sqrt{g^2 + 1}}{2g} \right], \frac{y^2}{2g} \right) \right)$$

**> psi[b] := eval(rhs(sol), \_C1=0);**

$$\psi_b := \frac{1}{\sqrt{y} e^{\frac{y^2}{4g}}} \left( -C2 \left( \Gamma \left( \right. \right. \right. \right. \tag{30.11}$$

$$- \frac{\sqrt{g^2 + 1}}{2g} \Big) \text{hypergeom} \left( \left[ \frac{\sqrt{g^2 + 1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \right], \right.$$

$$\left. \left[ \frac{2g + \sqrt{g^2 + 1}}{2g} \right], \frac{y^2}{2g} \right) \left( \frac{y^2}{2g} \right)^{-\frac{-2g + \sqrt{g^2 + 1}}{4g} + \frac{\sqrt{g^2 + 1}}{2g}} \Big) /$$

$$\left( \Gamma \left( \frac{-\sqrt{g^2 + 1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \right) \right)$$

$$\left( \Gamma \left( \frac{\sqrt{g^2 + 1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \right) \left( \frac{y^2}{2 g} \right)^{\frac{-2 g + \sqrt{g^2 + 1}}{4 g}} \right) \right)$$

Because the series represented by the hypergeometric functions must terminate, the contribution with two hypergeometric functions has disparate first arguments; for this reason, no choice of  $W$  can make them both terminate, and we therefore discard that contribution and work with the contribution that has only one hypergeometric function.

```
> _C2 := 0;
   _C1 := C;
   psi := psi[a];
```

```
_C2 := 0
```

```
_C1 := C
```

$\psi :=$  (30.12)

$$\frac{1}{\sqrt{y} e^{\frac{y^2}{4g}}} \left( C \left( \frac{y^2}{2g} \right)^{\frac{2g + \sqrt{g^2 + 1}}{4g}} \text{hypergeom} \left( \left[ \frac{1}{4 h c B_e g} \left( \sqrt{g^2 + 1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2 \right) \right], \left[ \frac{2g + \sqrt{g^2 + 1}}{2g} \right], \frac{y^2}{2g} \right) \right)$$

To proceed with applying a condition of discrete energies we separate the first solution into its parts.

```
> op(psi);
```

$$C, \frac{1}{\sqrt{y}}, \frac{1}{e^{\frac{y^2}{4g}}}, \left( \frac{y^2}{2g} \right)^{\frac{2g + \sqrt{g^2 + 1}}{4g}},$$
 (30.13)

$$\text{hypergeom} \left( \left[ \frac{\sqrt{g^2 + 1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \right], \left[ \frac{2g + \sqrt{g^2 + 1}}{2g} \right], \frac{y^2}{2g} \right)$$

Although the order of operands shown is unpredictable, one might isolate the first argument of the hypergeometric operator in  $\psi_a$ , by either applying **op** with appropriate numbers that would depend on the order of operands above, or specifying operands within a particular special function with **indets**, which we perform below. Because confluent hypergeometric polynomials are well behaved -- such that

these functions do not diverge as  $e^{\frac{y^2}{2g}}$  for large values of  $y$  -- only for values of their first argument being equal to zero or a negative integer, we extract that first argument, set it equal to an integer  $-v$ , and solve for discrete energies characterised by that quantum number.

```
> opl := op(op(1, indets(psi, 'specfunc(anything, hypergeom)')[1]))
;
```

$$opl := \frac{\sqrt{g^2 + 1} h c B_e + 2 c h \left( g - \frac{1}{2} \right) B_e - 2 E g^2}{4 h c B_e g} \quad (30.14)$$

```
> E[v] := collect(expand(solve(opl = -v, E)), [g,h,c,B[e]]);
# For Laguerre functions, opl = v, not -v.
```

$$E_v := \frac{(2v + 1) B_e c h}{g} + \frac{\left( \frac{\sqrt{g^2 + 1}}{2} - \frac{1}{2} \right) B_e c h}{g^2} \quad (30.15)$$

We simplify the second term by forming a Taylor series and truncating at the second power of  $g$ .

```
> E[v] := subs(sqrt(g^2+1) = taylor(sqrt(g^2+1), g, 3), E[v]);
```

$$E_v := \frac{(2v + 1) B_e c h}{g} + \frac{\left( \frac{\left( 1 + \frac{1}{2} g^2 + O(g^4) \right)}{2} - \frac{1}{2} \right) B_e c h}{g^2} \quad (30.16)$$

```
> E[v] := convert(E[v], polynom);
```

$$E_v := \frac{(2v + 1) B_e c h}{g} + \frac{h c B_e}{4} \quad (30.17)$$

The first neglected term through truncation of the Taylor series at  $g^3$  is  $-\frac{g^2}{16}$ , which is much smaller

than unity. We replace  $g$  with  $\frac{2 B_e}{\omega}$ ,

```
> E[v] := subs(g=2*B[e]/omega[e], E[v]);
```

$$E_v := \frac{(2v + 1) c h \omega_e}{2} + \frac{h c B_e}{4} \quad (30.18)$$

```
> psi := simplify(subs(E=E[v], omega[e]=2*B[e]/g, psi));
```

```
ψ :=
```

$$\frac{1}{\sqrt{y}} \left( C 2^{-\frac{2g + \sqrt{g^2 + 1}}{4g}} \left( \frac{y^2}{g} \right)^{\frac{2g + \sqrt{g^2 + 1}}{4g}} \text{hypergeom} \left( \left[ \frac{1}{8g} (-g^2 - 8vg) \right] \right) \right)$$

$$+ 2 \sqrt{g^2 + 1} - 2) \Big], \left[ \frac{2g + \sqrt{g^2 + 1}}{2g}, \frac{y^2}{2g} \right) e^{-\frac{y^2}{4g}} \Big)$$

**> psi := subs((-g^2-8\*v\*g+2\*(g^2+1)^(1/2)-2)/(8\*g) = -v, psi);**

**ψ :=**

**(30.20)**

$$\frac{1}{\sqrt{y}} \left( C 2^{-\frac{2g + \sqrt{g^2 + 1}}{4g}} \left( \frac{y^2}{g} \right)^{\frac{2g + \sqrt{g^2 + 1}}{4g}} \text{hypergeom} \left( [-v], \left[ \frac{2g + \sqrt{g^2 + 1}}{2g} \right], \frac{y^2}{2g} \right) e^{-\frac{y^2}{4g}} \right)$$

The total residual energy, for  $v=0$ , hence becomes  $\sim h c \left( \frac{\omega_e}{2} + \frac{B_e}{4} \right)$ . The total energy relative to zero at the minimum of potential energy  $V(R)$  is thus approximately

$$\frac{E_v}{h c} = \left( v + \frac{1}{2} \right) \omega_e + \frac{B_e}{4}$$

We incorporate the value of  $E_v$  in the argument of the confluent hypergeometric function and its corresponding normalising factor, which for a confluent hypergeometric function expressed as  $\text{hypergeom}(-v, k, y)$  is approximately

$$2 \sqrt{\frac{g \Gamma \left( \frac{2g + \sqrt{g^2 + 1} + 2vg}{2g} \right)}{\Gamma \left( \frac{2g}{2g + \sqrt{g^2 + 1}} \right) \Gamma \left( \frac{\sqrt{g^2 + 1}}{2g} \right) \Gamma(v+1) \Gamma \left( \frac{1}{2g} \right)}}$$

as  $k = 1 + \frac{\sqrt{g^2 + 1}}{2g}$  is generally not quite an integer, we employ a  $\Gamma$  function instead of a factorial,

and we include a factor  $(-1)^v$  to impose a particular convention on phase.

**> CC := simplify(sqrt(g\*GAMMA(1+1/2/g\*(g^2+1)^(1/2)+v)/(GAMMA(1/(1/2\*(2\*g+(g^2+1)^(1/2))/g))**  
**\*GAMMA(1/2\*(2\*g+(g^2+1)^(1/2))/g-1)\*GAMMA(1/(2\*g))\*v!/4)**  
**), symbolic);**

$$CC := \frac{2 \sqrt{g} \sqrt{\Gamma \left( \frac{(2v+2)g + \sqrt{g^2 + 1}}{2g} \right)}}{\sqrt{\Gamma \left( \frac{2g}{2g + \sqrt{g^2 + 1}} \right)} \sqrt{\Gamma \left( \frac{\sqrt{g^2 + 1}}{2g} \right)} \sqrt{\Gamma \left( \frac{1}{2g} \right)} \sqrt{\Gamma(1+v)}}$$

**(30.21)**

```
> psi := simplify((-1)^v*CC*psi, radical);
```

```
ψ :=
```

(30.22)

$$\left( 2 (-1)^v \sqrt{g} \sqrt{\Gamma\left(\frac{(2v+2)g + \sqrt{g^2+1}}{2g}\right)} C 2^{-\frac{2g + \sqrt{g^2+1}}{4g}} \left(\frac{y^2}{g}\right)^{\frac{2g + \sqrt{g^2+1}}{4g}} \right. \\ \left. \text{hypergeom}\left([-v], \left[\frac{2g + \sqrt{g^2+1}}{2g}\right], \frac{y^2}{2g}\right) e^{-\frac{y^2}{4g}} \right) / \\ \left( \sqrt{\Gamma\left(\frac{2g}{2g + \sqrt{g^2+1}}\right)} \sqrt{\Gamma\left(\frac{\sqrt{g^2+1}}{2g}\right)} \sqrt{\Gamma\left(\frac{1}{2g}\right)} \sqrt{\Gamma(1+v)} \sqrt{y} \right)$$

We notice that this amplitude function appears entirely real, i.e., containing no imaginary parts; hence  $\bar{\psi} = \psi$ , which condition we assume in further integrations. Because symbolic normalisation of this function is impracticable with *Maple*, we undertake numerical integration with  $g = \frac{1}{100}$  for several values of quantum number  $v$  to evaluate the integration constant by imposing normalisation such that  $\int_{-\infty}^{\infty} \psi_a(v)^2 dy = 1$  for each value of quantum number  $v$ .

```
> for j from 0 to 4 do
```

```
    C1 := sqrt(1/evalf(Int(eval(psi/C, [g=1/100., v=j])^2, y=0.20.
    .10, method=_Gquad)));
```

```
end do;
```

```
CI := 0.9994964551585279
```

```
CI := 0.9994964551585279
```

```
CI := 0.9994964551585274
```

```
CI := 0.9994964551585279
```

```
CI := 0.9994964551585274
```

(30.23)

An additional and numerical normalising factor hence is independent of  $v$  but slightly dependent on the value of  $g$ . As samples of these normalised amplitude functions for a few vibrational states we calculate accurately these formulae.

```
> 'psi[0]' = evalf(eval(psi, [g=1/100, v=0, C=C1]));
```

$$\psi_0 = \frac{1.708863006551672 \times 10^{11} (y^2)^{25.50124996875155} e^{-25.y^2}}{\sqrt{y}}$$

(30.24)

```
> 'psi[1]' = evalf(eval(psi, [g=1/100, v=1, C=C1]));
```

$$\psi_1 = -\frac{1}{\sqrt{y}} \left( 1.220402195518491 \times 10^{12} (y^2)^{25.50124996875155} \text{hypergeom}([-1.], \right.$$

(30.25)

$$[51.00249993750310], 50. y^2) e^{-25. y^2})$$

```
> 'psi[2]' = expand(evalf(eval(psi, [g=1/100, v=2, C=C1])));
```

$$\psi_2 = \frac{1}{\sqrt{y}} \left( 6.223004191694146 \times 10^{12} (y^2)^{25.50124996875155} \text{hypergeom}([-2.], \right. \quad (30.26)$$

$$[51.00249993750310], 50. y^2) e^{-25. y^2})$$

```
> 'psi[3]' = expand(evalf(eval(psi, [g=1/100, v=3, C=C1])));
```

$$\psi_3 = -\frac{1}{\sqrt{y}} \left( 2.615698258613656 \times 10^{13} (y^2)^{25.50124996875155} \text{hypergeom}([-3.], \right. \quad (30.27)$$

$$[51.00249993750310], 50. y^2) e^{-25. y^2})$$

```
> 'psi[4]' = expand(evalf(eval(psi, [g=1/100, v=4, C=C1])));
```

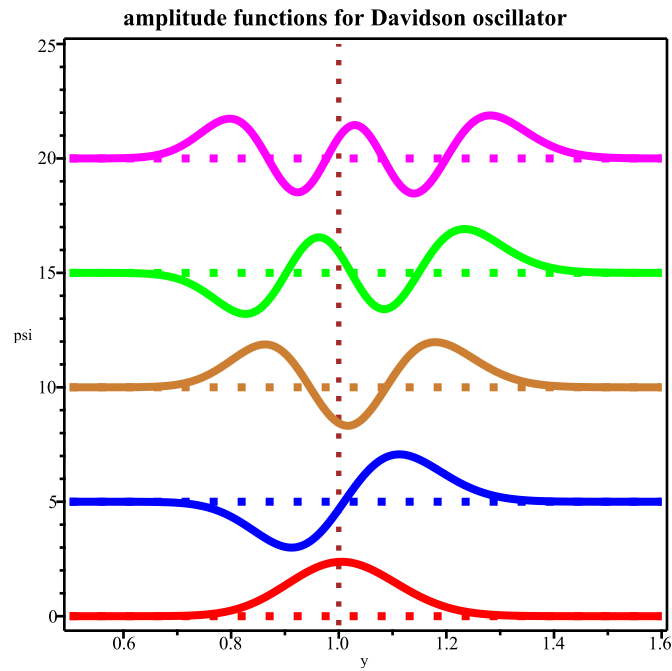
$$\psi_4 = \frac{1}{\sqrt{y}} \left( 9.610911543553486 \times 10^{13} (y^2)^{25.50124996875155} \text{hypergeom}([-4.], \right. \quad (30.28)$$

$$[51.00249993750310], 50. y^2) e^{-25. y^2})$$

Including a vertical brown dotted line placed at the equilibrium distance, we plot these first five amplitude functions, offset vertically for clarity; expand laterally this figure to improve the view.

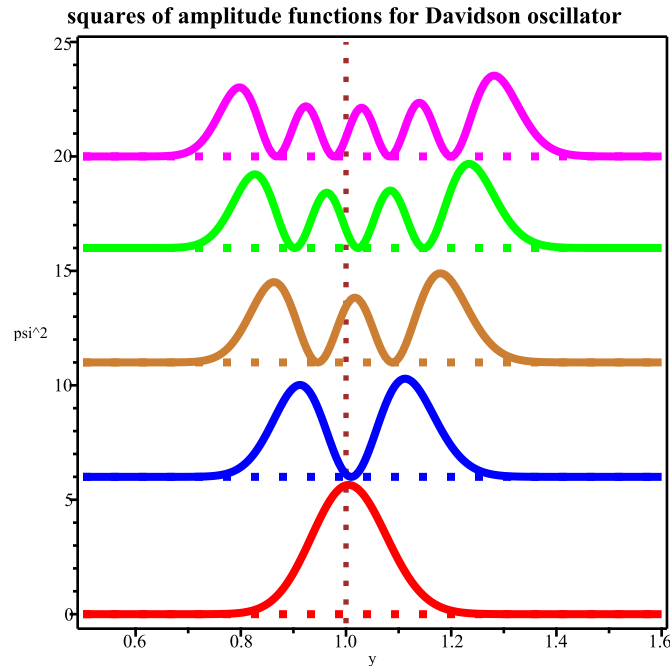
```
> lin := plottools[line]([1,-0.4], [1,25], colour=brown, linestyle=
2, thickness=2):
plo := plot([eval(psi, [g=1/100, v=0, C=C1]), 0,
eval(psi, [g=1/100, v=1, C=C1])+5, 5,
eval(psi, [g=1/100, v=2, C=C1])+10, 10,
eval(psi, [g=1/100, v=3, C=C1])+15, 15,
eval(psi, [g=1/100, v=4, C=C1])+20, 20],
y=0.5..1.6, -0.2..18.3, linestyle=[1,2,1,2,1,2,1,2],
thickness=[2,0,2,0,2,0,2,0,2,0], axes=boxed,
colour=[red,red,blue,blue,gold,gold,green,green,
magenta, magenta], thickness=[3$5], labels=["y", "psi"]):
plots[display](lin, plo, titlefont=[TIMES,BOLD,14],
title="amplitude functions for Davidson oscillator");
```





Including again a vertical brown dotted line placed at the equilibrium distance, we plot the squares of these first five amplitude functions, offset vertically for clarity; expand laterally this figure to improve the view.

```
> pls := plot([eval(psi^2, [g=1/100, v=0, C=C1]), 0,
    eval(psi^2, [g=1/100, v=1, C=C1])+6, 6,
    eval(psi^2, [g=1/100, v=2, C=C1])+11, 11,
    eval(psi^2, [g=1/100, v=3, C=C1])+16, 16,
    eval(psi^2, [g=1/100, v=4, C=C1])+20, 20],
    y=0.5..1.6, -0.2..24, linestyle=[1,2,1,2,1,2,1,2],
    thickness=[2,0,2,0,2,0,2,0,2,0], axes=boxed, thickness=
[3$5],
    colour=[red,red,blue,blue,gold,gold,green,green,
    magenta,magenta], labels=["y", "psi^2"]):
plots[display](lin, pls, titlefont=[TIMES,BOLD,14],
    title="squares of amplitude functions for Davidson
oscillator");
```



These curves in both preceding sets are evidently not symmetric about that vertical line at  $y = 1$ , but are shifted progressively to larger  $y$  with increasing values of  $v$ .

We test the normalisation and orthogonality.

```
> `<0|0>` := evalf(Int(eval(psi, [g=1/100, v=0, C=C1])*
    eval(psi, [g=1/100, v=0, C=C1]), y=0.0..infinity));
`<1|1>` := evalf(Int(eval(psi, [g=1/100, v=1, C=C1])*
    eval(psi, [g=1/100, v=1, C=C1]), y=0.0..infinity));
`<1|0>` := evalf(Int(eval(psi, [g=1/100, v=1, C=C1])*
    eval(psi, [g=1/100, v=0, C=C1]), y=0.0..infinity));
`<2|0>` := evalf(Int(eval(psi, [g=1/100, v=2, C=C1])*
    eval(psi, [g=1/100, v=0, C=C1]), y=0.0..infinity));
`<3|0>` := evalf(Int(eval(psi, [g=1/100, v=3, C=C1])*
    eval(psi, [g=1/100, v=0, C=C1]), y=0.0..infinity));
`<4|0>` := evalf(Int(eval(psi, [g=1/100, v=4, C=C1])*
    eval(psi, [g=1/100, v=0, C=C1]), y=0.0..infinity));
```

$$\langle 0|0 \rangle := 1.0000000000000099$$

$$\langle 1|1 \rangle := 1.0000000000000099$$

$$\langle 1|0 \rangle := -1.634614314138634 \times 10^{-19}$$

$$\langle 2|0 \rangle := -5.876669487925431 \times 10^{-19}$$

$$\langle 3|0 \rangle := -1.120504782962775 \times 10^{-17}$$

$$\langle 4|0 \rangle := -5.839 \times 10^{-17}$$

(30.29)

Within a possible small numerical error, these values are clearly unity and zero, respectively. As the amplitude functions are fully normalised, we test the values of energy according to the relation

$$\int_0^{\infty} \psi_v(y) H(y) \psi_v(y) dy = E_v.$$

```
> for j from 0 to 4 do
  Hpsi := eval(- diff(simplify(eval(psi, v=j)), y$2)
    + V*psi, [g=1/100, v=j, C=C1]);
  Ev[j] := h*c*B[e]*int(eval(psi, [g=1/100., v=j,
    C=C1])*Hpsi, y=0.0..infinity);
end do;
for v from 0 to 4 do
  E[v] := Ev[v];
end do;
v := 'v':
```

$$E_0 := 100.2499937503167 \, h \, c \, B_e$$

$$E_1 := 300.2499937503264 \, h \, c \, B_e$$

$$E_2 := 500.2499937503367 \, h \, c \, B_e$$

$$E_3 := 700.2499937503461 \, h \, c \, B_e$$

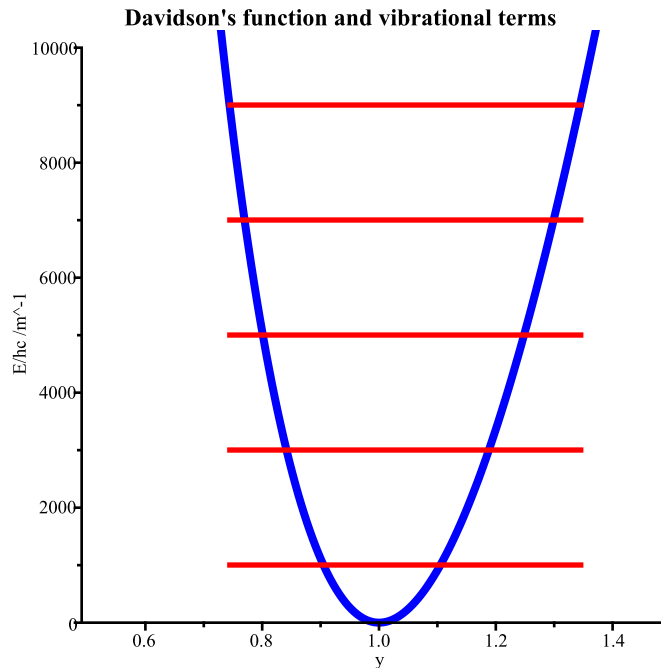
$$E_4 := 900.2499937503581 \, h \, c \, B_e$$

**(30.30)**

These values confirm numerically that the energies of adjacent quantum states clearly differ by a constant interval,  $200 B_e$  for the given conditions, from an initial state of least energy with term value  $100.25 B_e$ . The difference from integer values of energies arises from constant term  $\frac{h \, c \, B_e}{4}$  derived above in the residual energy. With a numerical value  $B_e = 10 \, \text{cm}^{-1}$  we plot here the curve for the function for potential energy and the values of the vibrational terms, which are the vibrational energies divided by  $hc$ .

```
> p5 := plot(eval(V*B[e], [g=1/100, B[e]=10]), y=0.5..1.5, 0..10000,
  colour=blue, thickness=3);
p6 := plot([seq(eval(E[v]/(h*c), B[e]=10), v=0..4)], y=0.74..1.35,

  colour=red, titlefont=[TIMES,BOLD,14], thickness=2,
  title="Davidson's function and vibrational terms"):
plots[display]([p5,p6], labels=["y", "E/hc /m^-1"],
  labeldirections=[horizontal,vertical]);
```



The intensity of a spectral transition between pure vibrational states  $v$  and  $v'$  according to an electric dipolar moment is proportional to the square of matrix element

$$\langle v'|y|v\rangle = \int_0^\infty \psi_{v'}(y) y \psi_v(y) dy ;$$

we calculate these matrix elements for transitions from state  $v=0$  to states with  $1 < v' < 4$  for  $g = \frac{1}{100}$ .

In some releases of *Maple*, these integrals might prove refractory.

```
> `<1|y|0>` := evalf[10](Int((eval(psi, [g=1/100, v=1, C=C1]))*y
                               *(eval(psi, [g=1/100, v=0, C=C1])), y=0.1..infinity,
                               method=_Gquad));
<1|y|0> := 0.07053759107 (30.31)
```

```
> `<2|y|0>` := evalf[10](Int((eval(psi, [g=1/100, v=2, C=C1]))*y
                               *(eval(psi, [g=1/100, v=0, C=C1])), y=0.1..infinity,
                               method=_Gquad));
<2|y|0> := -0.003458306806 (30.32)
```

```
> `<3|y|0>` := evalf[10](Int((eval(psi, [g=1/100, v=3, C=C1]))*y
                               *(eval(psi, [g=1/100, v=0, C=C1])), y=0.1..infinity,
                               method=_Gquad));
<3|y|0> := 0.0004113826519 (30.33)
```

```
> `<4|y|0>` := evalf[10](Int((eval(psi, [g=1/100, v=4, C=C1]))*y
                               *(eval(psi, [g=1/100, v=0, C=C1])), y=0.1..infinity,
                               method=_Gquad));
<4|y|0> := -0.00006997599195 (30.34)
```

These magnitudes decrease monotonically with increasing difference  $\Delta v$ . For comparison, the

corresponding values for  $^1\text{H}^{35}\text{Cl}$  are

$$\langle I|y|0\rangle = 0.066, \quad \langle 2|y|0\rangle = -0.0070, \quad \langle 3|y|0\rangle = 0.00047, \quad \langle 4|y|0\rangle = -0.000028.$$

We form a sum of the squares of these quantities weighted by the relative wavenumbers of the corresponding transitions.

```
> ` $\langle 1|y|0\rangle$ `^2 + 2*` $\langle 2|y|0\rangle$ `^2 + 3*` $\langle 3|y|0\rangle$ `^2 + 4*` $\langle 4|y|0\rangle$ `^2;
0.004999998819504046
```

(30.35)

For comparison, we form the same quantity for the canonical quadratic harmonic oscillator as calculated in section 1.31,

```
> `(sqrt(2.)/20)^2;
0.00500000000000000000
```

(30.36)

which yields practically the same value and  $f=1$ . We evaluate a few other matrix elements  $\langle v'|y|v\rangle$ .

```
> ` $\langle 2|y|1\rangle$ ` := evalf[10](Int((eval(psi, [g=1/100, v=2, C=C1]))*y
*(eval(psi, [g=1/100, v=1, C=C1])), y=0..infinity,
method=_Gquad));
 $\langle 2|y|1\rangle$  := 0.09951779528
```

(30.37)

```
> ` $\langle 3|y|1\rangle$ ` := evalf[10](Int((eval(psi, [g=1/100, v=3, C=C1]))*y
*(eval(psi, [g=1/100, v=1, C=C1])), y=0..infinity,
method=_Gquad));
 $\langle 3|y|1\rangle$  := -0.005904665386
```

(30.38)

```
> ` $\langle 4|y|1\rangle$ ` := evalf[10](Int((eval(psi, [g=1/100, v=4, C=C1]))*y
*(eval(psi, [g=1/100, v=1, C=C1])), y=0..infinity,
method=_Gquad));
 $\langle 4|y|1\rangle$  := 0.0008025247470
```

(30.39)

```
> ` $\langle 3|y|2\rangle$ ` := evalf[10](Int((eval(psi, [g=1/100, v=3, C=C1]))*y
*(eval(psi, [g=1/100, v=2, C=C1])), y=0..infinity,
method=_Gquad));
 $\langle 3|y|2\rangle$  := 0.1216027680
```

(30.40)

These values for  $\Delta v=1$  and  $\Delta v=2$  increase with  $v$ .

We evaluate expectation values  $\langle v | y^{-2} | v \rangle = \int_0^\infty \frac{\Psi_v(y) \Psi_v(y)}{y^2} dy$  that are equal to rotational

parameters  $B_v$  for states with  $0 \leq v \leq 4$ ;

```
> for j from 0 to 4 do
  ` $\langle 1/y^2\rangle$ `[j] = B[e]*evalf(Int((eval(psi, [v=j,
g=1/100., C=C1]))*1/y^2*(eval(psi,
[v=j,g=1/100.,C=C1])), y=0..infinity, method=_Gquad));
end do;
```

$$\langle 1/y^2 \rangle_0 = 0.9999500037496865 B_e$$

$$\langle 1/y^2 \rangle_1 = 0.9999500037496867 B_e$$

$$\begin{aligned}
\langle 1/y^2 \rangle_2 &= 0.9999500037496891 B_e \\
\langle 1/y^2 \rangle_3 &= 0.9999500037496873 B_e \\
\langle 1/y^2 \rangle_4 &= 0.9999500037496878 B_e
\end{aligned}
\tag{30.41}$$

these values are constant and essentially equal to  $B_e$  because all corrections dependent on quantum number  $v$  are zero, indicating that this Davidson *harmonic oscillator* is also effectively a *rigid rotor*. The vibration-rotational energies are therefore expressible as

$$\frac{E_{v,J}}{h c} = \omega_e \left( v + \frac{1}{2} \right) + B_e \left( J + \frac{1}{2} \right)^2$$

with  $\omega_e = 2000 \text{ cm}^{-1}$  and  $B_e = 10 \text{ cm}^{-1}$ , with  $g = \frac{1}{100}$  for example.

We test expectation values of  $R/R_e$  to the first four powers for several vibrational states.

```

> for j from 0 to 4 do
  <y>`[j] = evalf(Int((eval(psi, [v=j,
    g=1/100., C=C1]))*y*(eval(psi,
    [v=j,g=1/100.,C=C1])), y=0..infinity, method=_Gquad));
end do;

```

$$\begin{aligned}
\langle y \rangle_0 &= 1.007503008800571 \\
\langle y \rangle_1 &= 1.022318503286653 \\
\langle y \rangle_2 &= 1.036955935486020 \\
\langle y \rangle_3 &= 1.051421184536485 \\
\langle y \rangle_4 &= 1.065719823384950
\end{aligned}
\tag{30.42}$$

```

> for j from 0 to 4 do
  <y^2>`[j] = evalf(Int((eval(psi, [v=j,
    g=1/100., C=C1]))*y^2*(eval(psi,
    [v=j,g=1/100.,C=C1])), y=0..infinity, method=_Gquad));
end do;

```

$$\begin{aligned}
\langle y^2 \rangle_0 &= 1.020049998750060 \\
\langle y^2 \rangle_1 &= 1.060049998750061 \\
\langle y^2 \rangle_2 &= 1.100049998750063 \\
\langle y^2 \rangle_3 &= 1.140049998750061 \\
\langle y^2 \rangle_4 &= 1.180049998750062
\end{aligned}
\tag{30.43}$$

```

> for j from 0 to 4 do
  <y^3>`[j] = evalf(Int((eval(psi, [v=j,
    g=1/100., C=C1]))*y^3*(eval(psi,

```

```

    [v=j,g=1/100.,C=C1])), y=0..infinity, method=_Gquad));
end do;

<y^3>_0 = 1.037778472955712
<y^3>_1 = 1.114081973340059
<y^3>_2 = 1.191669365131871
<y^3>_3 = 1.270522480913438
<y^3>_4 = 1.350623847129370
(30.44)

> for j from 0 to 4 do
    <y^4>[j] = evalf(Int((eval(psi, [v=j,
        g=1/100., C=C1]))*y^4*(eval(psi,
        [v=j,g=1/100.,C=C1])), y=0..infinity, method=_Gquad));
end do;

<y^4>_0 = 1.060902999925001
<y^4>_1 = 1.185708999775009
<y^4>_2 = 1.315314999625019
<y^4>_3 = 1.449720999475024
<y^4>_4 = 1.588926999325032
(30.45)

```

This Davidson function for potential energy has the property that expectation values of  $R/R_e$  to positive powers increase nearly linearly with vibrational quantum number  $v$ . For matrix elements of  $R^2$ ,

```

> for j from 0 to 7 do
    <`,`j+1,`|^2*y^2`,`j,`>` = evalf(Int((eval(psi, [v=j+1,
        g=1/100., C=C1]))*y^2*(eval(psi,
        [v=j,g=1/100.,C=C1])), y=0..infinity, method=_Gquad));
end do;

<`,`1,`|^2*y^2,0,`>` = 0.1428320691406562
<`,`2,`|^2*y^2,1,`>` = 0.2039656832655986
<`,`3,`|^2*y^2,2,`>` = 0.2521963519264379
<`,`4,`|^2*y^2,3,`>` = 0.2939455730233148
<`,`5,`|^2*y^2,4,`>` = 0.3316700165450686
<`,`6,`|^2*y^2,5,`>` = 0.3666142384714581
<`,`7,`|^2*y^2,6,`>` = 0.3995084477517450
<`,`8,`|^2*y^2,7,`>` = 0.4308224690055173
(30.46)

```

there is a tendency to converge with increasing vibrational quantum number  $v$ .

### 1.33 significance of comparison

> # no restart here!

What do these further results signify? For the cases of a canonical linear harmonic oscillator with this function for potential energy relative to a minimum at  $R = R_e$ ,

$$\frac{V_c(R)}{h c} = \frac{B_e \left( \frac{R - R_e}{R_e} \right)^2}{g^2}$$

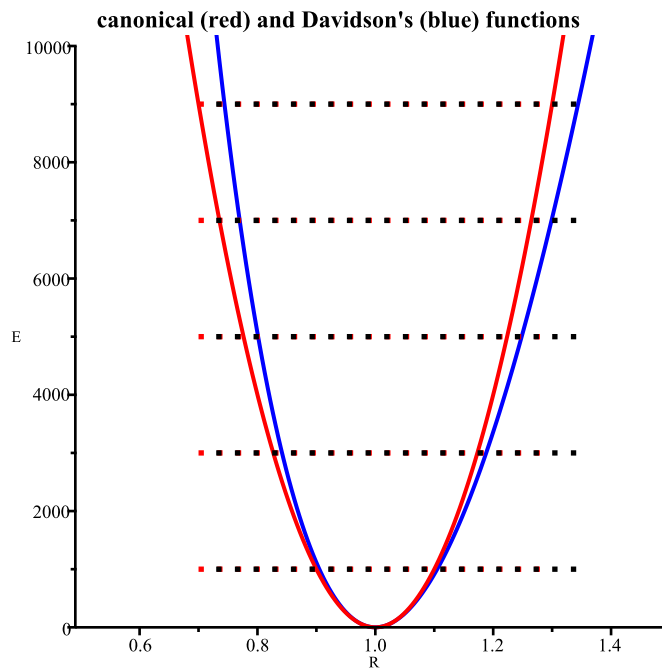
and of an oscillator according to Davidson's function for potential energy likewise relative to a minimum at  $R = R_e$ ,

$$\frac{V_D(R)}{h c} = \frac{B_e \left( \frac{R}{R_e} - \frac{R_e}{R} \right)^2}{g^2}$$

we compare in the following plot the curves for potential energy and lines for discrete values of energy with common values of parameters, taking  $R_e = 1$ ,  $B_e = 10$  in appropriate units and  $g = \frac{1}{100}$ , and recalling results for energies from section 1.32. Expand laterally this plot to improve viewing.

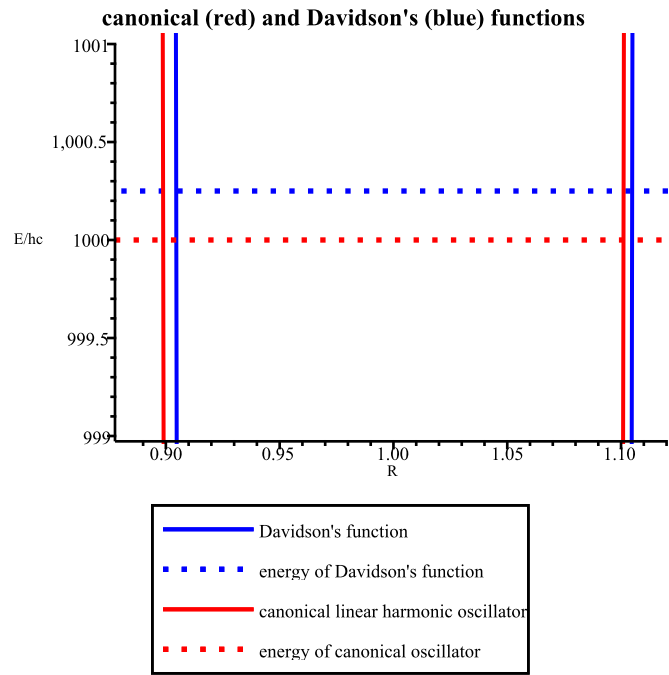
```
> VRy := eval(eval(B[e]*(y - 1/y)^2/(4*g^2), y=R/R[e]),
               [R[e]=1, B[e]=10, g=1/100]):
p5 := plot(VRy, R=3/5..3/2, 0..10000, colour=blue):
p6 := plot([seq(eval(k*2000+1000.25), k=0..4)], R=0.7..1.3,
           colour=red, linestyle=[2,2,2,2,2], thickness=[2,2,2,2,2]):
VRx := eval(eval(B[e]*x^2/g^2, [x=(R-R[e])/R[e], g=1/100]),
           [R[e]=1, B[e]=10]):
p7 := plot(VRx, R=1/2..3/2, 0..10000, colour=red):
p8 := plot([seq(eval((1+2*v)*B[e]/g, [B[e]=10, g=1/100]),
               v=0..4)], R=0.73..1.35, colour=black,
           linestyle=[2,2,2,2,2], thickness=[2,2,2,2,2]):
plots[display]([p5,p6,p7,p8], labels=["R", "E"], titlefont=[TIMES,
BOLD, 14],
               title="canonical (red) and Davidson's (blue) functions");
```





This plot demonstrates that, although the two curves representing these two functions for potential energy are clearly distinct, the corresponding energies appear to overlap exactly. To assess the nature of this overlap, we expand the ordinate scale in the vicinity of energies for  $v=0$ .

```
> p5 := plot(VRy, R=3/5..3/2, 0..10000, colour=blue,
             legend="Davidson's function"):
p6 := plot(1000.25, R=0.7..1.3, colour=blue,
           linestyle=[2,2,2,2,2], thickness=[2,2,2,2,2],
           legend="energy of Davidson's function"):
p7 := plot(VRx, R=1/2..3/2, 0..10000, colour=red,
           legend="canonical linear harmonic oscillator"):
p8 := plot(1000, R=0.73..1.35, colour=red,
           linestyle=[2,2,2,2,2], thickness=[2,2,2,2,2],
           legend="energy of canonical oscillator"):
plots[display]([p5,p6,p7,p8], view=[0.88..1.12, 999..1001],
               labels=["R","E/hc"], titlefont=[TIMES,BOLD,14],
               title="canonical (red) and Davidson's (blue) functions");
```



These plots confirm that the discrete energies of the corresponding quantum states according to the two functions for potential energy differ slightly, corresponding to a difference  $\sim \frac{h c B_e}{4}$  in residual energies, but that the differences of energy between adjacent states remain constant and equal.

There exists an uncountable number of confining classical functions of potential energy with a single minimum for which the classical angular velocity  $\omega_0 = \frac{B_e}{2\gamma}$  is independent of energy; there are likewise potential-energy functions of uncountable number for which, between adjacent quantum-mechanical eigenvalues, the differences of energy are equal [M. M. Nieto, Physical Review D24, 1030 -- 1032, 1981].

Among measurable quantities in spectral transitions are the differences of discrete energies between quantum states and the intensities of those transitions. These plots for particular harmonic functions of potential energy demonstrate clearly that a distinction between these particular functions for potential energy of harmonic oscillators is impossible purely on the basis of such differences of vibrational energy, but, because of a slight difference between numerical values of matrix elements for transitions, such as

$$\langle 1|x|0 \rangle = \int_{-\infty}^{\infty} \psi_1(x) x \psi_0(x) dx$$

for the canonical linear harmonic oscillator, equal to 0.07071067811865475 according to the calculation above, or

$$\langle 1|y|0 \rangle = \int_0^{\infty} \psi_1(y) y \psi_0(y) dy$$

for the linear harmonic oscillator with Davidson's function for potential energy according to numerical value 0.07053759109296482 for the particular case calculated above, one might formally distinguish these functions according to intensities of a transition according to an electric dipole  $\langle v+1|x|v \rangle$  or  $\langle v+1|y|v \rangle$  in sections 1.31 and 1.32, respectively. A striking distinction between these functions for potential energy is that, for the canonical harmonic oscillator, the only transition possible according to an

electric dipolar moment from state  $\nu = 0$  is to  $\nu = 1$ , whereas, for the harmonic oscillator according to Davidson's function, transitions from state  $\nu = 0$  to states with  $\nu > 0$  are possible but with rapidly decreasing intensities., comparable with experiment on diatomic molecules.

The two functions  $V(R, J)$  for *effective* potential energy pertinent to vibration-rotational transitions for the canonical linear harmonic oscillator,

$$\frac{V_c(R, J)}{h c} = B_e \left( \frac{\left( \frac{R - R_e}{R_e} \right)^2}{g^2} + \frac{R_e^2 J(J + 1)}{R^2} \right)$$

and for the Davidson oscillator,

$$\frac{V_D(R, J)}{h c} = B_e \left( \frac{\left( \frac{R}{R_e} - \frac{R_e}{R} \right)^2}{g^2} + \frac{R_e^2 J(J + 1)}{R^2} \right)$$

have a common further term depending on rotational quantum number  $J$ . The conclusion about indistinguishable functions of potential energy on the basis of differences of vibrational energies is inapplicable when vibration-rotational energies might be deduced. Hence, by analogy, the inversion of vibrational-rotational spectral data *of only frequency type* to both a unique function of potential energy and, equivalently, a unique structure corresponding to the equilibrium internuclear distance  $R_e$  at the minimum of the curves of potential energy is practicable in these two cases, and can be confirmed on the basis of an analysis of intensities of vibration-rotational transitions.

These two harmonic oscillators that have distinct functions of potential energy have hence exactly the same energies, although the intensities of transitions between states differ. Another example of systems of the same energies involves an infinite potential energy for a particle confined to a line segment, discussed in section 1.42, and a particle under the influence of potential energy  $V(x) = 2 \csc(x)^2$ ; the latter has one fewer bound state.

## 1.4 other oscillators, rotors and angular momenta

### 1.41 free particle in one dimension

> **restart:**

For a free particle constrained to move along axis  $x$ , the potential energy  $V_0$  is constant, i.e.

independent of  $x$ . To evaluate wave function  $\psi(x, t)$ , we apply to this system Schroedinger's equation dependent on time (cf. C. S. Johnson and L. G. Pedersen, *Problems and Solutions in Quantum Chemistry and Physics*, Addison-Wesley, 1974),

$$H \psi(x, t) = \frac{i h \left( \frac{\partial}{\partial t} \psi(x, t) \right)}{2 \pi}.$$

According to section 1.23, with hamiltonian operator  $H$  independent of time, we convert a partial differential equation in variables  $x$  and  $t$  into two ordinary differential equations on assuming a separation of the variables.

$$\psi(x, t) = X(x) T(t)$$

On making the latter substitution and dividing Schroedinger's equation by  $\psi(x)$ , we obtain

$$\frac{H X(x)}{X(x)} = \frac{i h \left( \frac{d}{dt} T(t) \right)}{2 \pi T(t)} = E.$$

As the two sides of this identity depend on separate independent variables, for arbitrary values of  $x$  and  $t$  these two sides must both be equal to the same constant, which has the dimensions of energy,  $E$ . The resulting equations are hence

$$H X(x) = E X(x)$$

and

$$\frac{i h \left( \frac{d}{dt} T(t) \right)}{2 \pi} = E T(t)$$

We solve first the latter equation, assuming an initial condition designed to avoid a constant of integration.

```
> Teq := I*h/(2*Pi)*diff(T(t),t) = E*T(t);
```

$$Teq := \frac{\frac{1}{2} h \left( \frac{d}{dt} T(t) \right)}{\pi} = E T(t) \quad (32.1)$$

```
> Tsol := dsolve({Teq, T(0)=1}, T(t));
```

$$Tsol := T(t) = e^{\frac{-2IE\pi t}{h}} \quad (32.2)$$

Hamiltonian  $H$  for the spatial equation is

```
> H(x) = -h^2/(2*m*(2*Pi)^2)*Diff(``,x$2) + V[0];
```

$$H(x) = -\frac{h^2 \left( \frac{\partial^2}{\partial x^2} \right)}{8 m \pi^2} + V_0 \quad (32.3)$$

which we insert into Schroedinger's equation for the spatial coordinate,

```
> Xeq := -h^2/(2*m*(2*Pi)^2)*diff(X(x),x$2) + V[0]*X(x) = E*X(x);
```

$$Xeq := -\frac{h^2 \left( \frac{d^2}{dx^2} X(x) \right)}{8 m \pi^2} + V_0 X(x) = E X(x) \quad (32.4)$$

solve it,

```
> Xsol := dsolve(Xeq, X(x));
```

$$Xsol := X(x) = \_C1 \sin\left(\frac{2 \sqrt{2} \pi \sqrt{E - V_0} \sqrt{m} x}{h}\right) + \_C2 \cos\left(\frac{2 \sqrt{2} \pi \sqrt{E - V_0} \sqrt{m} x}{h}\right) \quad (32.5)$$

and convert to exponential form.

```
> Xsol := simplify(convert(Xsol, exp));
```

$$Xsol := X(x) = \_C1 \sin\left(\frac{2 \sqrt{2} \pi \sqrt{E - V_0} \sqrt{m} x}{h}\right) + \_C2 \cos\left(\frac{2 \sqrt{2} \pi \sqrt{E - V_0} \sqrt{m} x}{h}\right) \quad (32.6)$$

As an ordinary differential equation of second order has two independent solutions, we combine the four terms having only two distinct coefficients  $\_C1$  and  $\_C2$  as constants of integration into the following form as a general solution of the spatial equation.

> Xsol := X(x) = subs(\_C1\*I+\_C2=2\*a, \_C1\*I-\_C2=-2\*b, rhs(Xsol));

$$Xsol := X(x) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) + \_C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) \quad (32.7)$$

The total solution  $\psi(x, t)$  is hence

> psi := rhs(Xsol)\*rhs(Tsol);

$$\psi := \left( \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) + \_C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) \right) e^{\frac{-2IE\pi t}{h}} \quad (32.8)$$

> psi := simplify(expand(psi));

$$\begin{aligned} \psi := & \left( 2\_C1 \sin\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) \right. \\ & \left. + 2 \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)^2 \_C2 - \_C2 \right) e^{\frac{-2IE\pi t}{h}} \end{aligned} \quad (32.9)$$

Normalization is inapplicable for this wave function of a free particle because the wave function has constant amplitude through all space, but a possibility is to normalise over a large length  $L$ , taken to be much greater than the size of the particle; then  $a = b = \sqrt{\frac{1}{2L}}$ .

A sum of classical traveling waves is expressible as

$$a e^{2\pi i \left( \frac{x}{\lambda} - vt \right)} + b e^{2\pi i \left( -\frac{x}{\lambda} - vt \right)}$$

This expression becomes identical to the expression for  $\psi(x, t)$  if

$$\frac{2\pi}{\lambda} = \frac{\sqrt{2m(E-V_0)}}{\frac{h}{2\pi}}$$

and

$$\frac{E}{\frac{h}{2\pi}} = 2\pi v$$

The quantity of which the square root appears in the former equation is  $p_x$ , component  $x$  of momentum  $p$ , yielding

$$\frac{1}{\lambda} = \frac{p_x}{h}$$

which is the relation of de Broglie for the wave length  $\lambda$  of a wave accompanying a particle having momentum  $p$ , as in  $\lambda = \frac{h}{p}$ , and the latter relation is Einstein's formula for the energy of a photon of frequency  $v$ ,

$$E = h v .$$

The second term in  $\psi(x, t)$ , having coefficient  $a$ , represents a wave traveling in the direction of  $+x$ , and

the other term, having coefficient  $b$ , represents a wave traveling in the direction of  $-x$ ; for the sum of classical traveling waves, setting the exponent equal to zero, as  $\frac{x}{\lambda} - v t = 0$ , and solving for  $\frac{x}{t} = v \lambda$  yields the velocity of the crest of the wave. Each energy of the particle is doubly degenerate, with amplitude functions corresponding to the particle moving toward  $+x$  or  $-x$ , but there is no quantization for this system as the energy can assume any value,  $0 \leq E \leq \infty$ .

Choosing an initial condition such that

$$\psi(x, 0) = a e^{-\frac{2I\sqrt{2}\pi\sqrt{-V_0+E}\sqrt{m}x}{h}}$$

requires that  $b = 0$ .

**> P1 := subs(b=0, psi);**

$$P1 := \left( 2\_C1 \sin\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) + 2 \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)^2 \_C2 - \_C2 \right) e^{\frac{-2IE\pi t}{h}} \quad (32.10)$$

We operate on  $P1$  with the operator for  $p_x$ , namely  $-\frac{i h \left( \frac{\partial}{\partial x} \right)}{2 \pi}$ ,

**> -I\*h/(2\*Pi)\*diff(P1,x);**

$$\frac{1}{\pi} \left( -\frac{1}{2} h \left( \frac{2\_C1 \sqrt{2}\pi\sqrt{E-V_0}\sqrt{m} \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)^2}{h} - \frac{2\_C1 \sin\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)^2 \sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}}{h} - \frac{1}{h} \left( 4 \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right) \_C2 \sqrt{2}\pi\sqrt{E-V_0}\sqrt{m} \sin\left(\frac{1}{h} \left( \sqrt{2}\pi \sqrt{E-V_0}\sqrt{m}x \right) \right) \right) \right) e^{\frac{-2IE\pi t}{h}} \right) \quad (32.11)$$

which yields a product of  $P1$  with  $\sqrt{2 m (E - V_0)}$ .

**> %/P1;**

$$\left( -\frac{1}{2} h \left( \frac{2\_C1 \sqrt{2}\pi\sqrt{E-V_0}\sqrt{m} \cos\left(\frac{\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)^2}{h} \right) \right) \quad (32.12)$$

$$\begin{aligned}
& - \frac{2\_C1 \sin\left(\frac{\sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right)^2 \sqrt{2} \pi \sqrt{E-V_0} \sqrt{m}}{h} \\
& - \frac{1}{h} \left( 4 \cos\left(\frac{\sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right) - C2 \sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} \sin\left(\frac{1}{h} \left( \sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x \right) \right) \right) \\
& \left( \pi \left( 2\_C1 \sin\left(\frac{\sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right) \cos\left(\frac{\sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right) \right. \right. \\
& \left. \left. + 2 \cos\left(\frac{\sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right)^2 - C2 \right) \right)
\end{aligned}$$

$PI$  is hence an eigenfunction of  $p_x$  with eigenvalue  $\sqrt{2 m (E - V_0)}$ , which is characteristic of the momentum of a free particle moving in direction  $+x$ . If we choose  $a=0$  in  $\Psi(x, t)$ , we find that the eigenvalue would correspond to the momentum of a particle moving in direction  $-x$ .

If we choose an initial condition such that, in  $Xsol$  above, coefficient  $\_C1 = 0$ , the expression for  $\Psi(x, t)$  becomes

**> psi := \_C2\*cos(2\*2^(1/2)\*Pi/h\*(-V[0]+E)^(1/2)\*m^(1/2)\*x)\*exp(-2\*I\*E/h\*Pi\*t);**

$$\psi := \_C2 \cos\left(\frac{2 \sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right) e^{\frac{-2iE\pi t}{h}} \quad (32.13)$$

The probability of the particle becomes  $|\Psi(x, t)|^2$  or  $\overline{\Psi(x, t)} \Psi(x, t)$ ,

**> simplify(conjugate(psi)\*psi) assuming real;**

$$\_C2^2 \cos\left(\frac{2 \sqrt{2} \pi \sqrt{E-V_0} \sqrt{m} x}{h}\right)^2 \quad (32.14)$$

which is independent of time.

Commutator  $[p_x, H(x)]$  of momentum operator  $p_x$  with hamiltonian operator  $H(x)$  is

$$\begin{aligned}
[p_x, H] &\equiv p_x H - H p_x = p_x \left( \frac{p_x^2}{2m} + V_0 \right) - \left( \frac{p_x^2}{2m} + V_0 \right) p_x = \frac{[p_x, p_x^2]}{2m} + [p_x, V_0] = \\
&\frac{p_x^3 - p_x^3}{2m} + p_x (V_0 - V_0) = 0
\end{aligned}$$

Because momentum operator  $p_x$  commutes with hamiltonian operator  $H(x)$ , these operators have simultaneous eigenfunctions in complete sets, whereas in general these operators fail to commute; for instance, for eigenfunction

$$\cos\left(\frac{2\sqrt{2}\pi\sqrt{-V_0+E}\sqrt{m}x}{h}\right)e^{-\frac{2IE\pi t}{h}}$$

as applied above, this solution of Schroedinger's equation is not an eigenfunction of  $p_x$ , as we show here,

```
> p[x]*psi = -I*h/(2*Pi)*diff(psi,x);
```

$$p_x - C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)e^{-\frac{2IE\pi t}{h}} \quad (32.15)$$

$$= I_C2\sqrt{2}\sqrt{E-V_0}\sqrt{m}\sin\left(\frac{2\sqrt{2}\pi\sqrt{E-V_0}\sqrt{m}x}{h}\right)e^{-\frac{2IE\pi t}{h}}$$

of which the resulting expression contains sine rather than cosine.

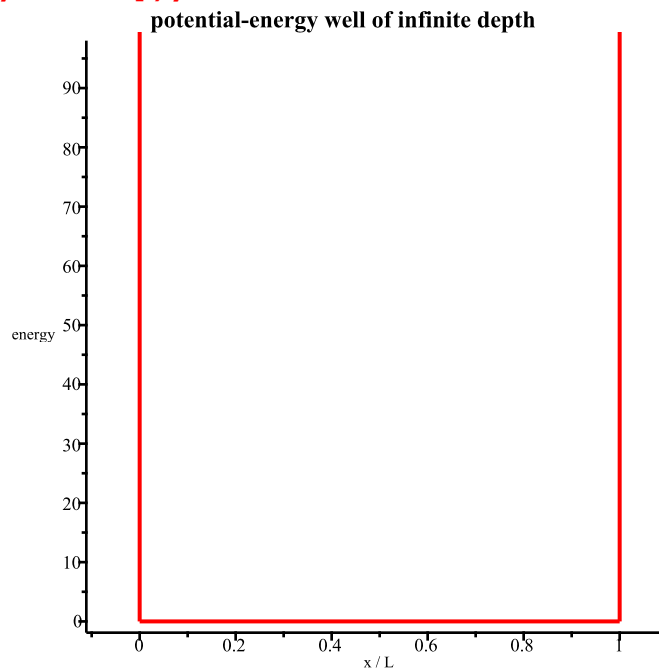
## 1.42 potential-energy wells treated with Schroedinger's equation and JBKW procedure

### 1 infinite well

```
> restart:
```

A traditional conventional exercise in quantum mechanics is the solution of Schroedinger's temporally independent equation for a particle of mass  $m$  constrained to a segment of a line of length  $L$ ; the potential energy is assumed to be zero within that segment and infinite elsewhere, as shown here.

```
> plot([[[0,0],[0,100]], [[0,0],[1,0]], [[1,0],[1,100]]], x=-0.1.  
.1.1,  
       colour=[red,red,red,red], titlefont=[TIMES,BOLD,14], labels=  
["x / L", "energy"],  
       axes=frame, title="potential-energy well of infinite depth",  
       view=[-0.1..1.1,-1..98]);
```





We write the applicable ordinary-differential equation for that segment,.

```
> de := -h^2/(8*Pi^2*m)*diff(psi(x),x$2) = E*psi(x);
```

$$de := -\frac{h^2 \left( \frac{d^2}{dx^2} \psi(x) \right)}{8 \pi^2 m} = E \psi(x) \quad (33.1.1)$$

and solve it.

```
> sol := dsolve(de, psi(x));
```

$$sol := \psi(x) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{E}\sqrt{m}x}{h}\right) + \_C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{E}\sqrt{m}x}{h}\right) \quad (33.1.2)$$

As the amplitude function must have zero amplitude at  $x=0$  and outside that segment, the cosine solution is physically unacceptable; we set the coefficient of the cosine term, which arose as an integration constant from solution of the differential equation, equal to zero.

```
> sol := subs(_C2=0, sol);
```

$$sol := \psi(x) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{E}\sqrt{m}x}{h}\right) \quad (33.1.3)$$

As the amplitude function must have zero amplitude at  $x=L$ , the coefficient of  $x$  as argument of sine must fulfill this condition,

```
> E := solve(subs(x=L, rhs(sol))=0, E, allsolutions);
```

$$E := \frac{Z1^2 h^2}{8 m L^2} \quad (33.1.4)$$

which enables evaluation of  $E$ ,

```
> E := subs(_Z1=n, E);
```

$$E := \frac{n^2 h^2}{8 m L^2} \quad (33.1.5)$$

which shows the energy to increase quadratically with quantum number  $n$ , and the amplitude function.

```
> sol := simplify(sol, symbolic);
```

$$sol := \psi(x) = \_C1 \sin\left(\frac{\pi n x}{L}\right) \quad (33.1.6)$$

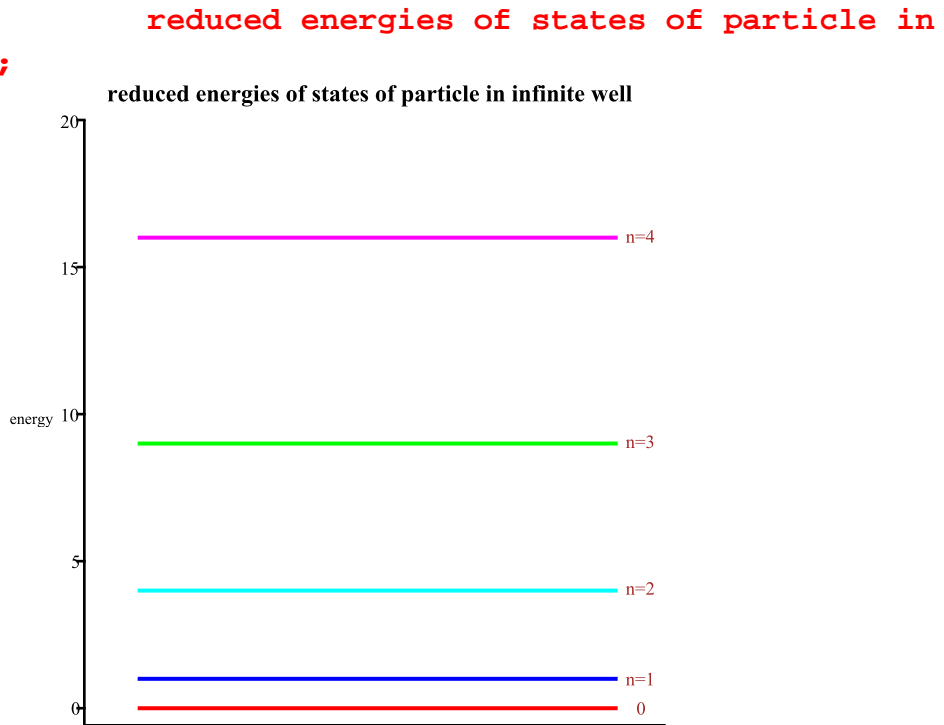
We plot the energy/ $h^2 m^{-1} L^{-2}$ , so reduced, as a function of quantum number  $n$ .

```
> pw1 := plot([seq(j^2, j=0..4)], x=0..0.2, -0.4..20,
  axes=frame, colour=[red,blue,cyan,green,magenta],
  thickness=[1$5, 2], tickmarks=[0,5], labels=[" ", "energy"]):
```

```
pw2 := plots[textplot]([0.21,0.003,"0"],[0.21,1+0.003,"n=1"],
  [0.21,4+0.003,"n=2"], [0.21,9+0.003,"n=3"], [0.21,16+0.003,
  "n=4"]],
  colour=brown):
```

```
plots[display]([pw1,pw2], titlefont=[TIMES,BOLD,14], view=[-0.02.
```

```
.0.22, -0.4..20],
      title="
infinite well");
```



As the particle is confined to the segment of the line, its total probability, according to Born, of being found in that region must be unity,

```
> nc := simplify(int(rhs(sol)^2, x=0..L)) assuming n::integer;
```

$$nc := \frac{L \cdot C1^2}{2} \quad (33.1.7)$$

which enables evaluation of the other integration constant.

```
> ic := solve(nc=1, _C1);
```

$$ic := \frac{\sqrt{2}}{\sqrt{L}}, -\frac{\sqrt{2}}{\sqrt{L}} \quad (33.1.8)$$

As an amplitude function is defined only within a modulus of unity, we accept the positive root,

```
> ic := op(map(abs,{ic})) assuming L>0;
```

$$ic := \frac{\sqrt{2}}{\sqrt{L}} \quad (33.1.9)$$

to complete the definition of the amplitude function.

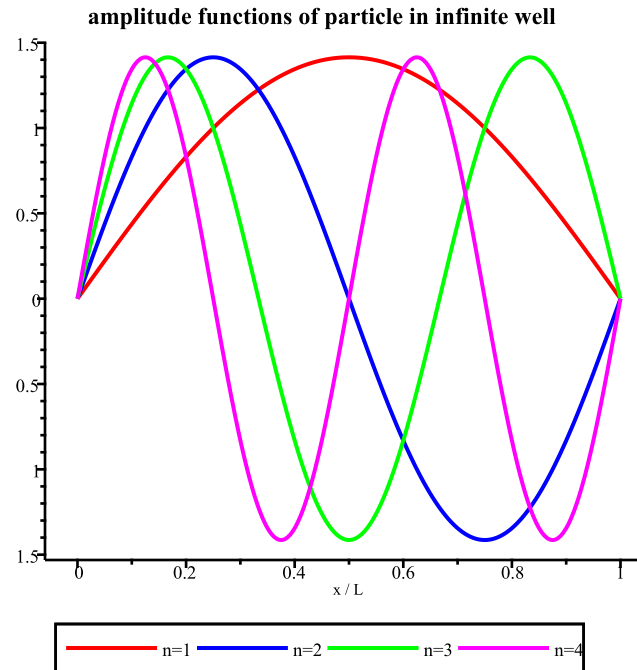
```
> sol := subs(_C1 = ic, sol);
```

$$sol := \psi(x) = \frac{\sqrt{2} \sin\left(\frac{\pi n x}{L}\right)}{\sqrt{L}} \quad (33.1.10)$$

As  $\psi(x)$  is identically zero everywhere for  $n = 0$ , the particle can not exist in such a condition; the state

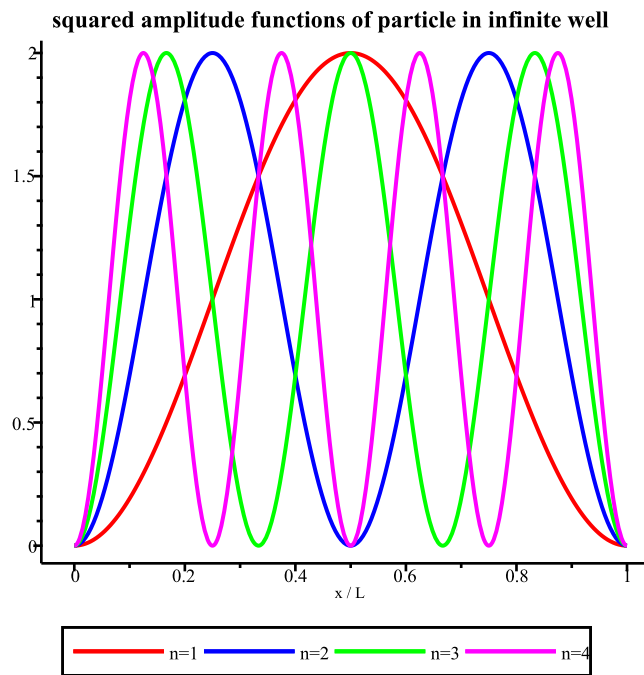
of least energy must correspond to  $n = 1$ , for which  $E = \frac{1}{8} \frac{h^2}{m L^2}$ . We plot the amplitude functions for  $x/L$  and  $n = 1, 2, 3, 4$ .

```
> plot([seq(eval(rhs(sol),L=1), n=1..4)], x=0..1, colour=[red,blue,
green,magenta],
      legend=["n=1","n=2","n=3","n=4"], titlefont=[TIMES,BOLD,14],
      view=[-0.05..1.05,-1.5..1.5],
      title="amplitude functions of particle in infinite well", axes=
frame, labels=["x / L"," "]);
```



We plot also the squares of these amplitude functions.

```
> plot([seq(eval(rhs(sol),L=1)^2, n=1..4)],x=0..1, colour=[red,blue,
green,magenta], legend=["n=1","n=2","n=3","n=4"], titlefont=
[TIMES,BOLD,14],
      title="squared amplitude functions of particle in infinite
well",
      axes=frame, view=[-0.05..1.05,-0.05..2.05], labels=["x / L","
"]);
```



These procedures and examples are kindly provided by Dr. J. Boiden Pedersen, Syddansk Universitet, 2010 August, as modified and extended by J. F. Ogilvie, 2011 January and 2013 February. These sections require *Maple* 13 or subsequent release.

## 2 finite well

### dimensionless Schroedinger equation

For numerical calculations, one requires the Schroedinger equation,

$$\frac{h^2}{8\pi^2 m} \frac{d^2}{dR^2} \Psi(R) + V(R) \Psi(R) = E \Psi(R) \quad (1)$$

to be expressed in a dimensionless form, which is convenient also for analytical purposes. We apply Schroedinger's temporally independent equation for one spatial dimension in the following dimensionless form,

$$\left( \frac{d^2}{dx^2} \Psi(x) \right) + v(x) \Psi(x) = \epsilon \Psi(x) \quad (2)$$

in which the dimensionless quantities are defined as

$$x = \frac{R}{L}, \quad v(x) = \frac{V(x, L)}{E^*}, \quad \epsilon = \frac{E}{E^*}, \quad \text{with } \psi(x) = \sqrt{L} \Psi(xL) \quad (3)$$

$L > 0$  is a characteristic length of the system, e.g. the length of the potential-energy 'well' if this length be appropriately defined.  $E^* > 0$  is a characteristic energy unit of the system, e.g. the depth or height of a potential-energy well or other characteristic energy of the system.

### inside the well

**> restart:**

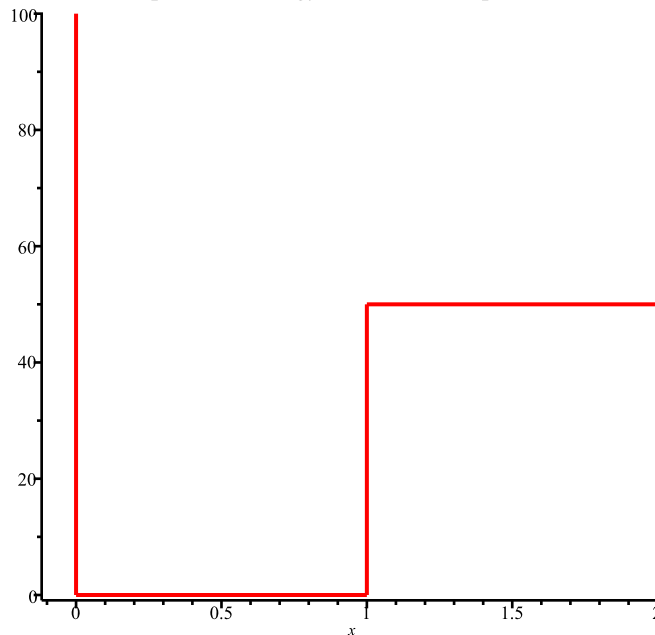
To contrast the energies of the states of a system comprising an infinitely deep well and another system with a well of finite depth, which has this shape,

**> plot([[[0,0],[0,100]], [[0,0],[1,0]], [[1,0],[1,50]], [[1,50],[2,**

```

50]]],
    x=-0.1..2, colour=[red,red,red,red], titlefont=[TIMES,BOLD,
14],
    axes=frame, title="potential-energy well of finite depth");
potential-energy well of finite depth

```



we define a well -- really, a line segment, of reduced length 1 unit, to have an infinitely high wall at the left side and a wall of finite height at the right side; inside the well  $V(x) = 0$ . We apply the

Schroedinger equation in dimensionless form, as derived above, with  $k^2 = \frac{8\pi^2 m E}{h^2}$ , and solve the

differential equation for even solutions with boundary conditions  $f_l = 1$  and  $\frac{\partial}{\partial x} f_l = 0$  both at  $x = 0$ ,

and odd solutions with boundary conditions  $f_l = 0$  and  $\frac{\partial}{\partial x} f_l = 1$  both at  $x = 0$ .

```
> deq1 := - diff(f1(x), x$2) = k^2*f1(x);
```

$$deq1 := -\frac{d^2}{dx^2} f_l(x) = k^2 f_l(x) \quad (33.3.1)$$

For the even solution the boundary conditions are

```
> BCEven := f1(0)=1, D(f1)(0)=0;
```

$$BCEven := f_l(0) = 1, D(f_l)(0) = 0 \quad (33.3.2)$$

and we solve the differential equation.

```
> f_even := unapply(eval(f1(x), dsolve({deq1, BCEven})), x);
```

$$f\_even := x \mapsto \cos(k \cdot x) \quad (33.3.3)$$

For the odd solution the boundary conditions are

```
> BCodd := f1(0)=0, D(f1)(0)=1;
```

$$BCodd := f_l(0) = 0, D(f_l)(0) = 1 \quad (33.3.4)$$

and we solve the differential equation.

```
> f_odd := unapply( eval(f1(x), dsolve({deq1, BCodd})), x);
```

$$f_{\text{odd}} := x \mapsto \frac{\sin(k \cdot x)}{k} \quad (33.3.5)$$

**outside the well**

```
> # no restart here
```

Outside the well we apply a boundary condition as  $f_2 \rightarrow 0$  at  $x \rightarrow \infty$ ,

```
> deq2 := diff(f2(x), x$2) = kappa^2*f2(x);
```

$$deq2 := \frac{d^2}{dx^2} f_2(x) = \kappa^2 f_2(x) \quad (33.4.1)$$

```
> BC2 := f2(infinity) = 0;
```

$$BC2 := f_2(\infty) = 0 \quad (33.4.2)$$

```
> sol2 := dsolve(deq2);
```

$$sol2 := f_2(x) = \_C1 e^{\kappa x} + \_C2 e^{-\kappa x} \quad (33.4.3)$$

```
> f2 := expand(eval(f2(x), sol2)/exp(kappa*x));
```

$$f_2 := \_C1 + \frac{\_C2}{(e^{\kappa x})^2} \quad (33.4.4)$$

so that coefficient  $\_C2$  of the positive exponential function is set to 0.

```
> bci := (limit(f2, x=infinity) assuming(kappa>0)) = 0;
```

$$bci := \_C1 = 0 \quad (33.4.5)$$

```
> f2 := simplify(subs(bci, f2)*exp(kappa*x));
```

$$f_2 := \_C2 e^{-\kappa x} \quad (33.4.6)$$

```
> f := unapply(subs(eval(f2,x=0)=C, f2), x);
```

$$f := x \mapsto C \cdot e^{-\kappa \cdot x} \quad (33.4.7)$$

**matching interior and exterior solutions, even solution**

```
> # no restart here
```

We match the interior and exterior solutions at  $x = 1$ , so that  $f_{\text{even}}(x) = f(x)$  at  $x = 1$ .

```
> match1 := f_even(1) = f(1);
```

$$match1 := \cos(k) = C e^{-\kappa} \quad (33.5.1)$$

```
> match2 := D(f_even)(1) = D(f)(1);
```

$$match2 := -k \sin(k) = -C \kappa e^{-\kappa} \quad (33.5.2)$$

```
> c := solve(match1, C);
```

$$c := \frac{\cos(k)}{e^{-\kappa}} \quad (33.5.3)$$

```
> res_eq := subs(C=c, match2);
```

$$res\_eq := -k \sin(k) = -\cos(k) \kappa \quad (33.5.4)$$

```
> even_eq := kappa = solve(res_eq, kappa);
```

$$even\_eq := \kappa = \frac{k \sin(k)}{\cos(k)} \quad (33.5.5)$$

One method of solution involves recognition that  $\kappa = \sqrt{v0 - k^2}$ , so that a circle of radius  $\sqrt{v0}$  represents  $v0$  in plane  $k, \kappa$ , which we plot below.

```
> trans_even := subs(kappa=sqrt(v0 - k^2), even_eq);
```

$$trans\_even := \sqrt{-k^2 + v0} = \frac{k \sin(k)}{\cos(k)} \quad (33.5.6)$$

### matching interior and exterior solutions, odd solution

```
> # no restart here
```

We analogously match the interior and exterior solutions at  $x = 1$ , so that  $f_{odd}(x) = f(x)$  at  $x = 1$ .

```
> match1 := f_odd(1) = f(1);
```

$$match1 := \frac{\sin(k)}{k} = C e^{-\kappa} \quad (33.6.1)$$

```
> match2 := D(f_odd)(1) = D(f)(1);
```

$$match2 := \cos(k) = -C \kappa e^{-\kappa} \quad (33.6.2)$$

```
> c := solve(match1, C);
```

$$c := \frac{\sin(k)}{e^{-\kappa} k} \quad (33.6.3)$$

```
> res_eq := subs(C=c, match2);
```

$$res\_eq := \cos(k) = -\frac{\sin(k) \kappa}{k} \quad (33.6.4)$$

```
> odd_eq := kappa = solve(res_eq, kappa);
```

$$odd\_eq := \kappa = -\frac{\cos(k) k}{\sin(k)} \quad (33.6.5)$$

One method of solution involves recognition again that  $\kappa = \sqrt{v0 - k^2}$ , so that a circle of radius  $\sqrt{v0}$  represents  $v0$  in plane  $k, \kappa$ , which we plot below.

```
> trans_odd := subs(kappa = sqrt(v0 - k^2), odd_eq);
```

$$trans\_odd := \sqrt{-k^2 + v0} = -\frac{\cos(k) k}{\sin(k)} \quad (33.6.6)$$

### graphical solutions

```
> # no restart here
```

We plot the values of  $k^2$  for the odd and even cases, choosing the height of the wall on the right side of the well to be 50 units.

```
> height := 50;
```

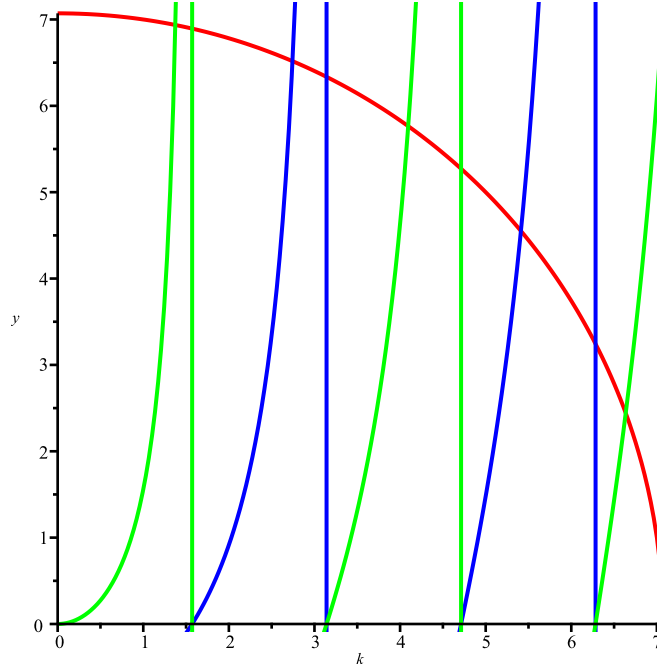
$$height := 50 \quad (33.7.1)$$

```
> k_range := sqrt(height);
```

$$k\_range := 5\sqrt{2} \quad (33.7.2)$$

Here is the plot for the odd solution. The solutions occur at the intersection of the red and blue or green curves, not the straight lines.

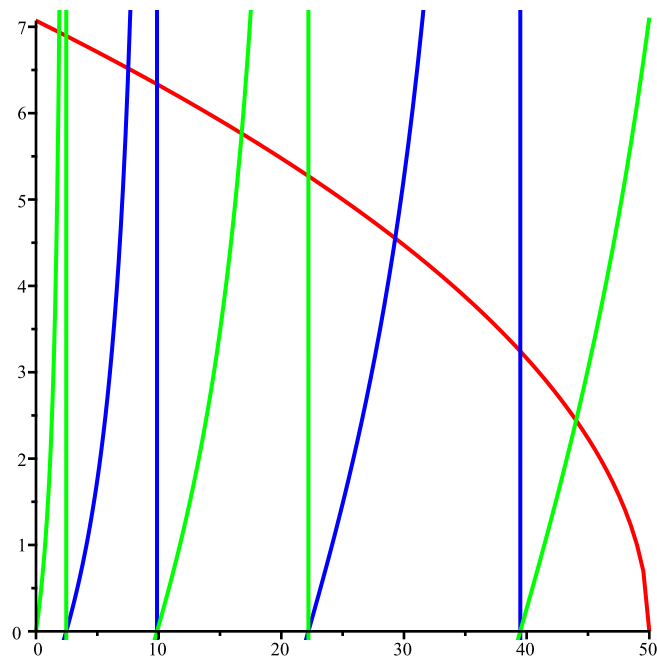
```
> plot(subs(v0=height, [lhs(trans_odd), rhs(trans_odd), rhs
  (trans_even)]),
  k=0..k_range, y=0..k_range, colour=[red, blue, green]);
```



Here we form the plot for the even solution. The solutions occur at the intersection of the red and blue or green curves, not the straight lines.

```
> p1 := plot([k^2, subs(v0=height, lhs(trans_odd)), k=0..k_range],
  colour=red):
> p2 := plot([k^2, subs(v0=height, rhs(trans_odd)), k=0..k_range],
  view=[0..k_range^2, 0..k_range], colour=blue):
> p3 := plot([k^2, subs(v0=height, rhs(trans_even)), k=0..k_range],
  view=[0..k_range^2, 0..k_range], colour=green):
> plots[display](p1,p2,p3);
```





### numerical solutions

```
> # no restart here
> k_range := sqrt(height):
> no_states := trunc(sqrt(height*4/Pi^2) + 1);
    no_states := 5
```

(33.8.1)

We calculate the values of  $k$  for the infinite well,

```
> for i from 0 to no_states do
    Ku[i] := sqrt(evalf((i+1)^2*Pi^2/4));
end do;
```

$$Ku_0 := 1.570796327$$

$$Ku_1 := 3.141592654$$

$$Ku_2 := 4.712388981$$

$$Ku_3 := 6.283185308$$

$$Ku_4 := 7.853981635$$

$$Ku_5 := 9.424777962$$

(33.8.2)

and apply these values as limits in seeking numerical solutions.

```
> for i from 0 to no_states -1 do
    if (i mod 2) = 0 then
        K[i] := fsolve(subs(v0=height, trans_even), k=Ku[i]-1.5..Ku[i]
    );
    else
```

```

        K[i] := fsolve(subs(v0=height, trans_odd), k=Ku[i]-1.5..Ku[i])
    ;
    end if;
end do;

```

For a specified height of the finite well, we calculate the energies of the states for both the finite and infinite wells, and the relative difference.

```

> printf("The height of the potential well is %a\n", height);
for j from 0 to no_states - 1 do
    printf("E(%d)=%7.4f, Einf=%5.2f, per cent difference = %3.0f\n",
        j, K[j]^2, Ku[j]^2, (Ku[j]^2 - K[j]^2)/Ku[j]^2*100);
end do;

```

The height of the potential well is 50

```

E(0)= 1.8909, Einf= 2.47, per cent difference = 23
E(1)= 7.5251, Einf= 9.87, per cent difference = 24
E(2)=16.7672, Einf=22.21, per cent difference = 24
E(3)=29.2859, Einf=39.48, per cent difference = 26
E(4)=44.0346, Einf=61.69, per cent difference = 29

```

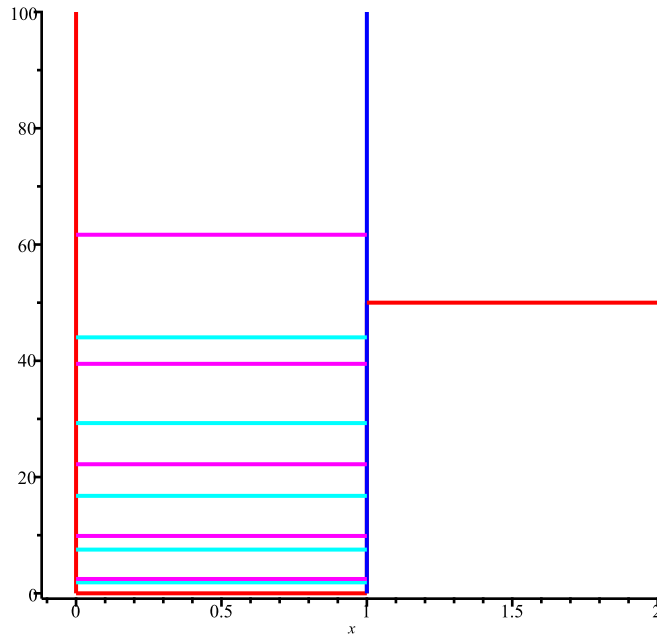
This plot compares the calculated energies for states with  $j=0..4$  for the finite well, in cyan colour, and the infinite well, in green colour; the red line shows the boundary of the finite well, and the blue line for the infinite well at points at which these two boundaries differ.

```

> plot([[0,0],[0,100]], [[0,0],[1,0]], [[1,0], [1,50]], [[1,0],[1,
100]],
    [[1,50], [3,50]], seq([[0,K[j]^2], [1,K[j]^2]], j=0..4),
    seq([[0,Ku[j]^2], [1,Ku[j]^2]], j=0..4)], x=-0.1..2,
    colour=[red,red,red,blue,red,cyan$5,magenta$5], axes=frame,
    title="comparison of well energies, cyan for finite, magenta
for infinite", titlefont=[TIMES,BOLD,14]);

```

comparison of well energies, cyan for finite, magenta for infinite



The plot shows graphically the comparative results for the energies according to the calculations above. For each value of quantum number  $n$ , the energy of the state pertaining to the finite well, marked with a cyan line, is less than the energy of the state pertaining to the infinite well.

### 3 JBKW method

#### JBKW approximation and procedure

> restart;

The conditions for quantisation of energy of the stationary states in an infinitely deep, rectangular well of width  $L$  are

$$k L = n \pi \quad \text{with } k, n \text{ in set of integers } \mathbf{Z} \quad \text{and} \quad E = \frac{h^2 k^2}{8 \pi^2 m}$$

The corresponding amplitude functions are standing waves characterized with

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin(kx) = \sqrt{\frac{2}{L}} \sin\left(\frac{n \pi x}{L}\right)$$

According to the conventional formula for linear momentum  $p$ ,

$$p = \sqrt{2 m E}$$

we write

$$p = k \frac{h}{2 \pi}$$

which agrees with de Broglie's relation,

$$\lambda = \frac{h}{p}$$

and the standard wave relation between wavenumber and wave length,

$$k = \frac{2 \pi}{\lambda}$$

The condition for quantisation becomes rewritten as

$$p L = n \pi \frac{h}{2 \pi} \quad \text{with } n \text{ in } \mathbf{Z}$$

As the potential energy  $V$  and thus  $p$  are constant in the well, an equivalent form is

$$\int_0^L p \, dx = n \pi \frac{h}{2 \pi} \quad \text{with } n \text{ in } \mathbf{Z}$$

The idea of the approximation that evolved from independent work of Brillouin, Kramers and Wentzel, 1926, based on a general method of solving differential equations by Jeffreys in 1923, is simple: a stationary state must be represented as a standing wave; with this approximation one assumes that a local wavenumber  $k$  is determined according to the above formulae; thus

$$p(x) = \sqrt{2 m (E - V)}$$

For a region in which the potential energy is bounded with two infinite barriers, the JBKW approximation, also known as WKB or BWK or semiclassical or quasiclassical method, for arbitrary potential energy  $V(x)$  bounded with two infinite walls at  $x=0$  and  $x=L$  is this phase integral, as above.

$$\int_0^L p(x) \, dx = n \pi \frac{h}{2 \pi}$$

The method is extensible to potential-energy functions with one or zero infinite wall; although the derivation is long, the results are simple:

$$\begin{aligned} \int_0^L p(x) \, dx &= \left( n - \frac{1}{4} \right) \pi \frac{h}{2 \pi} && \text{for a potential with one infinite barrier} \\ &= \left( n - \frac{1}{2} \right) \pi \frac{h}{2 \pi} && \text{for a potential with no infinite barrier} \end{aligned}$$

In all cases the domain of integration is over the classically allowed region bounded by the classical turning points, at which  $V(x) = E$ .

In the succeeding calculations, the energy is applied in a reduced form,  $\frac{E}{E^*}$ , for which

$$\frac{h^2 E^*}{8 \pi^2 m L^2} = 1 \quad \text{and with a reduced length coordinate, } x = \frac{R}{L}.$$

For use with procedure BKW below, the potential energy should be passed as an array function or other procedure, but containing no **if** statement. If the formula for potential energy include parameters with no fixed value, they should be denoted  $a$  and  $b$ , and their signs should be defined in parameter list *signs*; the first element in *signs* is the sign of the energy, which must always be specified; i.e. the shortest list of signs contains one element.

- `no_infinite_walls = 2` -- two infinite walls, located at  $x=0$  and  $x=L$
- `no_infinite_walls = 1` -- one hard wall at  $x=0$ ; the other turning point is evaluated by the procedure.
- `no_infinite_walls = 0` -- both classical turning points are evaluated by the procedure.
- `no_infinite_walls = -1` -- implies that the classical turning points are manually set at  $x=0$  and  $x=width$ .

This procedure operates satisfactorily under *Maple* 13 or subsequent release, but under *Maple* 11 **solve** fails to work in some cases.

```
> BKW := proc(pot, signs::list, no_infinite_walls::integer, width)
    local n, energy_sign, sign_a, sign_b, xt, x1, p, QC, qcn;
```

```

global a, b;
description "BKW approximation for energies of one-dimensional
            stationary states, J. Boiden Pedersen, 2010";
energy_sign := signs[1];
if energy_sign = +1 then
    assume(epsilon::positive);
elif energy_sign = -1 then
    assume(epsilon::negative);
end if;
if nops(signs) >= 2 then
    if signs[2] = +1 then
        assume(a::positive)
    elif signs[2] = -1 then
        assume(a::negative);
    end if;
end if;
if nops(signs) = 3 then
    if signs[3] = +1 then
        assume(b::positive)
    elif signs[3] = -1 then
        assume(b::negative);
    end if;
end if;
p := unapply(sqrt(epsilon - pot(x)), x);
if no_infinite_walls = -1 then
    QC := int(p(x), x=0..width);
    qcn := solve(QC = (n-1/2)*Pi, epsilon) assuming positive;
elif no_infinite_walls = 0 then
    xt := [solve(epsilon=pot(x), x, dropmultiplicity=true)];
    QC := int(p(x), x=xt[2] .. xt[1]);
    qcn := [solve(QC = (n-1/2)*Pi, epsilon)];
    qcn := remove(has, qcn, I)[1];
elif no_infinite_walls = 1 then
    xt := [solve(epsilon=pot(x), x, dropmultiplicity=true,
                useassumptions)] assuming x>0;
    QC := int(p(x), x=0..xt[1]);
    qcn := [solve(QC = (n-1/4)*Pi, epsilon)];
    qcn := remove(has, qcn, I)[1];
elif no_infinite_walls = 2 then
    xl := width;
    QC := int(p(x), x=0..xl);
    qcn := solve(QC = n*Pi, epsilon) assuming positive;

```

```

    end if;
    unapply(qcn, n);
end proc:
> Describe(BKW);

# BKW approximation for energies of one-dimensional stationary states, J.
# Boiden Pedersen, 2010
BKW( pot, signs::list, no_infinite_walls::integer, width )

```

Here we apply the BKW method in only one dimension; for its application in multiple dimensions, see Maslov and Fedoriuk [*Semiclassical Approximation in Quantum Mechanics*, Mathematical Physics and Applied Mathematics, 7, Reidel, Dordrecht, Netherlands, 1981].

### harmonic oscillator

```

> # no restart here
number of infinite walls 0, 1
> Vhosc := x -> x^2/4; # assume(epsilon::positive);

```

$$V_{hosc} := x \mapsto \frac{x^2}{4} \quad (33.10.1)$$

```

> BKW(Vhosc, [+1], 0);

```

$$n \mapsto n - \frac{1}{2} \quad (33.10.2)$$

That the result is  $n - \frac{1}{2}$  rather than the conventional  $n + \frac{1}{2}$  results from the ground state being numbered  $n = 1$ .  
for the half potential,

```

> BKW(Vhosc, [+1], 1);

```

$$n \mapsto 2 \cdot n - \frac{1}{2} \quad (33.10.3)$$

### triangular potential

```

> # no restart here
number of infinite walls 0, 1

```

```

> Vtriangle := x -> a*abs(x);

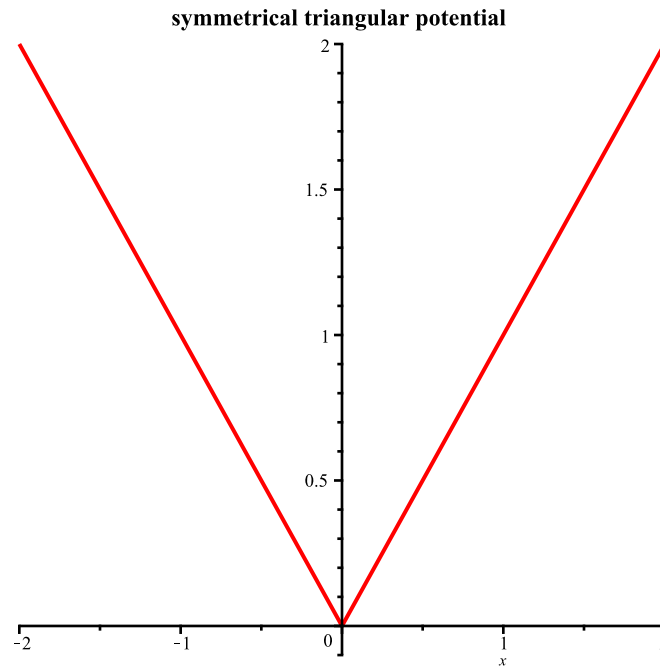
```

$$V_{triangle} := x \mapsto a \cdot |x| \quad (33.11.1)$$

```

> plot(abs(x), x=-2..2, -0.1..2, colour=red, titlefont=[TIMES,BOLD,
14],
    title="symmetrical triangular potential");

```



```
> assume(a > 0);
```

```
> E_triangle := BKW(Vtriangle, [+1,+1],0);
```

$$E_{\text{triangle}} := n \mapsto \frac{(6 \cdot \pi \cdot a \cdot n - 3 \cdot \pi \cdot a)^{2/3}}{4} \quad (33.11.2)$$

```
> factor(E_triangle(n));
```

$$\frac{3^{2/3} (\pi a (2n - 1))^{2/3}}{4} \quad (33.11.3)$$

The energy of the ground state is poorly estimated, but the energies of excited states become increasingly accurate.

We test next the infinite, unsymmetric triangular potential.

```
> BKW(Vtriangle,[+1,+1],1);
```

$$n \mapsto \frac{(12 \cdot \pi \cdot a \cdot n - 3 \cdot \pi \cdot a)^{2/3}}{4} \quad (33.11.4)$$

Nearly the same values appear here as those for even  $n$  for the symmetrical triangular potential.

### finite rectangular potential

```
> # no restart here
```

For number of infinite walls 0, 1, the potential energy is zero inside; only the number of boundaries are adjustable -- i.e two infinite walls, or one infinite wall or no infinite wall.

For the infinite rectangular potential,

```
> FW := BKW(0, [+1], 2,2);
```

$$FW := n \mapsto \frac{\pi^2 \cdot n^2}{4} \quad (33.12.1)$$

this result is exact and correct.

We consider next the finite rectangular well having two soft walls, i.e. no hard wall.

```
> fw := BKW(0, [+1], -1, 2);
```

$$f_w := n \mapsto \frac{1}{4} \cdot \pi^2 \cdot n^2 - \frac{1}{4} \cdot \pi^2 \cdot n + \frac{1}{16} \cdot \pi^2 \quad (33.12.2)$$

```
> 'fw' = factor(fw(n));
```

$$f_w = \frac{\pi^2 (2n - 1)^2}{16} \quad (33.12.3)$$

The finite well hence yields  $\frac{\pi^2 \left(n - \frac{1}{2}\right)^2}{4}$ , which is the same result as for the infinite well except that  $n - \frac{1}{2}$  appears instead of  $n$ , but the result conveys no information about the height or depth of the well, which is an obvious fault.

These values are inaccurate for depth = 50. The energy of the ground state is poorly estimated, of the intermediate states is satisfactory, but of the most excited state is again poorly estimated as the tail of the amplitude function is long for this state.

### coulombic potential energy

```
> # no restart here
```

number of infinite walls 1

```
> Vc := x -> -2/x;
```

$$V_c := x \mapsto -\frac{2}{x} \quad (33.13.1)$$

```
> E[c] := BKW(Vc, [-1], 1);
```

$$E_c := n \mapsto -\frac{16}{(4 \cdot n - 1)^2} \quad (33.13.2)$$

```
> E[c](1);
```

$$-\frac{16}{9} \quad (33.13.3)$$

### alternative treatment of JBKW method

```
> restart:
```

For the Schrodinger equation in one spatial dimension written as

$$\frac{d^2}{dx^2} \psi(x) + \frac{8 \pi^2 m}{h^2} (E - V(x)) \psi(x) = 0$$

an approximate solution due separately to Brillouin, Kramers and Wentzel emanates from the theory of ordinary differential equations. This method is known also as a *semiclassical* version of quantum mechanics. For a problem in three dimensions, this method requires only a spherically symmetric potential energy and a radial differential equation.



If  $V(x)$  be a constant quantity independent of  $x$ , we solve the differential equation as follows,

> `deq := diff(psi(x), x$2) + 8*Pi^2*m/(h^2)*(E - V)*psi(x) = 0;`

$$deq := \frac{d^2}{dx^2} \psi(x) + \frac{8 \pi^2 m (E - V) \psi(x)}{h^2} = 0 \quad (33.14.1)$$

> `dsolve(deq, psi(x));`

$$\psi(x) = _C1 \sin\left(\frac{2\sqrt{2} \pi \sqrt{m} \sqrt{E - V} x}{h}\right) + _C2 \cos\left(\frac{2\sqrt{2} \pi \sqrt{m} \sqrt{E - V} x}{h}\right) \quad (33.14.2)$$

> `simplify(eval(convert(%, exp), _C2=_C1));`

$$\psi(x) = _C1 \left( \cos\left(\frac{2\sqrt{2} \pi \sqrt{m} \sqrt{E - V} x}{h}\right) + \sin\left(\frac{2\sqrt{2} \pi \sqrt{m} \sqrt{E - V} x}{h}\right) \right) \quad (33.14.3)$$

to obtain a solution of the form  $e^{\pm i k x}$ , with  $k = \frac{2\sqrt{2} \pi m^{\frac{1}{2}} (E - V)^{\frac{1}{2}}}{h}$  and in which "+" in the exponent implies  $\pm i k x$ . If  $V(x)$  vary only slowly with  $x$ , a trial solution is  $\psi(x) = e^{i u(x)}$ , with  $u(x)$  not linear in spatial variable  $x$ . Substitution of this trial solution into the original differential equation yields an equation for the *phase*,  $u(x)$ . If we denote

$$k(x) = \left( \frac{8 \pi^2 m (E - V(x))}{h^2} \right)^{\frac{1}{2}} \quad \text{for } E > V(x)$$

and

$$k(x) = -i \left( \frac{8 \pi^2 m (E - V(x))}{h^2} \right)^{\frac{1}{2}} = -i \kappa(x) \quad \text{for } E < V(x)$$

we find that  $u(x)$  satisfies this equation.

$$i \left( \frac{d^2}{dx^2} u(x) \right) - \left( \frac{d}{dx} u(x) \right)^2 + k(x)^2 = 0$$

This differential equation is equivalent to the original differential equation, but the boundary conditions are more readily expressible in terms of  $\psi(x)$  than of  $u(x)$ . Unlike the Schroedinger equation that is linear, this equation resembles the classical Hamilton-Jacobi equation in being non-linear. As an approximation that might be viable if potential energy  $V(x)$  varies not too rapidly, we ignore the second derivative; under this condition, we obtain  $u_0(x)$  as a crude approximation for  $u(x)$  according to this equation,

$$\left( \frac{d}{dx} u_0(x) \right)^2 = k(x)^2$$

which becomes on integration,

$$u_0(x) = \pm \int^x k(x) dx + C$$

If  $V(x)$  be constant, the latter is an exact solution, whereas, if  $V(x)$  vary with  $x$ , we generate a successive approximation with

$$\left( \frac{d}{dx} u(x) \right)^2 = k(x)^2 + i \frac{d^2}{dx^2} u(x)$$

When we substitute approximation  $n$  of the right side of the latter equation, approximation  $n + 1$  arises from mere quadrature.

$$u_{n+1}(x) = \pm \int^x \sqrt{k(x)^2 + i \left( \frac{d^2}{dx^2} u_n(x) \right)^n} dx + C_{n+1}$$

We hence obtain, for  $n = 0$ ,

$$u_1(x) = \pm \int^x \sqrt{k(x)^2 + i \left( \frac{d^2}{dx^2} u_0(x) \right)^n} dx + C_1 = \pm \int^x \sqrt{k(x)^2 + i \left( \frac{d}{dx} k(x) \right)} dx + C_1$$

in which the sign before  $i$  in the integral on the right should be  $\pm$ . Those two signs in the preceding four equations yield approximations to two particular solutions of the original differential equation for  $u(x)$  above, which we denote as  $u_{+,}$  and  $u_{-,}$  for a general solution,

$$u(x) = u_{+,} - i \ln \left( 1 + A e^{i(u_{-,} - u_{+,})} \right) + B = u_{-,} - i \ln \left( A + e^{i(u_{+,} - u_{-,})} \right) + B$$

in which appear arbitrary constants  $A$  and  $B$ , appropriate for an ordinary differential equation of second order. The corresponding solution of the Schrodinger equation is

$$\psi(x) = e^{iu(x)} = e^{iB} e^{iu_{+,}(x)} + A e^{iB} e^{iu_{-,}(x)},$$

which constitutes two particular approximate solutions of the original differential equation in a simple superposition. For the approximation procedure for  $u_{n+1}(x)$  to tend toward the correct  $u(x)$  depends on  $u_1(x)$  being near  $u_0(x)$ , which implies that

$$\left| \frac{d}{dx} k(x) \right| \ll |k(x)^2|$$

Both signs in the equation for  $u_1(x)$  on the right, i.e. the external sign and the internal sign before  $i$ , must be chosen the same as for  $u_0(x)$  above, for which  $u_1(x)$  serves as an improvement. If the great inequality, above, holds, we expand the integrand to obtain

$$u_1(x) = \int^x \left( \pm k(x) + \frac{i \left( \frac{d}{dx} k(x) \right)}{2 k(x)} \right) dx + C_1 = \pm \int^x k(x) dx + \frac{i}{2} \ln(k(x)) + C_1$$

Constant  $C_1$  of integration is immaterial because it affects only the normalisation of  $\psi(x)$ , which, if required, is implemented after completion of the approximations. The above derivation is known as the BKW approximation, and yields an approximate BKW amplitude function

$$\psi(x) = \frac{1}{\sqrt{k(x)}} e^{\pm \left( \int^x k(x) dx \right)}$$

In a classically accessible region in which  $E > V(x)$  is real, the two waves implied by the two signs in the preceding exponent before the integral propagate independently in opposite directions. When this BKW approximation is valid, potential energy  $V(x)$  varies so slowly with  $x$  that no reflected or scattered wave is generated as these waves propagate.

> restart:

In the following, adapted from *Quantum Mechanics using Computer Algebra* by W.-H. Steeb, World Scientific, Singapore, 1994, for the eigenvalue equation in one dimension,

$$\frac{d^2}{dx^2} u(x) + \frac{2m(E - V(x))u(x)}{\hbar^2} = 0,$$

in which, and in the commands below,  $\hbar = \frac{h}{2\pi}$ , we set

$$u(x) = e^{\frac{i w}{\hbar}}$$

and

$$w(x) = S(x) + \frac{\hbar}{i} \ln(A(x))$$

Both  $S(x)$  and  $\ln(A(x))$  are even functions of  $\hbar$ . When we insert the latter expressions into the eigenvalue equation, we obtain a system of equations as presented below.

$$\begin{aligned} &> \text{alias}(u=u(x), S=S(x), A=A(x), V=V(x)); \\ &u, S, A, V \end{aligned} \quad (33.14.4)$$

$$\begin{aligned} &> w := S + \hbar/(i) * \ln(A); \\ &w := S - i \hbar \ln(A) \end{aligned} \quad (33.14.5)$$

$$\begin{aligned} &> u := \exp(i*w/\hbar); \\ &u := e^{\frac{i(S - i \hbar \ln(A))}{\hbar}} \end{aligned} \quad (33.14.6)$$

$$\begin{aligned} &> R1 := \text{factor}(\text{expand}(\text{diff}(u, x\$2) + 2*m*(E-V(x))*u)); \\ R1 &:= \frac{1}{\hbar^2} \left( e^{\frac{iS}{\hbar}} \left( 2EA\hbar^2 m - 2AV(x)\hbar^2 m + iA \left( \frac{\partial^2}{\partial x^2} S \right) \hbar + 2i \left( \frac{\partial}{\partial x} S \right) \left( \frac{\partial}{\partial x} A \right) \hbar - A \left( \frac{\partial}{\partial x} S \right)^2 + \left( \frac{\partial^2}{\partial x^2} A \right) \hbar^2 \right) \right) \end{aligned} \quad (33.14.7)$$

$$\begin{aligned} &> R1a := \text{subs}(i=j, R1); \\ R1a &:= \frac{1}{\hbar^2} \left( e^{\frac{jS}{\hbar}} \left( 2EA\hbar^2 m - 2AV(x)\hbar^2 m + jA \left( \frac{\partial^2}{\partial x^2} S \right) \hbar + 2j \left( \frac{\partial}{\partial x} S \right) \left( \frac{\partial}{\partial x} A \right) \hbar - A \left( \frac{\partial}{\partial x} S \right)^2 + \left( \frac{\partial^2}{\partial x^2} A \right) \hbar^2 \right) \right) \end{aligned} \quad (33.14.8)$$

$$\begin{aligned} &> R1b := R1a * \hbar^2 / \exp(j*S/\hbar); \\ R1b &:= 2EA\hbar^2 m - 2AV(x)\hbar^2 m + jA \left( \frac{\partial^2}{\partial x^2} S \right) \hbar + 2j \left( \frac{\partial}{\partial x} S \right) \left( \frac{\partial}{\partial x} A \right) \hbar \\ &\quad - A \left( \frac{\partial}{\partial x} S \right)^2 + \left( \frac{\partial^2}{\partial x^2} A \right) \hbar^2 \end{aligned} \quad (33.14.9)$$

$$> R2 := \text{subs}(j=i, \text{simplify}(R1b - \text{subs}(j=0, R1b)) / j / \hbar^2 * \exp(j*S/\hbar));$$

$$R2 := \frac{\left( A \left( \frac{\partial^2}{\partial x^2} S \right) + 2 \left( \frac{\partial}{\partial x} S \right) \left( \frac{\partial}{\partial x} A \right) \right) e^{\frac{IS}{\hbar b}}}{\hbar b} \quad (33.14.10)$$

> R3 := R2/exp(1/hb\*S\*I);

$$R3 := \frac{A \left( \frac{\partial^2}{\partial x^2} S \right) + 2 \left( \frac{\partial}{\partial x} S \right) \left( \frac{\partial}{\partial x} A \right)}{\hbar b} \quad (33.14.11)$$

> R4 := simplify(subs(I=0,R1/exp(1/hb\*S\*I))\*exp(1/hb\*S\*I));

$$R4 := \frac{2 \left( \frac{\left( \frac{\partial^2}{\partial x^2} A \right) \hbar b^2}{2} + \left( -\frac{\left( \frac{\partial}{\partial x} S \right)^2}{2} + \hbar b^2 m (E - V(x)) \right) A \right) e^{\frac{IS}{\hbar b}}}{\hbar b^2} \quad (33.14.12)$$

> R5 := expand(R4/exp(1/hb\*S\*I)/A);

$$R5 := \frac{\frac{\partial^2}{\partial x^2} A}{A} - \frac{\left( \frac{\partial}{\partial x} S \right)^2}{\hbar b^2} + 2 E m - 2 V(x) m \quad (33.14.13)$$

The result with label R3, equation of continuity, can be integrated to yield

$$A(x) = C \left( \frac{d}{dx} S(x) \right)^{-\frac{1}{2}}$$

When we substitute this expression for  $A(x)$  into the result  $R5=0$ , we obtain this equation.

$$\left( \frac{d}{dx} S(x) \right)^2 = 2 m (E - V(x)) + \hbar b^2 \left( \frac{3 \left( \frac{\frac{d^2}{dx^2} S(x)}{\frac{d}{dx} S(x)} \right)^2}{4} + \frac{1 \left( \frac{d^3}{dx^3} S(x) \right)}{2 \left( \frac{d}{dx} S(x) \right)} \right)$$

This non-linear differential equation of third order in  $S(x)$  is equivalent to the initial eigenvalue equation. According to the BKW approximation, we expand  $S(x)$  in a power series in  $\hbar b^2$ .

$$S(x) = S_0(x) + \hbar b^2 S_1(x) + \hbar b^4 S_2(x) + \dots$$

#### e1.41 exercise

i) By substituting definitions 3 into equation 1, show that the units of energy  $E^{**}$  and length  $L$  are not independent; i.e. only one of these can be freely chosen. Show that the relation between  $L$  and  $E^{**}$  is

$$E^{**} = \frac{\hbar^2}{8 \pi^2 m L^2}, \text{ for a particle of mass } m \text{ subject to Schroedinger's equation.}$$

ii) Write the dimensionless Schroedinger equation for an infinite rectangular well of width  $2a$ .

iii) Write the dimensionless form of the potential energy for a finite rectangular well of width  $2a$  and depth  $V_0$  on choosing  $a$  as the length unit.

iv) Derive the dimensionless form of the harmonic potential energy  $V(r) = \frac{1}{2} m \omega^2 r^2$ , using  $\frac{h \omega}{2 \pi}$  as the unit of energy.

v) Derive the dimensionless form of the coulombic potential energy for the hydrogen atom,

$V_c(r) = -\frac{e^2}{4 \pi \epsilon_0} \frac{1}{r}$ , using as length the Bohr radius,  $a_0 = \frac{4 \pi \epsilon_0}{e^2} \frac{h^2}{4 \pi^2 m} \simeq 0.529 \cdot 10^{-10} \text{ m}$ , with mass  $m$  of the electron.

### 1.43 tunneling through a potential barrier

> **restart:**

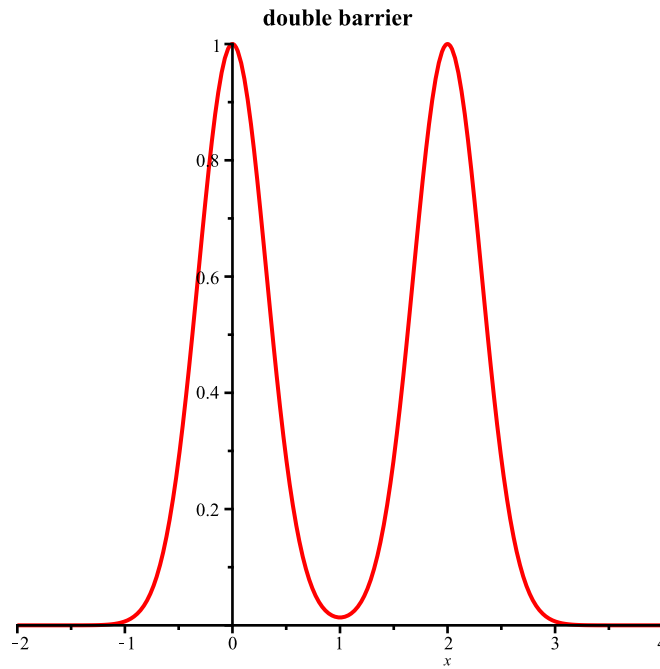
We solve the Schroedinger wave equation with scattering boundary conditions for an arbitrary potential function in one dimension. The boundary conditions (incident and reflected and transmitted waves) require the solution to have complex values. Our approach is to apply knowledge about a general solution to an ordinary differential equation of second order, requiring two independent solutions, and then to match to the physically imposed boundary conditions. This example is adapted from a worksheet prepared by Professor M. Horbatsch and appears here with his kind permission.

A conventional treatment begins with a simple potential shape (square barrier) for which an exact solution is obtainable. For a symbolic solution along these lines we refer the reader to M. Horbatsch: *Quantum Mechanics using Maple*, chapter 3.2, (Springer 1995). We here rely on numerical techniques included in *Maple*, namely to solve initial-value problems for systems of differential equations of first order. The tunneling problem requires us to solve a boundary-value problem, which is achieved on generating two independent unphysical solutions based on initial values, and then to match a linear combination of these to the physical boundary conditions. *Maple* has capability in **dsolve[numeric]** to handle a complex-valued differential equation, which permits a direct solution of the Schroedinger equation for scattering boundary conditions. To remain compatible with *Maple V* we stay, however, with real-valued boundary conditions for the solution of the differential equation, and introduce the complex-valued nature of the physical solution in the step in which linear combinations of two fundamental solutions are formed.

We could begin with simple barrier penetration, but we assume that the reader is already familiar with the basics of tunneling. We hence proceed with the more interesting double barrier. An example of a double-barrier potential is

$$\begin{aligned} > V := \exp(-5*x^2) + \exp(-5*(x-2)^2); \\ & \quad V := e^{-5x^2} + e^{-5(x-2)^2} \end{aligned} \tag{35.1}$$

```
> Vp := plot(V, x=-2..4, title="double barrier",
  colour=red, titlefont=[TIMES,BOLD,14]):
Vp;
```



Our interest is to discover transmission resonances. According to the plot, we safely assume that the interaction vanishes at  $x = -2$  and  $x = 4$  in this example. We work in units in which  $\frac{h}{2\pi} = m = 1$ , which simplifies relations between momentum and wavenumber as they become identical. The wavenumber (momentum) is obtained from the non-relativistic energy as

```
> kE := En -> sqrt(2*En);
```

$$kE := En \mapsto \sqrt{2 \cdot En} \quad (35.2)$$

We propagate two independent solutions, and then apply matching conditions. Schroedinger's amplitude equation is given as

```
> SE := En -> -1/2*diff(u(x),x$2) + (V - En)*u(x)=0;
```

$$SE := En \mapsto -\frac{\frac{d^2}{dx^2} u(x)}{2} + (V - En) \cdot u(x) = 0 \quad (35.3)$$

The boundary condition states that

- i) from the left is incident a free plane wave of wavenumber  $k$  and of known amplitude, and a reflected free plane wave of unknown amplitude; its magnitude squared eventually becomes the reflection probability and the choice of side from which the wave enters is arbitrary;
- ii) to the right of the potential region is outgoing a free plane wave of wavenumber  $k$  and unknown magnitude; the squared magnitude of the transmitted wave becomes the transmission probability when the incident wave is normalised to unity.

According to ii), the transmitted flux has the form  $T e^{ikx}$ ; the ratio of the derivative of the physical solution to the solution itself must hence equal  $i k$ . A strategy is thus to generate two independent solutions, and to form a linear combination that satisfies the requested relation. The initial and final values of the range of independent variables in the numerical integration of the differential equation are

```
> x_i := -2;
```

```
x_f := 4;
```

```
 $x_i := -2$ 
```

```
 $x_f := 4$ 
```

(35.4)

We choose a value of energy,

```
> En := 1/2;
```

```
 $En := \frac{1}{2}$ 
```

(35.5)

If complex-valued boundary conditions are desired, complex-valued solutions can result from use of

```
`dsolve/numeric/init_y0`:=subs();  
numeric=complex(numeric), eval(`dsolve/numeric/init_y0`));
```

We choose two initial conditions that provide independent solutions.

```
> IC1 := u(x_i)=1, D(u)(x_i)=1;
```

```
 $IC1 := u(-2) = 1, D(u)(-2) = 1$ 
```

(35.6)

```
> IC2 := u(x_i)=1, D(u)(x_i)=0;
```

```
 $IC2 := u(-2) = 1, D(u)(-2) = 0$ 
```

(35.7)

```
> sol1 := dsolve({SE(En), IC1}, u(x), numeric, output=listprocedure)  
:
```

```
> u1 := subs(sol1, u(x));
```

```
> ulp := subs(sol1, diff(u(x),x));
```

To demonstrate a result of calculation we evaluate these quantities.

```
> u1(x_f);
```

```
 $-1.00246529209570$ 
```

(35.8)

```
> ulp(x_f);
```

```
 $0.872615349234764$ 
```

(35.9)

For the second solution,

```
> sol2 := dsolve({SE(En), IC2}, u(x), numeric, output=listprocedure);
```

```
 $sol2 := \left[ x = \text{proc}(x) \dots \text{end proc}, u(x) = \text{proc}(x) \dots \text{end proc}, \frac{d}{dx} u(x) = \text{proc}(x) \right]$  (35.10)
```

```
...
```

```
end proc]
```

```
> #`dsolve/numeric/init_y0`:=subs(numeric=complex(numeric), eval  
(`dsolve/numeric/init_y0`));
```

```
> sol2 := dsolve({SE(En), IC2}, u(x), numeric, output=listprocedure):
```

```
> u2 := subs(sol2, u(x));
```

```
> u2p := subs(sol2, diff(u(x),x));
```

```
> u2(x_f);
```

```
 $-0.964456503435828$ 
```

(35.11)

```
> u2p(x_f);
```

-----

$$1.83707179567510$$

(35.12)

Having generated the two independent solutions using real boundary conditions, we proceed to assemble the complex-valued solution that satisfies the physical boundary condition of only a transmitted wave existing to the right of  $x_f$ . A necessary single mixing coefficient is determined on imposing that the ratio of the derivative over the solution equals  $i k$ .

```
> k := kE(En);
```

$$k := 1$$

(35.13)

```
> c2 := 'c2':
```

```
c2 := solve((u1p(x_f)+c2*u2p(x_f))/(u1(x_f)+c2*u2(x_f))=I*k,c2);
```

$$c2 := -0.5969537206 - 0.2322878153 I$$

(35.14)

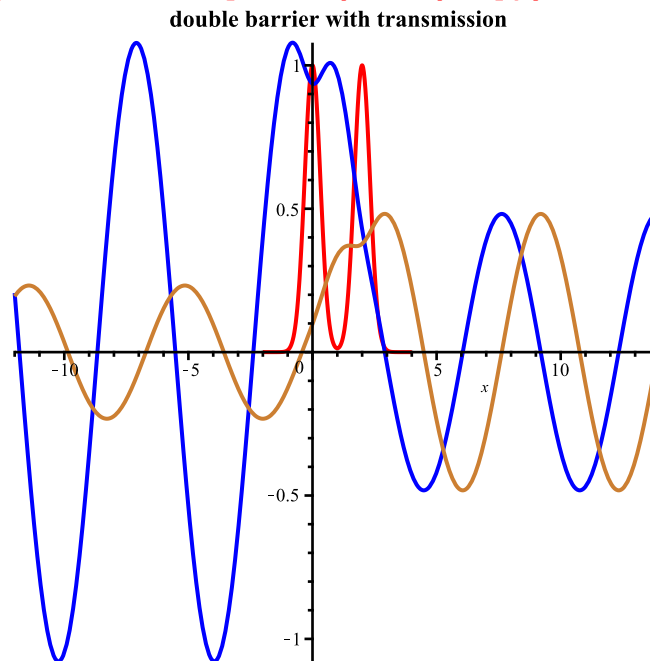
We form the physical solution, which has arbitrary normalisation at this point, and graph the real and imaginary parts:

```
> P1 := plot('Re(u1(x)+c2*u2(x))',x=-12..14, colour=blue):
```

```
> P2 := plot('Im(u1(x)+c2*u2(x))',x=-12..14, colour=gold):
```

```
> plots[display](Vp, P1,P2,title="double barrier with transmission",
```

```
colour=red, titlefont=[TIMES,BOLD,14]);
```



From this solution we proceed to extract the physical information. To the right of the potential there is a traveling plane wave, traveling to the right with momentum  $k$ ; we recognize the periodicity as about  $2\pi$ , corresponding to  $k=1$ ; we see that the imaginary part precedes the real part, corresponding to motion to the right; we can read amplitude  $T$ . On the left we must have the sum of an incident and reflected wave, which is characterized by unequal amplitudes for real and imaginary parts. In the middle we have a complicated connecting piece in which **dsolve[numeric]** and forming the linear combination have done the work for us. So far the incident wave has arbitrary normalisation; we calculate the normalisation from the solution in region I (at  $x = x_i$ ). We match at  $x_i$  a solution that has independent amplitudes for



the incoming and reflected waves, named  $V$  and  $R$  respectively:

```
> eq1 := N*exp(I*k*x_i)+R*exp(-I*k*x_i) = u1(x_i)+c2*u2(x_i);
      eq1 := N e-2I + R e2I = 0.403046279400000 - 0.232287815300000 I
```

(35.15)

```
> eq2 := I*(k*N*exp(I*k*x_i)-k*R*exp(-I*k*x_i)) = u1p(x_i)+c2*u2p(x_i);
      eq2 := I (N e-2I - R e2I) = 1. - 0. I
```

(35.16)

```
> sol := solve({eq1,eq2},{N,R});
      sol := {N=0.4763948527 + 0.4396508104 I, R=0.2651761400 - 0.3429849709 I}
```

(35.17)

```
> assign(sol);
```

We observe that  $N$  and  $R$  are amplitudes, which have complex values. The properly normalised reflection coefficient becomes

```
> r := R/N;
      r := -0.05821622771 - 0.6662333932 I
```

(35.18)

and the transmission coefficient is,

```
> t := evalf((u1(x_f)+c2*u2(x_f))/exp(I*k*x_f)/N);
      t := -0.367065730347691 - 0.646534864197233 I
```

(35.19)

A test whether this procedure all makes sense is to sum the magnitude squared for reflection and transmission.

```
> abs(r)^2 + abs(t)^2;
      1.00000064441822
```

(35.20)

Within numerical accuracy we preserve the norm; we hence interpret as reflection and transmission probabilities,

```
> abs(r)^2, abs(t)^2;
      0.4472560634, 0.552744581018218
```

(35.21)

We convert the calculation into a procedure that, for given energy, calculates the reflection and transmission coefficients. Our previously developed commands are used step by step as before.

```
> Tunnel := proc(En)
  local IC1,IC2,sol1,sol2,u1,u1p,u2,u2p,k,c2,N,R,r,t,sol,eq1,eq2;
  global V,kE,x_i,x_f;
  IC1 := u(x_i) = 1, D(u)(x_i) = 1;
  IC1 := u(x_i) = 1, D(u)(x_i) = 1;
  IC2 := u(x_i) = 1, D(u)(x_i) = 0;
  sol1 := dsolve({SE(En),IC1},u(x),numeric,output=listprocedure);
  u1 := subs(sol1,u(x));
  u1p := subs(sol1,diff(u(x),x));
  u1p := subs(sol1,diff(u(x),x));
  sol2 := dsolve({SE(En),IC2},u(x),numeric,output=listprocedure);
  u2 := subs(sol2,u(x));
  u2p := subs(sol2,diff(u(x),x));
```

```

k := kE(En);
c2 := solve((ulp(x_f)+c2*u2p(x_f))/(u1(x_f)+c2*u2(x_f))=I*k,c2);
N := 'N':
R := 'R':
eq1 := N*exp(I*k*x_i)+R*exp(-I*k*x_i) = u1(x_i)+c2*u2(x_i);
eq2 := I*(k*N*exp(I*k*x_i)-k*R*exp(-I*k*x_i)) = ulp(x_i)+c2*u2p
(x_i);
sol := solve({eq1,eq2}, {N,R});
assign(sol);
r := R/N;
t := evalf((u1(x_f) + c2*u2(x_f))/exp(I*k*x_f)/N);
#print(" R= ",abs(r)^2," T= ",abs(t)^2," R+T= ",abs(r)^2+abs(t)
^2," norm equal to 1.0 ?");
[abs(r)^2,abs(t)^2];
end proc:

```

We test for the previously calculated energy value.

```

> Tunnel(1/2);
[0.4472560634, 0.552744581018218]
(35.22)

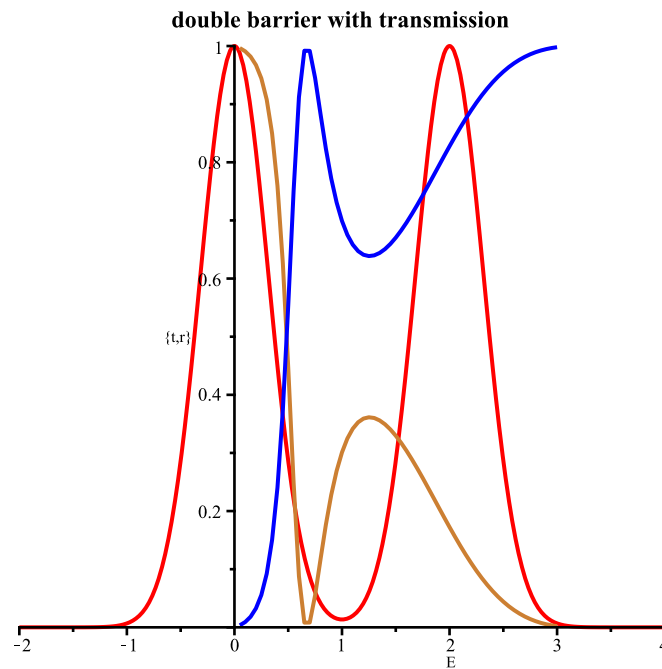
```

We proceed to scan the energy range from zero to above the peak height of the barrier. The results are accumulated in lists for subsequent plotting.

```

> Tr := [];
Rf := [];
for iE from 1 to 60 do
  En := iE/20;
  res := Tunnel(En);
  Tr := [op(Tr), [En,res[2]]];
  Rf := [op(Rf), [En,res[1]]];
end do;
> P1 := plot(Rf, colour=gold);
P2 := plot(Tr, colour=blue);
> plots[display](Vp, P1, P2, labels=["E","{t,r}"], title="double
barrier with transmission",
  colour=red, titlefont=[TIMES,BOLD,14]);

```



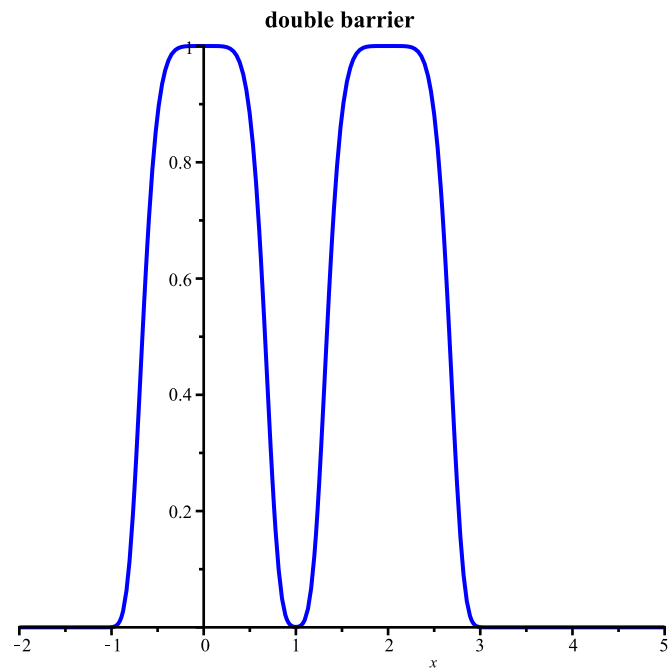
We observe the features that for sufficiently great energies only transmission occurs, whereas that classically this condition would apply for  $E > 1$ , and that for  $E = 0.66$  perfect transmission and no reflection is observed. This phenomenon is a transition resonance. The resonance structure has a width associated with it. Most physical phenomena that have their associated lifetime -- unstable elementary particles, alpha decay, nuclear gamma lines, atomic optical transitions, excitations in semiconductors, etc. -- can be understood as processes in which the amplitude equation describing the matter (or radiation) field involves tunneling. Broad resonances are associated with small lifetimes, sharp resonances with large lifetimes, according to Heisenberg's uncertainty relation for energy and time. The transmission resonance is broad. We can make the walls of the two barriers thicker, and observe what the effect is on the transmission probability.

```
> V := exp(-8*x^6) + exp(-8*(x-2)^6);
```

$$V := e^{-8x^6} + e^{-8(x-2)^6}$$

(35.23)

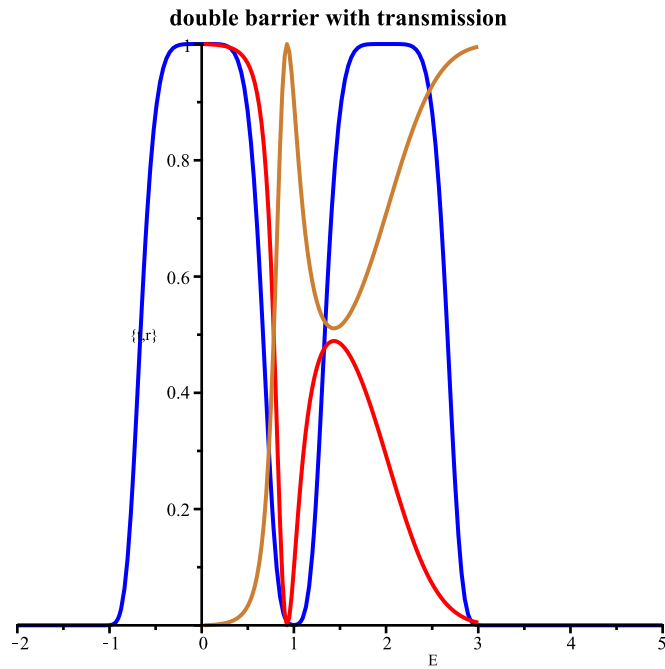
```
> Vp := plot(V, x=-2..5, title="double barrier",
  colour=blue, titlefont=[TIMES,BOLD,14]):
Vp;
```



```

> Tr := []:
Rf := []:
for iE from 1 to 120 do
  En := iE/40;
  res := Tunnel(En);
  Tr := [op(Tr), [En,res[2]]]:
  Rf := [op(Rf),[En,res[1]]]:
end do:
> P1 := plot(Rf, colour=red):
P2 := plot(Tr, colour=gold):
> plots[display](Vp, P1, P2, labels=["E","{t,r}"], title="double
barrier with transmission",
  colour=red, titlefont=[TIMES,BOLD,14]);

```



The transmission resonance sharpens, and occurs just below the classical value for the boundary of energy. We include an option in procedure Tunnel to graph the solution, to assist to understand how reflection and transmission occur.

```
> Tunnel := proc(En,iplot)
    local IC1,IC2,sol1,sol2,u1,ulp,u2,u2p,k,c2,N,R,r,t,sol,eq1,eq2;
    global V,kE,x_i,x_f,PL;
    IC1 := u(x_i) = 1, D(u)(x_i) = 1;
    IC2 := u(x_i) = 1, D(u)(x_i) = 0;
    sol1 := dsolve({SE(En),IC1},u(x), numeric,output=listprocedure);

    u1 := subs(sol1,u(x));
    ulp := subs(sol1,diff(u(x),x));
    sol2 := dsolve({SE(En),IC2},u(x), numeric,output=listprocedure);
    u2 := subs(sol2,u(x));
    u2p := subs(sol2,diff(u(x),x));
    k := kE(En);
    c2 := solve((ulp(x_f)+c2*u2p(x_f))/(u1(x_f)+c2*u2(x_f))=I*k, c2)
;
    N := 'N':
    R := 'R':
    eq1 := N*exp(I*k*x_i)+R*exp(-I*k*x_i) = u1(x_i)+c2*u2(x_i);
    eq2 := I*(k*N*exp(I*k*x_i)-k*R*exp(-I*k*x_i)) = ulp(x_i)+c2*u2p
(x_i);
    sol := solve({eq1,eq2}, {N,R});
    assign(sol);
    r := R/N;
```

```

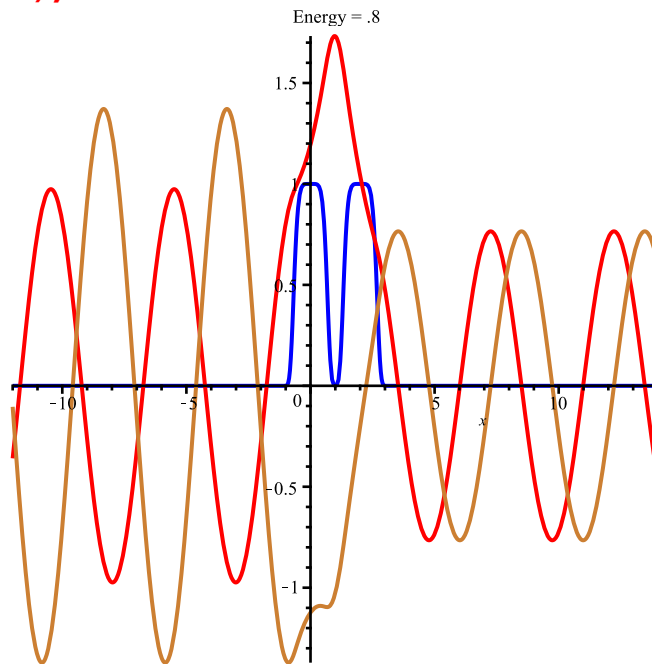
t := evalf((u1(x_f)+c2*u2(x_f))/exp(I*k*x_f)/N);
if iplot = 2 then print(" R= ",abs(r)^2," T= ",abs(t)^2," R+T=
",
                        abs(r)^2+abs(t)^2," norm equal to 1.0 ?")
end if;
if iplot = 1 then
  PL := plot([V,'Re((u1(x)+c2*u2(x))/N)','Im((u1(x)+c2*u2(x))/N)
'],
            x=x_i-10..x_f+10,colour=[blue,red,gold],
            title=cat("Energy = ",convert(evalf(En,3),string))):
end if;
[abs(r)^2, abs(t)^2];
end proc:
> Tunnel(0.8,1);
[0.4145493411, 0.585450568482717]
(35.24)

```

```

> plots[display](PL);

```

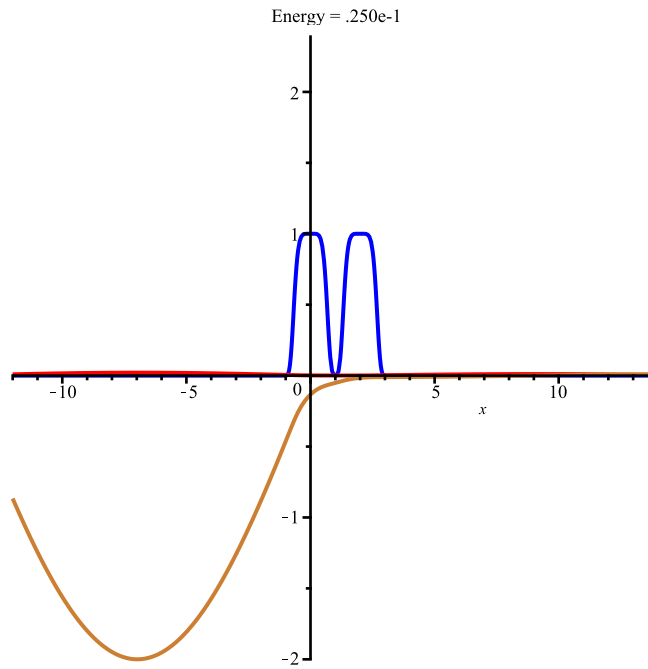


Can we form an animation as a function of energy? After an interval of computation, the result appears.

```

> PPL := 'PPL':
for iE from 1 to 120 do
  En := iE/40;
  res := Tunnel(En,1);
  PPL[iE] := PL:
end do:
> plots[display](seq(PPL[i],i=1..120),insequence=true);

```



The possibilities to explore scattering from various potentials with this worksheet appear to be unlimited. Transmission resonances appear to play a significant role in newly developed semiconductor devices, and might provide opportunities for computing hardware in future generations.

#### e1.42 exercise

Observe the result when the gap is widened between the potential maxima; be careful with the values of  $x_p$ ,  $x_f$  when the potential is altered.

#### 1.44 particle confined to a cuboid

> restart:

In this treatment of a particle confined to a cuboid with edges of lengths  $L_x$ ,  $L_y$ ,  $L_z$ , adapted from a derivation kindly provided by Dr. E. Castellon, we specify Schrodinger's temporally independent equation in three dimensions according to cartesian coordinates,

```
> pdeq := -h^2/(8*Pi^2*mu)*(diff(psi(x,y,z), x$2) + diff(psi(x,y,z),
y$2)
+ diff(psi(x,y,z), z$2)) + V*psi(x,y,z) = E*psi(x,y,z);
```

$$pdeq := - \frac{h^2 \left( \frac{\partial^2}{\partial x^2} \psi(x, y, z) + \frac{\partial^2}{\partial y^2} \psi(x, y, z) + \frac{\partial^2}{\partial z^2} \psi(x, y, z) \right)}{8 \pi^2 \mu} + V \psi(x, y, z) = E \psi(x, y, z) \quad (37.1)$$

z)

which we rearrange to free the derivative of coefficients.

```
> pdeq := diff(psi(x,y,z), x$2) + diff(psi(x,y,z), y$2) + diff(psi
(x,y,z), z$2)
+ 8*Pi^2*mu*V/h^2*psi(x,y,z) = 8*Pi^2*mu/h^2*E*psi(x,y,z);
```

(37.2)

$$\begin{aligned}
 pdeq &:= \frac{\partial^2}{\partial x^2} \psi(x, y, z) + \frac{\partial^2}{\partial y^2} \psi(x, y, z) + \frac{\partial^2}{\partial z^2} \psi(x, y, z) + \frac{8 \pi^2 \mu V \psi(x, y, z)}{h^2} \\
 &= \frac{8 \pi^2 \mu E \psi(x, y, z)}{h^2}
 \end{aligned} \tag{37.2}$$

We express the potential energy as a sum of contributions in directions  $x$ ,  $y$  and  $z$ ,

$$\begin{aligned}
 > \mathbf{V} := \mathbf{Vx(x)} + \mathbf{Vy(y)} + \mathbf{Vz(z)}; \\
 &V := Vx(x) + Vy(y) + Vz(z)
 \end{aligned} \tag{37.3}$$

and the total energy as a sum of contributions; although a dependence of these energies on a coordinate is implied in this separation purely for the purpose of separating the contributions to the total energy, that dependence is eliminated in the separate equations.

$$\begin{aligned}
 > \mathbf{E} := \mathbf{Ex(x)} + \mathbf{Ey(y)} + \mathbf{Ez(z)}; \\
 &E := Ex(x) + Ey(y) + Ez(z)
 \end{aligned} \tag{37.4}$$

This separation of potential energy and total energy into contributions according to the axes allows *Maple* to solve the partial differential equation.

$$\begin{aligned}
 > \mathbf{sol} := \mathbf{pdsolve(pdeq)}; \\
 sol &:= \psi(x, y, z) = \_F1(x) \_F2(y) \_F3(z) \textbf{ where } \left\{ \begin{aligned} &\frac{d^2}{dx^2} \_F1(x) = - \frac{\_F1(x) \_c1}{h^2} \\ &- \frac{8 \_F1(x) \pi^2 \mu (Vx(x) - Ex(x))}{h^2}, \frac{d^2}{dy^2} \_F2(y) = - \frac{\_F2(y) \_c2}{h^2} \\ &- \frac{8 \_F2(y) \pi^2 \mu (Vy(y) - Ey(y))}{h^2}, \frac{d^2}{dz^2} \_F3(z) = \frac{\_F3(z) \_c1}{h^2} + \frac{\_F3(z) \_c2}{h^2} \\ &- \frac{8 \_F3(z) \pi^2 \mu (Vz(z) - Ez(z))}{h^2} \end{aligned} \right\}
 \end{aligned} \tag{37.5}$$

$$\begin{aligned}
 > \mathbf{sols} := \mathbf{op(1, op(2, sol))}; \\
 sols &:= \left\{ \begin{aligned} &\frac{d^2}{dx^2} \_F1(x) = - \frac{\_F1(x) \_c1}{h^2} - \frac{8 \_F1(x) \pi^2 \mu (Vx(x) - Ex(x))}{h^2}, \frac{d^2}{dy^2} \_F2(y) = \\ &- \frac{\_F2(y) \_c2}{h^2} - \frac{8 \_F2(y) \pi^2 \mu (Vy(y) - Ey(y))}{h^2}, \frac{d^2}{dz^2} \_F3(z) = \frac{\_F3(z) \_c1}{h^2} \\ &+ \frac{\_F3(z) \_c2}{h^2} - \frac{8 \_F3(z) \pi^2 \mu (Vz(z) - Ez(z))}{h^2} \end{aligned} \right\}
 \end{aligned} \tag{37.6}$$

We separate the three differential equations,

$$\begin{aligned}
 > \textbf{for i from 1 to 3 do} \\
 &\quad \textbf{for j from 1 to nops(sols) do} \\
 &\quad \quad \textbf{if has(op(j, sols), [x,y,z][i]) = true}
 \end{aligned}$$



```

    then cat(Deq, [x,y,z][i]) := op(j, sols);
    else;
    end if;
end do;
end do;

```

into an equation dependent on x,

```
> Deqx;
```

$$\frac{d^2}{dx^2} F1(x) = -\frac{F1(x) - c_1}{h^2} - \frac{8 F1(x) \pi^2 \mu (Vx(x) - Ex(x))}{h^2} \quad (37.7)$$

an equation dependent on y, and

```
> Deqy;
```

$$\frac{d^2}{dy^2} F2(y) = -\frac{F2(y) - c_2}{h^2} - \frac{8 F2(y) \pi^2 \mu (Vy(y) - Ey(y))}{h^2} \quad (37.8)$$

an equation dependent on z.

```
> Deqz;
```

$$\frac{d^2}{dz^2} F3(z) = \frac{F3(z) - c_1}{h^2} + \frac{F3(z) - c_2}{h^2} - \frac{8 F3(z) \pi^2 \mu (Vz(z) - Ez(z))}{h^2} \quad (37.9)$$

We eliminate spurious terms, eliminate the dependence of total energies on coordinates and define the potential energy to be zero inside the cuboid and at its boundaries:  $V(x, y, z) = 0$  for  $0 \leq x \leq a$ ,  $V(x, y, z) = 0$  for  $0 \leq y \leq b$ ,  $V(x, y, z) = 0$  for  $0 \leq z \leq c$ .

```

> Deqx := subs(_c[1]=0, _c[2]=0, Ex(x)=-Ex, Ey(y)=-Ey, Ez(z)=-Ez, Vx
(x)=0,
    Vy(y)=0, Vz(z)=0, _F1=X, Deqx);
Deqy := subs(_c[1]=0, _c[2]=0, Ex(x)=-Ex, Ey(y)=-Ey, Ez(z)=-Ez, Vx
(x)=0,
    Vy(y)=0, Vz(z)=0, _F2=Y, Deqy);
Deqz := subs(_c[1]=0, _c[2]=0, Ex(x)=-Ex, Ey(y)=-Ey, Ez(z)=-Ez, Vx
(x)=0,
    Vy(y)=0, Vz(z)=0, _F3=Z, Deqz);

```

$$Deqx := \frac{d^2}{dx^2} X(x) = -\frac{8 X(x) \pi^2 \mu Ex}{h^2}$$

$$Deqy := \frac{d^2}{dy^2} Y(y) = -\frac{8 Y(y) \pi^2 \mu Ey}{h^2}$$

$$Deqz := \frac{d^2}{dz^2} Z(z) = -\frac{8 Z(z) \pi^2 \mu Ez}{h^2} \quad (37.10)$$

We solve these three ordinary-differential equations.

```
> solx := dsolve(Deqx);
```

$$solx := X(x) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ex}x}{h}\right) + \_C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ex}x}{h}\right) \quad (37.11)$$

> soly := dsolve(Deqy);

$$soly := Y(y) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ey}y}{h}\right) + \_C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ey}y}{h}\right) \quad (37.12)$$

> solz := dsolve(Deqz);

$$solz := Z(z) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ez}z}{h}\right) + \_C2 \cos\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ez}z}{h}\right) \quad (37.13)$$

One corner of the box is at the origin at which  $(x,y,z) = (0,0,0)$ ; at this point amplitude function  $\psi = X(x) Y(y) Z(z)$  must be zero, as a boundary condition; hence  $\_C2 = 0$ .

> solx := subs(\_C2=0, solx);

soly := subs(\_C2=0, soly);

solz := subs(\_C2=0, solz);

$$\begin{aligned} solx &:= X(x) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ex}x}{h}\right) \\ soly &:= Y(y) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ey}y}{h}\right) \\ solz &:= Z(z) = \_C1 \sin\left(\frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ez}z}{h}\right) \end{aligned} \quad (37.14)$$

We separate the coefficient of  $x, y, z$  in the sine formulae.

> sinxarg := op(op(2,op(2,solx)))/x;

sinyarg := op(op(2,op(2,soly)))/y;

sinzarg := op(op(2,op(2,solz)))/z;

$$\begin{aligned} sinxarg &:= \frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ex}}{h} \\ sinyarg &:= \frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ey}}{h} \\ sinzarg &:= \frac{2\sqrt{2}\pi\sqrt{\mu}\sqrt{Ez}}{h} \end{aligned} \quad (37.15)$$

As other boundary conditions, at  $x = Lx, y = Ly, z = Lz$ , the functions must be zero for each of  $X(x), Y(y), Z(z)$  different from zero; otherwise the amplitude function  $\psi$  is zero everywhere. As the sine functions must hence be equal to zero according to these boundary conditions, the arguments of the sine functions must be multiples of  $\pi$  when  $x = Lx, y = Ly, z = Lz$ .

> assume(nx::posint, ny::posint, nz::posint, h>0, Lx>0, Ly>0, Lz>0);

Ex := solve(sinxarg\*Lx=nx\*Pi, Ex);

Ey := solve(sinyarg\*Ly=ny\*Pi, Ey);

```
Ez := solve(sinzarg*Lz=nz*Pi, Ez);
```

$$E_x := \frac{\hbar^2 n_x^2}{8 L_x^2 \mu}$$

$$E_y := \frac{\hbar^2 n_y^2}{8 L_y^2 \mu}$$

$$E_z := \frac{\hbar^2 n_z^2}{8 L_z^2 \mu}$$

**(37.16)**

We normalise the amplitude functions such that the particle must be found somewhere within the box;

$\int_0^{L_x} X(x)^2 dx = 1$ ,  $\int_0^{L_y} Y(y)^2 dy = 1$ ,  $\int_0^{L_z} Z(z)^2 dz = 1$ . For the same reason each of  $X(x)$ ,  $Y(y)$ ,  $Z(z)$  must be zero for values of coordinates  $x$ ,  $y$ ,  $z$  outside the cuboid; otherwise the products  $V(x) X(x)$ ,  $V(y) Y(y)$  and  $V(z) Z(z)$  would be infinite, and the corresponding probability of finding the particle outside the cuboid would also be infinite.

```
> nrmx := simplify(int(rhs(solx)^2, x=0..Lx), symbolic) = 1;  
nrmy := simplify(int(rhs(soly)^2, y=0..Ly), symbolic) = 1;  
nrmz := simplify(int(rhs(solz)^2, z=0..Lz), symbolic) = 1;
```

$$nrmx := \frac{L_x \hbar^2 C_1^2}{2} = 1$$

$$nrmy := \frac{L_y \hbar^2 C_1^2}{2} = 1$$

$$nrmz := \frac{L_z \hbar^2 C_1^2}{2} = 1$$

**(37.17)**

We solve for coefficients  $C_1$ ;

```
> solve(nrmx, _C1):  
Ax := [%][1];  
solve(nrmy, _C1):  
Ay := [%][1];  
solve(nrmz, _C1):  
Az := [%][1];
```

$$A_x := \frac{\sqrt{2}}{\sqrt{L_x}}$$

$$A_y := \frac{\sqrt{2}}{\sqrt{L_y}}$$

$$A_z := \frac{\sqrt{2}}{\sqrt{L_z}}$$

**(37.18)**

The solutions  $X(x)$ ,  $Y(y)$  and  $Z(z)$  become

```
> solx := simplify(subs(_C1=Ax, solx), symbolic);
soly := simplify(subs(_C1=Ay, soly), symbolic);
solz := simplify(subs(_C1=Az, solz), symbolic);
```

$$\begin{aligned} solx &:= X(x) = \frac{\sqrt{2} \sin\left(\frac{\pi nx \sim x}{Lx \sim}\right)}{\sqrt{Lx \sim}} \\ soly &:= Y(y) = \frac{\sqrt{2} \sin\left(\frac{\pi ny \sim y}{Ly \sim}\right)}{\sqrt{Ly \sim}} \\ solz &:= Z(z) = \frac{\sqrt{2} \sin\left(\frac{\pi nz \sim z}{Lz \sim}\right)}{\sqrt{Lz \sim}} \end{aligned} \quad (37.19)$$

The total amplitude function is the product of these quantities.

```
> psi := simplify(rhs(solx)*rhs(soly)*rhs(solz));
```

$$\psi := \frac{2\sqrt{2} \sin\left(\frac{\pi nx \sim x}{Lx \sim}\right) \sin\left(\frac{\pi ny \sim y}{Ly \sim}\right) \sin\left(\frac{\pi nz \sim z}{Lz \sim}\right)}{\sqrt{Lx \sim} \sqrt{Ly \sim} \sqrt{Lz \sim}} \quad (37.20)$$

When we undertake inversion by replacing each coordinate with its negative value, equivalent to reflexion through a point, and divide by the amplitude function,

```
> simplify(subs(x=-x,y=-y,z=-z, psi))/psi;
-1 \quad (37.21)
```

we obtain  $-1$ , which indicates a negative parity. A scalar quantity or a polar vector has negative parity whereas an axial vector or pseudovector has positive parity. The minimum value of  $nx$  or  $ny$  or  $nz$  must be unity; the total amplitude function is otherwise identically zero so that the particle does not exist. We test the normalisation to ensure that the total probability of finding the particle somewhere within the box is unity.

```
> Int('psi'*psi', x=0..Lx, y=0..Ly, z=0..Lz) = int(psi*psi, x=0..
Lx, y=0..Ly, z=0..Lz);
```

$$\int_0^{Lz \sim} \int_0^{Ly \sim} \int_0^{Lx \sim} \psi^2 dx dy dz = 1 \quad (37.22)$$

To calculate the Heisenberg uncertainty, we define the momentum operator in three dimensions,

```
> p := F -> h/(I*2*Pi)*(diff(F, x) + diff(F, y) + diff(F, z));
```

$$p := F \mapsto -\frac{1}{2} I h \left( \frac{\partial}{\partial x} F + \frac{\partial}{\partial y} F + \frac{\partial}{\partial z} F \right) \quad (37.23)$$

and the position operator in three dimensions.

```
> q := F -> (x+y+z)*F;
```

$$q := F \mapsto (x + y + z) \cdot F \quad (37.24)$$

The mean momentum  $\langle p \rangle$  is

$$\begin{aligned} &> \text{p\_av} := \text{int}(\text{psi} * \text{p}(\text{psi}), \text{x}=0..\text{Lx}, \text{y}=0..\text{Ly}, \text{z}=0..\text{Lz}); \\ &\quad \text{p\_av} := 0 \end{aligned} \quad (37.25)$$

The mean squared momentum  $\langle p^2 \rangle$  is

$$\begin{aligned} &> \text{p2\_av} := \text{expand}(\text{int}(\text{psi} * \text{p}(\text{p}(\text{psi})), \text{x}=0..\text{Lx}, \text{y}=0..\text{Ly}, \text{z}=0..\text{Lz})); \\ &\quad \text{p2\_av} := \frac{\hbar^2 n_{z\sim}^2}{4 L_{z\sim}^2} + \frac{\hbar^2 n_{y\sim}^2}{4 L_{y\sim}^2} + \frac{\hbar^2 n_{x\sim}^2}{4 L_{x\sim}^2} \end{aligned} \quad (37.26)$$

The mean position  $\langle q \rangle$  is

$$\begin{aligned} &> \text{q\_av} := \text{simplify}(\text{int}(\text{psi} * \text{q}(\text{psi}), \text{x}=0..\text{Lx}, \text{y}=0..\text{Ly}, \text{z}=0..\text{Lz})); \\ &\quad \text{q\_av} := \frac{L_{x\sim}}{2} + \frac{L_{y\sim}}{2} + \frac{L_{z\sim}}{2} \end{aligned} \quad (37.27)$$

which corresponds to the centre of the cuboid. The mean squared position  $\langle q^2 \rangle$  is

$$\begin{aligned} &> \text{q2\_av} := \text{expand}(\text{simplify}(\text{int}(\text{psi} * \text{q}(\text{q}(\text{psi})), \text{x}=0..\text{Lx}, \text{y}=0..\text{Ly}, \text{z}=0.. \\ &\quad \text{Lz}))); \\ &\quad \text{q2\_av} := \frac{L_{x\sim}^2}{3} + \frac{L_{x\sim} L_{y\sim}}{2} + \frac{L_{x\sim} L_{z\sim}}{2} + \frac{L_{y\sim}^2}{3} + \frac{L_{y\sim} L_{z\sim}}{2} + \frac{L_{z\sim}^2}{3} - \frac{L_{x\sim}^2}{2 \pi^2 n_{x\sim}^2} \\ &\quad - \frac{L_{y\sim}^2}{2 \pi^2 n_{y\sim}^2} - \frac{L_{z\sim}^2}{2 \pi^2 n_{z\sim}^2} \end{aligned} \quad (37.28)$$

The uncertainty in position ( $\Delta q$ ) is hence

$$\begin{aligned} &> \text{Delta\_q} := (\text{q2\_av} - (\text{q\_av})^2)^{(1/2)}; \\ &\text{Delta\_q} := \\ &\quad \left( - \left( \frac{L_{x\sim}}{2} + \frac{L_{y\sim}}{2} + \frac{L_{z\sim}}{2} \right)^2 + \frac{L_{x\sim}^2}{3} + \frac{L_{x\sim} L_{y\sim}}{2} + \frac{L_{x\sim} L_{z\sim}}{2} + \frac{L_{y\sim}^2}{3} + \frac{L_{y\sim} L_{z\sim}}{2} \right. \\ &\quad \left. + \frac{L_{z\sim}^2}{3} - \frac{L_{x\sim}^2}{2 \pi^2 n_{x\sim}^2} - \frac{L_{y\sim}^2}{2 \pi^2 n_{y\sim}^2} - \frac{L_{z\sim}^2}{2 \pi^2 n_{z\sim}^2} \right)^{1/2} \end{aligned} \quad (37.29)$$

and the uncertainty in momentum ( $\Delta p$ ) is

$$\begin{aligned} &> \text{Delta\_p} := (\text{p2\_av} - (\text{p\_av})^2)^{(1/2)}; \\ &\quad \text{Delta\_p} := \sqrt{\frac{\hbar^2 n_{z\sim}^2}{4 L_{z\sim}^2} + \frac{\hbar^2 n_{y\sim}^2}{4 L_{y\sim}^2} + \frac{\hbar^2 n_{x\sim}^2}{4 L_{x\sim}^2}} \end{aligned} \quad (37.30)$$

The product of these uncertainties is  $\Delta q \Delta p$ .

$$\begin{aligned} &> \text{DqDp} := \text{expand}(\text{simplify}(\text{Delta\_q} * \text{Delta\_p})); \\ &\text{DqDp} := \end{aligned} \quad (37.31)$$

$$\frac{1}{12 \pi n_{x\sim} n_{y\sim} n_{z\sim} L_{z\sim} L_{y\sim} L_{x\sim}} \left( \sqrt{3} \left( L_{x\sim}^2 \pi^2 n_{x\sim}^2 n_{y\sim}^2 n_{z\sim}^2 + L_{y\sim}^2 \pi^2 n_{x\sim}^2 n_{y\sim}^2 n_{z\sim}^2 \right. \right.$$

$$+ Lz^2 \pi^2 nx^2 ny^2 nz^2 - 6 Lx^2 ny^2 nz^2 - 6 Ly^2 nx^2 nz^2 - 6 Lz^2 nx^2 ny^2) \\^{1/2} h \sqrt{Lx^2 Ly^2 nz^2 + ny^2 Lz^2 Lx^2 + nx^2 Lz^2 Ly^2}$$

For the state of least energy and a cubic box of length  $L$ ,

```
> DqDp_3D := simplify(subs(nx=1, ny=1, nz=1, Lx=L, Ly=L, Lz=L,
(Delta_q*Delta_p))) assuming L>0;
```

$$DqDp_{3D} := \frac{\sqrt{\pi^2 - 6} \sqrt{3} h}{4 \pi} \quad (37.32)$$

```
> DqDp_3D2p := %*2*Pi:
```

```
evalf(DqDp_3D2p)/`2*Pi`;
```

$$\frac{1.703585426 h}{2 \pi} \quad (37.33)$$

which is greater than  $\frac{1}{2} \frac{h}{2 \pi}$ . We repeat the calculations for a particle confined to a line segment, using the above result for  $X(x)$ .

$$\langle p_x \rangle$$

```
> px_av := int(rhs(solx) * h/(2*Pi*I)*diff(rhs(solx),x), x=0..Lx);
```

$$px_{av} := 0 \quad (37.34)$$

$$\langle p_x^2 \rangle$$

```
> px2_av := int(rhs(solx) * h/(2*Pi*I)*diff(h/(2*Pi*I)*diff(rhs
(solx),x),x), x=0..Lx);
```

$$px2_{av} := \frac{h^2 nx^2}{4 Lx^2} \quad (37.35)$$

$$\langle q_x \rangle$$

```
> qx_av := simplify(int(rhs(solx) * x * rhs(solx), x=0..Lx));
```

$$qx_{av} := \frac{Lx}{2} \quad (37.36)$$

$$\langle q_x^2 \rangle$$

```
> qx2_av := simplify(int(rhs(solx) * x^2 * rhs(solx), x=0..Lx));
```

$$qx2_{av} := \frac{2 Lx^2 \pi^2 nx^2 - 3 Lx^2}{6 nx^2 \pi^2} \quad (37.37)$$

$$\Delta q$$

```
> Delta_qx := (qx2_av - (qx_av)^2)^(1/2);
```

$$(37.38)$$

$$\Delta q_x := \sqrt{-\frac{Lx^2}{4} + \frac{2 Lx^2 \pi^2 nx^2 - 3 Lx^2}{6 nx^2 \pi^2}} \quad (37.38)$$

$\Delta p$

```
> Delta_px := (px2_av - (px_av)^2)^(1/2);
```

$$\Delta p_x := \frac{\sqrt{4} \sqrt{\frac{h^2 nx^2}{Lx^2}}}{4} \quad (37.39)$$

$\Delta q_x \Delta p_x$

```
> DqDp_1D := simplify(subs(nx=1, Delta_qx*Delta_px));
```

$$DqDp_{1D} := \frac{\sqrt{\pi^2 - 6} \sqrt{3} h}{12 \pi} \quad (37.40)$$

The product of uncertainties in the box is hence

```
> DqDp_3D/DqDp_1D;
```

3

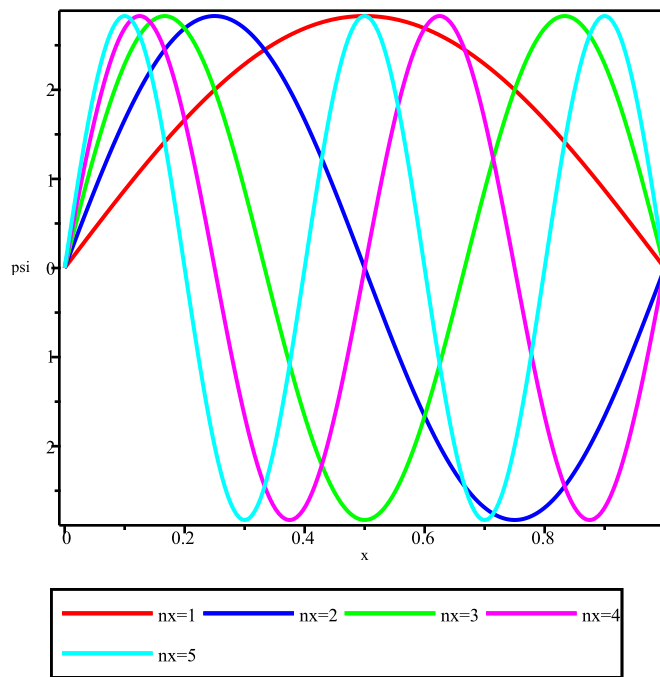
(37.41)

three times the corresponding value for the case of a particle confined to a line segment. **Hence the more dimensions has the enclosure of the particle, the greater is the uncertainty.**

We seek to plot the amplitude function, but it is impossible to plot the total value of an object in three dimensions as a function of each coordinate, which requires four spatial dimensions. We hence first plot the normalised amplitude functions for a cube with sides of unit length for a few values of  $nx$  along axis

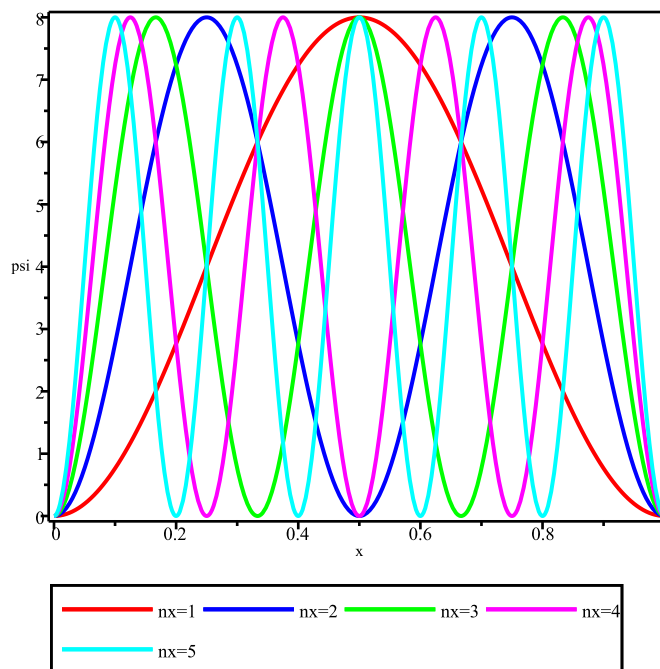
$x$ , with  $y = z$  fixed at  $\frac{1}{2}$  and  $ny = nz = 1$ ,

```
> plot([seq(eval(psi, [nx=j, ny=1, nz=1, Lx=1, Ly=1, Lz=1, y=0.5, z=
0.5]), j=1..5)],
       x=0..1, colour=[red,blue,green,magenta,cyan], labels=["x",
"psi"],
       legend=["nx=1", "nx=2", "nx=3", "nx=4", "nx=5"], axes=boxed);
```



and then their squares.

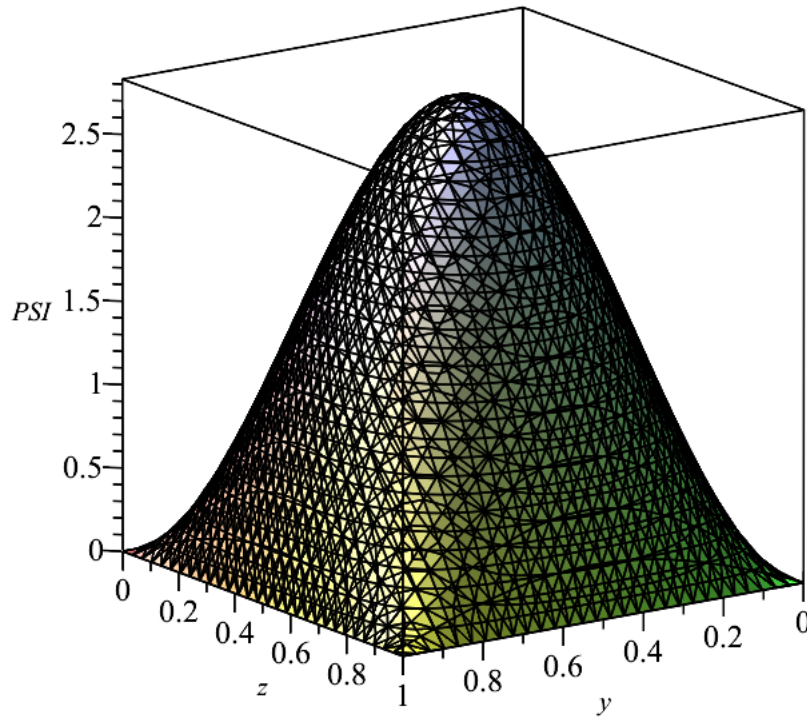
```
> plot([seq(eval(psi^2, [nx=j, ny=1, nz=1, Lx=1, Ly=1, Lz=1, y=0.5,
z=0.5])), j=1..5)],
       x=0..1, colour=[red,blue,green,magenta,cyan], labels=["x",
"psi"],
       legend=["nx=1", "nx=2", "nx=3", "nx=4", "nx=5"], axes=boxed);
```



We plot also in two dimensions the amplitude function for a cube for the state of least energy with  $x$  fixed at  $\frac{1}{2}$ .



```
> plots:-implicitplot3d(PSI = subs(nx=1, ny=1, nz=1, Lx=1, Ly=1, Lz=
1, x=0.5, psi), y=0..1, z=0..1, PSI=0..2.83, axes=boxed);
```



Here we animate the amplitude function showing how the total amplitude function  $\psi(x, y, z)$  varies as  $x$  varies from 0 to  $Lx = 1$ .

```
> ns := [2,1,1];
   Ls := [1,1,1];
   substitutions := nx = ns[1], ny = ns[2], nz = ns[3],
                     Lx = Ls[1], Ly = Ls[2], Lz = Ls[3]:
   MAX := maximize( subs(substitutions, psi), x=0..1, y=0..1, z=0..1
);
   MIN := minimize( subs(substitutions, psi), x=0..1, y=0..1, z=0..1
);
   plots:-animate(plots:-implicitplot3d, [PSI = subs(substitutions,
x=t, psi),
                     y=0..Ls[2], z=0..Ls[3], PSI=MIN..MAX], t=0..Ls[1], grid=
[30,30,30],axes=boxed);
```

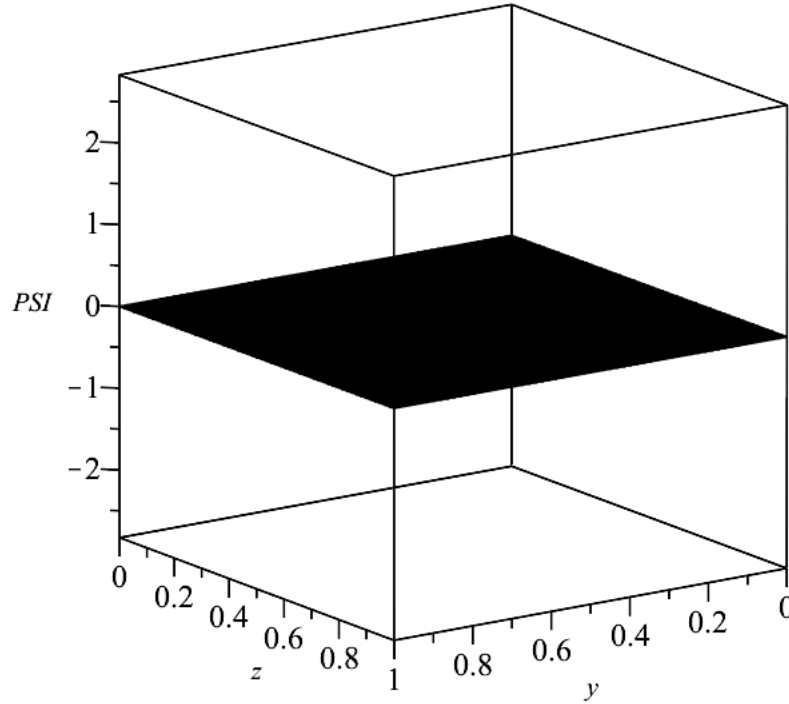
$ns := [2, 1, 1]$

$Ls := [1, 1, 1]$

$MAX := 2\sqrt{2}$

$$MIN := -2\sqrt{2}$$

$t=0.$



The total energy is the sum of the three contributions,

**> Et := collect(Ex + Ey + Ez, [h,mu]);**

$$Et := \frac{\left( \frac{nx^2}{8 Lx^2} + \frac{ny^2}{8 Ly^2} + \frac{nz^2}{8 Lz^2} \right) h^2}{\mu} \quad (37.42)$$

For the particle to exist within the enclosure, the value of each quantum number  $nx$ ,  $ny$ ,  $nz$  must be at least unity; otherwise  $\psi = 0$  and  $\psi^2 = 0$ , so that the particle does not exist. The minimum energy of the system hence corresponds to the case  $nx = ny = nz = 1$ ,

**> Etr := eval(Et, [nx=1, ny=1, nz=1]);**

$$Etr := \frac{\left( \frac{1}{8 Lx^2} + \frac{1}{8 Ly^2} + \frac{1}{8 Lz^2} \right) h^2}{\mu} \quad (37.43)$$

which implies a *residual energy*, relative to the zero of potential energy, similarly to the case of the canonical linear harmonic oscillator in section group 1.2. This residual energy is here inversely proportional to the squared length of the enclosure in each direction; for a large enclosure, the differences of energy between states of adjacent energy become small, and this residual energy likewise

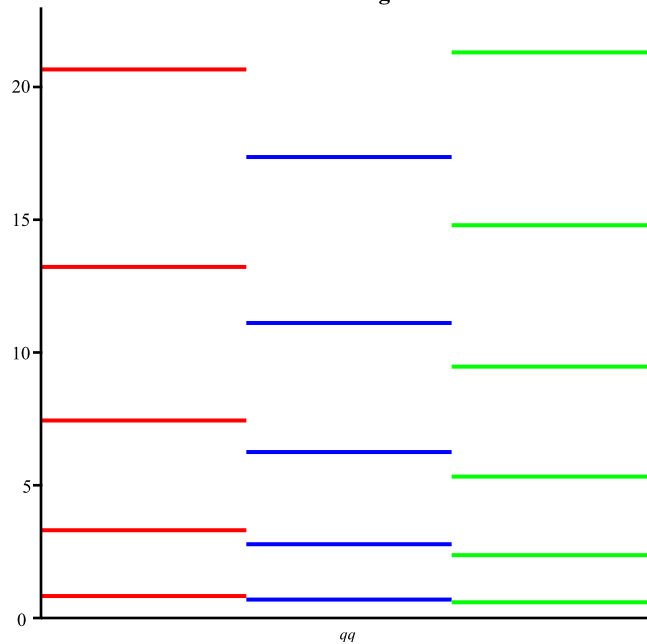
tends to become small.

For lengths  $L_x = 1.1$ ,  $L_y = 1.2$ ,  $L_z = 1.3$ , we prepare to plot the energies, reduced as  $\frac{8 E_j L_j^2 \mu}{h^2}$  with  $j = x, y, z$ , as vertical manifolds, one for each quantum number.

```
> plx := plot([seq(eval(Ex*8*Lx^2/1.1^2*mu/h^2, nx=j), j=1..5)], qq=
  0..1, colour=red):
  ply := plot([seq(eval(Ey*8*Ly^2/1.2^2*mu/h^2, ny=j), j=1..5)], qq=
  1..2, colour=blue):
  plz := plot([seq(eval(Ez*8*Lz^2/1.3^2*mu/h^2, nz=j), j=1..6)], qq=
  2..3, colour=green):
```

We plot these manifolds.

```
> plots[display]({plx,ply,plz}, title="relative reduced energies of
  states", titlefont=[TIMES,BOLD,14],
  view=[0..3,0..23], tickmarks=[0,5]);
```



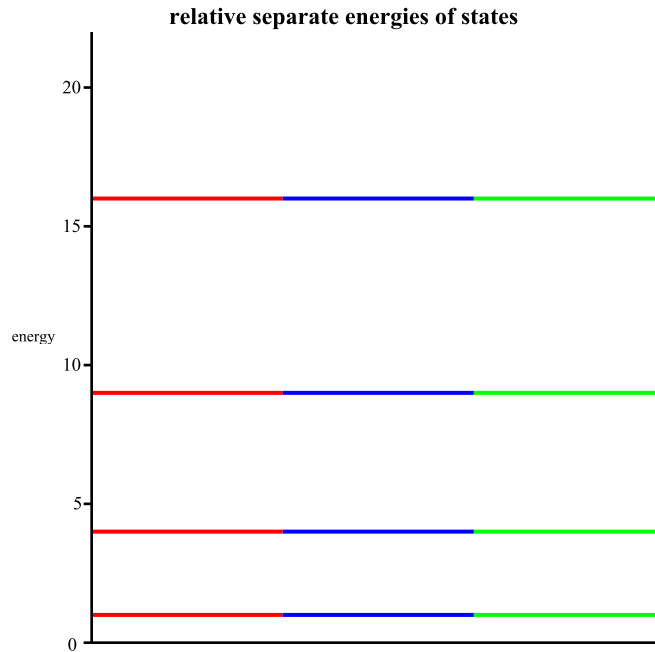
When no two of edges  $L_x, L_y, L_z$  are in the ratio of integers, the energies corresponding to values of three quantum numbers  $n_x, n_y, n_z$  in various sets are all distinct, as shown above. When an integral relation among  $L_x, L_y, L_z$  exists, particular values of energy corresponding to the three quantum numbers in two or more distinct sets occur, and their respective amplitude functions are independent: such an energy has an associated [degeneracy](#) and the system is described as being in a [degenerate state](#); the degree of degeneracy is specified as the number of independent sets of quantum numbers, and the degeneracy of states of a system is a consequence of symmetry. If the cuboid be a regular cube, we plot the individual values of energy, in unit  $\frac{h^2}{8 \mu L^2}$ , associated with the three quantum numbers as follows.

```
> plx := plot([seq(eval(Ex*8*Lx^2*mu/h^2, nx=j), j=1..5)], qq=0..1,
  colour=red):
  ply := plot([seq(eval(Ey*8*Ly^2*mu/h^2, ny=j), j=1..5)], qq=1..2,
```

```

colour=blue):
plz := plot([seq(eval(Ez*8*Lz^2*mu/h^2, nz=j), j=1..5)], qq=2..3,
colour=green):
> #plt := plot([seq(eval(Ex*8*Lx^2*mu/h^2+Ey*8*Ly^2*mu/h^2+Ez*8*
Lz^2*mu/h^2,
# [mu=1,h=1,Lz=1/sqrt(8),nz=j]), j=1..5)], qq=2..3,
colour=green):
plots[display]({plx,ply,plz}, title="relative separate energies of
states", titlefont=[TIMES,BOLD,14],
view=[0..3,0..22], labels=["","energy"], tickmarks=
[0,5]);

```



The minimum energy of the particle confined to a cubic enclosure in three dimensions is

```
> Etm := eval(Et, [nx=1, ny=1, nz=1, Lx=L, Ly=L, Lz=L]);
```

$$E_{tm} := \frac{3 \hbar^2}{8 L^2 \mu} \quad (37.44)$$

for comparison with the minimum energy of the particle confined to a line segment.

```
> Exm := eval(Ex, [nx=1, Lx=L]);
```

$$E_{xm} := \frac{\hbar^2}{8 L^2 \mu} \quad (37.45)$$

The residual energy of the particle confined symmetrically in three dimensions is thus three times that of a particle confined to one dimension.

We permute the squares of the quantum numbers to indicate the various possible sets.

```
> E1 := combinat[permute]([seq(nx^2, nx=1..5), seq(ny^2, ny=1..5),
seq(nz^2, nz=1..5)], 3);
```

(37.46)

$E1 := [ [1, 4, 9], [1, 4, 16], [1, 4, 25], [1, 4, 1], [1, 4, 4], [1, 9, 4], [1, 9, 16], [1, 9, 25], [1, 9, 1], [1, 9, 9], [1, 16, 4], [1, 16, 9], [1, 16, 25], [1, 16, 1], [1, 16, 16], [1, 25, 4], [1, 25, 9], [1, 25, 16], [1, 25, 1], [1, 25, 25], [1, 1, 4], [1, 1, 9], [1, 1, 16], [1, 1, 25], [1, 1, 1], [4, 1, 9], [4, 1, 16], [4, 1, 25], [4, 1, 1], [4, 1, 4], [4, 9, 1], [4, 9, 16], [4, 9, 25], [4, 9, 4], [4, 9, 9], [4, 16, 1], [4, 16, 9], [4, 16, 25], [4, 16, 4], [4, 16, 16], [4, 25, 1], [4, 25, 9], [4, 25, 16], [4, 25, 4], [4, 25, 25], [4, 4, 1], [4, 4, 9], [4, 4, 16], [4, 4, 25], [4, 4, 4], [9, 1, 4], [9, 1, 16], [9, 1, 25], [9, 1, 1], [9, 1, 9], [9, 4, 1], [9, 4, 16], [9, 4, 25], [9, 4, 4], [9, 4, 9], [9, 16, 1], [9, 16, 4], [9, 16, 25], [9, 16, 9], [9, 16, 16], [9, 25, 1], [9, 25, 4], [9, 25, 16], [9, 25, 9], [9, 25, 25], [9, 9, 1], [9, 9, 4], [9, 9, 16], [9, 9, 25], [9, 9, 9], [16, 1, 4], [16, 1, 9], [16, 1, 25], [16, 1, 1], [16, 1, 16], [16, 4, 1], [16, 4, 9], [16, 4, 25], [16, 4, 4], [16, 4, 16], [16, 9, 1], [16, 9, 4], [16, 9, 25], [16, 9, 9], [16, 9, 16], [16, 25, 1], [16, 25, 4], [16, 25, 9], [16, 25, 16], [16, 25, 25], [16, 16, 1], [16, 16, 4], [16, 16, 9], [16, 16, 25], [16, 16, 16], [25, 1, 4], [25, 1, 9], [25, 1, 16], [25, 1, 1], [25, 1, 25], [25, 4, 1], [25, 4, 9], [25, 4, 16], [25, 4, 4], [25, 4, 25], [25, 9, 1], [25, 9, 4], [25, 9, 16], [25, 9, 9], [25, 9, 25], [25, 16, 1], [25, 16, 4], [25, 16, 9], [25, 16, 16], [25, 16, 25], [25, 25, 1], [25, 25, 4], [25, 25, 9], [25, 25, 16], [25, 25, 25]] ]$  (37.46)

Here is a list of the sums of components.

```
> sort([seq(add(E1[j,k], k=1..3), j=1..nops(E1))]);
[3, 6, 6, 6, 9, 9, 9, 11, 11, 11, 12, 14, 14, 14, 14, 14, 14, 17, 17, 17, 18, 18, 18, 19, 19, 19, 21, 21, 21, 21, 21, 22, 22, 22, 24, 24, 24, 26, 26, 26, 26, 26, 26, 27, 27, 27, 27, 29, 29, 29, 29, 29, 29, 30, 30, 30, 30, 30, 30, 33, 33, 33, 33, 33, 33, 34, 34, 34, 35, 35, 35, 35, 35, 35, 36, 36, 36, 38, 38, 38, 38, 38, 38, 41, 41, 41, 42, 42, 42, 42, 42, 42, 43, 43, 43, 45, 45, 45, 45, 45, 45, 48, 50, 50, 50, 50, 50, 50, 51, 51, 51, 54, 54, 54, 57, 57, 57, 59, 59, 59, 66, 66, 66, 75]
```

 (37.47)

We sort them according to increasing order of the sum of their components.

```
> sort({seq(add(E1[j,k], k=1..3), j=1..nops(E1))});
{3, 6, 9, 11, 12, 14, 17, 18, 19, 21, 22, 24, 26, 27, 29, 30, 33, 34, 35, 36, 38, 41, 42, 43, 45, 48, 50, 51, 54, 57, 59, 66, 75}
```

 (37.48)

To count the number of states, defined by these permutations of squares of integers chosen three at a time, we generate a series in some variable  $v$ ,

```
> Order := 37;
s1 := series(add(v^(i^2), i=1..isqrt(Order)), v);
Order := 37
s1 := v + v^4 + v^9 + v^16 + v^25 + v^36
```

 (37.49)

```
> s2 := series(s1*s1, v);
```

$$s_2 := v^2 + 2v^5 + v^8 + 2v^{10} + 2v^{13} + 2v^{17} + v^{18} + 2v^{20} + 2v^{25} + 2v^{26} + 2v^{29} + v^{32} + 2v^{34} + O(v^{37}) \quad (37.50)$$

```
> s3 := series(s1*s2, v);
```

$$s_3 := v^3 + 3v^6 + 3v^9 + 3v^{11} + v^{12} + 6v^{14} + 3v^{17} + 3v^{18} + 3v^{19} + 6v^{21} + 3v^{22} + 3v^{24} + 6v^{26} + 4v^{27} + 6v^{29} + 6v^{30} + 6v^{33} + 3v^{34} + 6v^{35} + 3v^{36} + O(v^{38}) \quad (37.51)$$

The number of states for a particular energy, or the degree of degeneracy, is given by the coefficient of  $v$  with that energy as exponent; for instance, the number of states for  $E = 14$  is

```
> coeff(s3, v, 14);
```

$$6 \quad (37.52)$$

which we confirm by calculating the number of permutations of  $[1^2, 2^2, 3^2]$  such that  $1^2 + 2^2 + 3^2 = 14$ .

```
> combinat[permute]([1^2, 2^2, 3^2]);
```

$$[[1, 4, 9], [1, 9, 4], [4, 1, 9], [4, 9, 1], [9, 1, 4], [9, 4, 1]] \quad (37.53)$$

```
> nops(%);
```

$$6 \quad (37.54)$$

When we extract the operands of series  $s_3$ ,

```
> ol := seq(op(s3)[i], i=1..40);
```

$$ol := 1, 3, 3, 6, 3, 9, 3, 11, 1, 12, 6, 14, 3, 17, 3, 18, 3, 19, 6, 21, 3, 22, 3, 24, 6, 26, 4, 27, 6, 29, 6, 30, 6, 33, 3, 34, 6, 35, 3, 36 \quad (37.55)$$

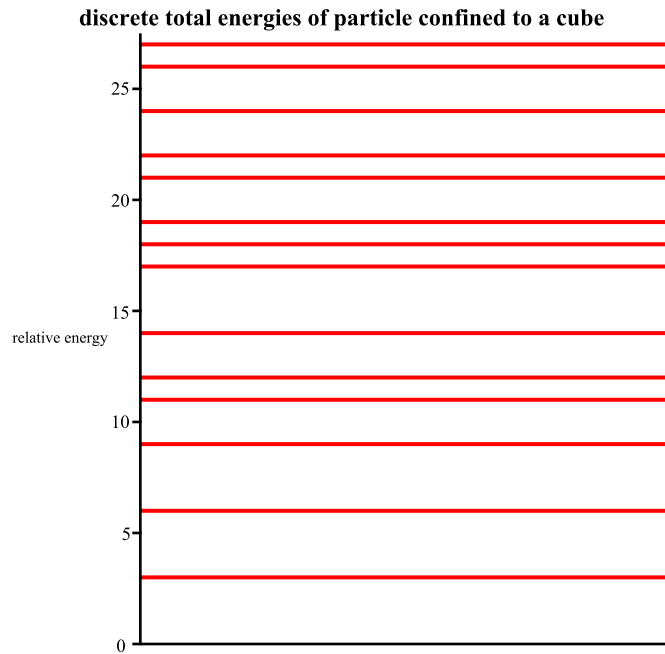
we find that the odd entries are the coefficients of the terms of which the even entries are the exponents. We add the coefficients to find the number of permutations of quantum numbers that specify states up to energy 36 units.

```
> ol1 := add(ol[2*j-1], j=1..20);
```

$$ol1 := 78 \quad (37.56)$$

To plot the discrete total energies, on a relative scale, that correspond to those exponents, we extract the operands from sum  $s_3$  and plot the even values that specify those exponents.

```
> plot([seq(ol[2*j], j=1..14)], qq=0..1, 0..27.5, colour=red,
      tickmarks=[0,5],
      labels=["", "relative energy"], titlefont=[TIMES,BOLD,14],
      view=[0..0.1, 0..27.5],
      title="discrete total energies of particle confined to a
      cube");
```



The numbers on the abscissal axis have no significance. For a cube with side of length  $L$ , the number of states of which the energy is less than or equal to  $E_n$  is equal to the number of sets of three positive integers  $nx, ny, nz$  satisfying this inequality.

$$> \text{nx}^2 + \text{ny}^2 + \text{nz}^2 \leq 8 \cdot \mu \cdot L^2 / h^2 \cdot E_n;$$

$$nx^2 + ny^2 + nz^2 \leq \frac{8 \mu L^2 E_n}{h^2} \quad (37.57)$$

For the cube with one corner at the origin of axes in a cartesian system of coordinates, number  $N$  of states is purported to be numerically equal to the volume of the first quadrant of a sphere of radius

$$\sqrt{\frac{8 \mu L^2 E_n}{h^2}}, \text{ provided that } N \geq 1.$$

$$> N := 1/8 \cdot 4 \cdot \text{Pi} / 3 \cdot (8 \cdot \mu \cdot L^2 \cdot E_n / h^2)^{(3/2)};$$

$$N := \frac{4 \pi \sqrt{8} \left( \frac{\mu L^2 E_n}{h^2} \right)^{3/2}}{3} \quad (37.58)$$

For  $E_n = 27$  and a cube of length  $L = \frac{h}{\sqrt{8 \mu}}$ ,

$$> \text{evalf}(\text{simplify}(\text{eval}(N, [L=h/\text{sqrt}(8 \cdot \mu), E_n=36])));$$

$$113.0973355 \quad (37.59)$$

which overestimates the result of the direct addition above by a factor  $\sim \sqrt{2}$ , but that formula might hold in a limit of large quantum numbers.

$$> \text{evalf}(\%o11);$$

$$1.449965840 \quad (37.60)$$

Comparing the system of a particle confined to a line segment, i.e. one dimension, and another system of a particle confined to a cuboid, i.e. three dimensions, we find that the total amplitude function in three spatial dimensions is expressible as a product of three amplitude functions, one for each spatial coordinate, whereas for one dimension the total amplitude function involves only a single coordinate; in three dimensions, three quantum numbers are required, obtained from a condition for each coordinate, whereas only one condition is necessary in one dimension; in three dimensions with a cuboid of which the sides have equal lengths, the number of separate values of discrete energies is much less than the number for a cuboid of sides of unequal lengths, and in the former case multiple amplitude functions, defined by their quantum numbers in a list, have the same energy, a phenomenon known as degeneracy; an amplitude function in three dimensions might have surfaces of zero amplitude, and likewise a probability function as the square of that amplitude function has such surfaces of zero density, whereas for one dimension the amplitude or probability function has zero value at only points.

#### 1.45 anharmonic oscillator according to matrix mechanics

> restart:

> with(LinearAlgebra):

*Matrix mechanics* is the original form of quantum mechanics that Werner Heisenberg initiated in 1925 and elaborated subsequently in association with Max Born and Pascual Jordan. Heisenberg's original paper was concerned with the solution of an anharmonic oscillator, but according to an approach with perturbation theory different from the one developed below. With perturbation theory one can solve physical problems, such as that of an anharmonic oscillator that usefully models the vibrational properties of a diatomic molecule as we demonstrate here. The full calculation is practicable with *Maple* statements and procedures that follow, and an augmented description and explanation appears in a published paper. Alternative procedures in *Maple* to generate energies of vibration-rotational states of a diatomic molecule, based on BKW or quasi-classical theory and hypervirial perturbation theory in wave mechanics, are described separately.

In *wave mechanics*, the perturbation theory for discrete non-degenerate energies takes the following form. We assume that, for a particular hamiltonian  $H^{(0)}$  of zero order, the amplitude functions  $\psi^{(0)}$  and energies  $E_n^{(0)}$  of states of an unperturbed system are known exactly, according to

$$H^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}.$$

We seek solutions for the perturbed system,  $H \psi_n = E_n \psi_n$  in which  $H = H^{(0)} + H^{''}$ ; perturbation theory is appropriate when  $H^{(0)} \gg H^{''}$ . We form a series of both energies,  $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$  and amplitude functions  $\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \dots$ , in which the parenthetically enclosed superscripts indicate the order of the correction; the latter two series are substituted into the equation for the perturbed system  $H \psi_n = E_n \psi_n$ . Separation of the terms in this expanded equation according to order, multiplying by  $\psi_n^{(0)*}$  and integrating yields

$$\begin{aligned} E_n^{(0)} &= \langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(0)} \rangle \\ E_n^{(1)} &= \langle \psi_n^{(0)} | H^{''} | \psi_n^{(0)} \rangle \\ E_n^{(2)} &= \langle \psi_n^{(0)} | H^{''} - E_n^{(1)} | \psi_n^{(1)} \rangle \end{aligned}$$

and analogously for higher orders.

Here we apply a perturbation to an anharmonic oscillator according to *matrix mechanics*, for which the energies are known directly from section 1.22. For additional information, please consult a textbook



of quantum mechanics that explains perturbation theory and its application to solve physical problems; the application of perturbation theory in both wave mechanics and matrix mechanics is explained in detail by T.-Y. Wu, Quantum Mechanics, World Scientific, Singapore, 1986; we follow the latter treatment here. According to matrix mechanics, each physical quantity is represented with a matrix, which are here of infinite rank; the general theory to solve a problem is to transform, with a unitary transformation  $\mathbf{U}$ , hamiltonian matrix  $\mathbf{H}$  into diagonal form  $\mathbf{E}$  as expressed in this matrix equation.

$$\mathbf{U} \mathbf{H} = \mathbf{E} \mathbf{U}$$

of which the solution is

$$\mathbf{U} \mathbf{H} \mathbf{U}^{-1} = \mathbf{E}$$

For the canonical linear harmonic oscillator,  $\mathbf{H}$  is diagonal, so  $\mathbf{U}$  is an identity matrix; hence  $\mathbf{H} = \mathbf{E}$ ; as, for the anharmonic oscillator,  $\mathbf{H}$  is no longer diagonal, the solution of the problem requires explicit diagonalization. In applying perturbation theory, we develop each matrix in a series with parameter  $\lambda$ ; the term of order zero captures the harmonic oscillator.

$$\begin{aligned}\mathbf{H} &= \mathbf{H}^{(0)} + \lambda \mathbf{H}^{(1)} + \lambda^2 \mathbf{H}^{(2)} + \dots \\ \mathbf{U} &= \mathbf{U}^{(0)} + \lambda \mathbf{U}^{(1)} + \lambda^2 \mathbf{U}^{(2)} + \dots \\ \mathbf{E} &= \mathbf{E}^{(0)} + \lambda \mathbf{E}^{(1)} + \lambda^2 \mathbf{E}^{(2)} + \dots \\ \mathbf{H}^{(0)} &= \mathbf{E}^{(0)}\end{aligned}$$

Matrix  $\mathbf{H}$  is a known quantity, determined according to the nature of the physical problem, here an anharmonic oscillator in one dimension. Matrix  $\mathbf{E}$  must be diagonal. Matrix  $\mathbf{U}$  is unitary such that  $\mathbf{U}^t \mathbf{U} = \mathbf{1}$ , a unit matrix. The application of the matrices in the preceding series for a purpose analogous to that succinctly outlined for wave mechanics is explained in detail during the following calculations.

The calculation undertaken here, adapted from a paper by M. B. Monagan and J. F. Ogilvie [*Mathematics of Computation and Simulation*, 1999, volume 49, pages 221-234], employs perturbation theory of multiple orders; the calculation, according to the order, is extensible by a user within the limitations of machine capacity and acceptable duration of calculation. We illustrate here how matrix mechanics in association with perturbation theory can serve effectively to solve an important problem in quantum mechanics. Because matrix  $\mathbf{H}^{(0)}$  that is the hamiltonian of the canonical linear harmonic oscillator is diagonal, for a diatomic molecule modeled as an anharmonic oscillator the requisite matrix algebra is simple; a consequence is that computations are readily performed to high order with a symbolic processor such as *Maple*.

A general hamiltonian for a system of effective mass  $\mu$  in one spatial dimension is

$$H = \frac{p^2}{2\mu} + V(x)$$

in which  $x$  denotes the displacement from equilibrium. For our anharmonic oscillator, we express the potential energy as

$$V(x) = k_2 x^2 + k_3 x^3 + k_4 x^4 + \dots$$

In this case,

$$H^{(0)} = \frac{p^2}{2\mu} + k_2 x^2, \quad H^{(1)} = k_3 x^3, \quad H^{(2)} = k_4 x^4, \quad \dots$$

Displacement coordinate  $x$  becomes matrix  $\mathbf{X}$  in subsequent calculations, of which elements  $X_{k,l}$  are defined in a solution for the canonical linear harmonic oscillator that we assume as an initial point of this calculation; cf section 1.22. Accordingly, symmetric matrix  $\mathbf{X}$  has two non-zero bands given by

$$X_{m, m+1} = \sqrt{\frac{h}{2 \mu \omega_0}} \sqrt{m+1}. \text{ The solution for that harmonic oscillator is } H^{(0)} = E_n^{(0)}, \text{ and}$$

$$H_{m, m}^{(0)} = \left(m + \frac{1}{2}\right) \omega_0 \text{ for } m = 0, 1, 2, \dots$$

To calculate terms of perturbative order  $K$  in series for matrices  $\mathbf{E}$  and  $\mathbf{U}$ , we proceed as follows. We construct first a matrix  $H^{(K)}$  to a given rank. We next create a matrix equation for the coefficient of  $\lambda^K$  by expanding an equation  $\mathbf{U} \mathbf{H} = \mathbf{E} \mathbf{U}$  symbolically as a power series in  $\lambda$ . We insert all known matrices truncated to a specified rank, and solve this equation for  $E^{(K)}$  and off-diagonal entries of  $U^{(K)}$ . To solve for diagonal entries of  $U^{(K)}$  we make use of an equation  $U^T U = 1$ , which we expand symbolically as a power series in  $\lambda$  and select the coefficient of  $\lambda^K$ . We insert all known quantities calculated to this point and solve for diagonal entries of  $U^{(K)}$ . After solving for  $E^{(K)}$  and  $U^{(K)}$ , we proceed to calculate terms of order  $K+1$ .

The following procedure serves to simplify matrices of formulae; it factors any common factor present in each entry of a matrix.

```
> factormatrix := proc(A)
  local multigcd, B, L, N, DD, G;
  multigcd := proc(aa)
    local i, g;
    g := aa[1];
    for i from 2 to nops(aa) while g <> 1 do
      g := frontend(gcd, [g, aa[i]]);
    end do;
    g;
  end;
  B := map(factor, A);
  L := {op(map(op, convert(B, listlist)))} minus {0};
  if nops(L) = 0 then
    RETURN( eval(B) );
  end if;
  N := multigcd(map(numer, L));
  if N <> 0 then
    N := N / icontent(N);
  end if;
  if N = 0 then
    RETURN(eval(B));
  end if;
  DD := multigcd(map(denom, L));
  if DD <> 0 then
    DD := DD / icontent(DD);
  end if;
  if DD = 0 then
```

```

    RETURN(eval(B));
end if;
G := N/DD;
if G = 1 or G = -1 then
    RETURN(eval(B));
end if;
G &* map( unapply( x/G, x ), B );
end proc:

```

In the construction of these two matrix equations, in the following procedure we assign coefficients of  $\lambda^k$  to variables  $G.k$  and  $UC.k$  to a specified order  $k = DD$ . This part of the computation is truly *symbolic* in that equations appear in terms of unknown matrices. We fix subsequently the rank of these matrices, insert known entries and solve for unknown entries.

```

> makeEquations := proc(DD)
    local i,H,U,E,G,Ut,UC;
    global constants;
    constants := constants, lambda;
    H := add(H||i*lambda^i,i=0..DD);
    U := 1+add(U||i*lambda^i,i=1..DD);
    E := H0 + add(E||i*lambda^i,i=1..DD);
    G := expand(U &* H - E &* U);
    G := algsubs(lambda^(DD+1)=0, G);
    Ut := 1 + add(tr(U||i)*lambda^i, i=1..DD );
    UC := expand( U &* Ut - 1 );
    UC := algsubs(lambda^(DD+1)=0, UC);
    for i from 1 to DD do
        G||i := coeff(G,lambda,i);
        UC||i := coeff(UC,lambda,i);
    end do;
    constants := op(subs(lambda=NULL, [constants]));
    RETURN();
end proc:

```

```

> makeEquations(3);

```

For instance, here are linear coefficients as determined previously,

```

> G1;
UC1;

```

$$\begin{aligned}
 & -E1 + H1 + U1 \&* H0 - (H0 \&* U1) \\
 & \quad \quad \quad tr(U1) + U1
 \end{aligned}$$

(38.1)

and here are quadratic coefficients.

```

> G2;
UC2;

```

$$-E2 + H2 + U2 \&* H0 - (H0 \&* U2) + U1 \&* H1 - (E1 \&* U1)$$

(38.2)

$$U1 \&* tr(U1) + tr(U2) + U2 \quad (38.2)$$

Matrix  $H^{(0)}$  is diagonal; this condition makes the algorithm work so simply. In the linear coefficient of  $\lambda$  above, quantity  $U^{(1)} H^{(0)} - H^{(0)} U^{(1)}$  has diagonal entries that are zero; diagonal entries of  $E^{(1)}$  are thus equal to those in  $H^{(1)}$ . In the quadratic coefficient, the unknown quantities are  $U^{(2)} H^{(0)} - H^{(0)} U^{(2)}$  and  $E^{(2)}$ ; diagonal entries of the former expression are again zero. Diagonal entries of  $E^{(2)}$  are hence given by diagonal entries of matrix  $H^{(2)} + U^{(1)} H^{(1)} - E^{(1)} U^{(1)}$ . This observation holds for terms of greater order that have a general form  $E^{(K)} + U^{(K)} H^{(0)} - H^{(0)} U^{(K)} + \dots = 0$ . Diagonal entries of  $E^{(K)}$  are simply determined and off-diagonal entries of  $U^{(K)}$  produce simple linear equations. Here is the cubic coefficient.

```
> G3;
UC3;
-E3 + H3 + U3 &* H0 - (H0 &* U3) + U2 &* H1 + U1 &* H2 - (E2 &* U1) - (E1 &*
U2)
```

$$U2 \&* tr(U1) + U1 \&* tr(U2) + tr(U3) + U3 \quad (38.3)$$

In the following procedure, we construct matrix  $H^{(K)}$  for  $K > 0$ , bearing in mind that all matrices have formally an infinite rank. Parameter  $N$  specifies the rank of a truncated matrix. To obtain  $H^{(K)}$  correct to  $N$  rows and  $N$  columns, we compute  $x^{K+2}$ ; we begin with  $N+K$  rows and columns for  $X$ .

```
> makeH := proc(K,N)
local m,X,H;
X := Matrix(N+K);
for m from 0 to N+K-2 do
X[m+1,m+2] := A*sqrt(m+1);
X[m+2,m+1] := X[m+1,m+2];
end do;
H := k | (K+2) * X^(K+2); #k | (K+2) instead of a | (K)
SubMatrix(H,1..N,1..N);
end proc;
```

Here is matrix  $H^{(1)}$  truncated to rank 6.

```
> HH1 := makeH(1, 6);
factormatrix(HH1);
```

$$(k3 A^3) \&* \begin{bmatrix} 0 & 3 & 0 & \sqrt{2} \sqrt{3} & 0 & 0 \\ 3 & 0 & 6\sqrt{2} & 0 & 2\sqrt{2} \sqrt{3} & 0 \\ 0 & 6\sqrt{2} & 0 & 9\sqrt{3} & 0 & 2\sqrt{3} \sqrt{5} \\ \sqrt{2} \sqrt{3} & 0 & 9\sqrt{3} & 0 & 24 & 0 \\ 0 & 2\sqrt{2} \sqrt{3} & 0 & 24 & 0 & 15\sqrt{5} \\ 0 & 0 & 2\sqrt{3} \sqrt{5} & 0 & 15\sqrt{5} & 0 \end{bmatrix} \quad (38.4)$$

Formulae for bands we obtain by interpolation:

$$\frac{H1_{m,m+1}}{A^3 k3} = 3 m \sqrt{m+1} \quad \text{for } 0 \leq m$$

and

$$\frac{H1_{m,m+3}}{A^3 k3} = \sqrt{(m+1)(m+2)(m+3)} \quad \text{for } 0 \leq m$$

in which  $A = \sqrt{\frac{h}{4 \pi \mu \omega_0}}$ . Here is likewise matrix  $H^{(2)}$  truncated to rank 6.

```
> HH2 := makeH(2, 6):
    factormatrix(HH2);
```

$$(k4 A^4) \&* \begin{bmatrix} 3 & 0 & 6\sqrt{2} & 0 & 2\sqrt{2}\sqrt{3} & 0 \\ 0 & 15 & 0 & 10\sqrt{2}\sqrt{3} & 0 & 2\sqrt{2}\sqrt{3}\sqrt{5} \\ 6\sqrt{2} & 0 & 39 & 0 & 28\sqrt{3} & 0 \\ 0 & 10\sqrt{2}\sqrt{3} & 0 & 75 & 0 & 36\sqrt{5} \\ 2\sqrt{2}\sqrt{3} & 0 & 28\sqrt{3} & 0 & 123 & 0 \\ 0 & 2\sqrt{2}\sqrt{3}\sqrt{5} & 0 & 36\sqrt{5} & 0 & 183 \end{bmatrix} \quad (38.5)$$

Diagonal entries are given by

$$\frac{H2_{m,m}}{A^4 k4} = 6 m^2 + 6 m + 3 \quad \text{for } 0 \leq m$$

The next band is given by

$$\frac{H2_{m,m+2}}{A^4 k4} = 2 (2 m + 3) \sqrt{(m+1)(m+2)} \quad \text{for } 0 \leq m$$

and

$$\frac{H2_{m,m+4}}{A^4 k2} = \sqrt{(m+1)(m+2)(m+3)(m+4)} \quad \text{for } 0 \leq m$$

In general, matrices  $H$  are banded and symmetric with  $K+3$  non-zero bands and with bands with zero entries between non-zero bands; formulae for bands can be determined by inspection and interpolation.

With  $H^{(0)}$  defined here as a diagonal matrix according to the canonical linear harmonic oscillator with elements  $H_{m+1,m+1} = \left(m + \frac{1}{2}\right) \omega$ , in which  $\omega$  has the significance of  $h \omega_0$ , this procedure calculates matrices  $E$  and  $U$  to order  $K$  (entered as  $DD$ ) truncated to rank  $N$ .

```
> AnHarmonic := proc(DD,N)
    global U0,H0,E0,Order,tr,Hh0,Uu0,Ee0;
    local i,j,m,x,K,T,Z,u,U,e,E,H,eqns,vars,sols;
    tr := evaln(tr);
    makeEquations(DD);
```

```

# tr := LinearAlgebra:-Transpose;
Uu0 := Matrix(N,shape=identity);
Hh0 := Matrix(N,shape=diagonal);
for m from 0 to N-1 do
    Hh0[m+1,m+1] := (m+1/2)*omega    #    definition of H^(0)
end do;
Ee0 := Hh0;
for K from 1 to DD do
    print("Solving for the coefficient of", lambda^K);
    Hh||K := makeH(K,N);
    Ee||K := Matrix(N,shape=diagonal);
    for i to N do
        Ee||K[i,i] := e[i,i];
    end do;
    Uu||K := Matrix(N);
    for i to N do
        for j to N do
            Uu||K[i,j] := u[i,j];
        end do;
    end do;
    U := evaln(U||K);
    E := evaln(E||K);
    H := evaln(H||K);
    printf("matrix %s\n",H);
    if N<9 then print(factorMatrix(Hh||K)) end if;
    printf("matrix equation to be solved\n");
    if N<9 then print(G||K) end if;
    Z := subs([seq(U||i=Uu||i,i=0..K),seq(E||i=Ee||i,i=0..K),seq
(H||i=Hh||i,i=0..K)],G||K);
    Z := subs(tr=LinearAlgebra:-Transpose,Z);
    Z := subs(`&*=LinearAlgebra:-MatrixMatrixMultiply,Z);
    Z := eval(Z);
    if K=1 then printf("expanded matrix equation to be solved\n");
        if N<9 then print(Z) end if;
    end if;
    eqns := normal(convert(Z,set));
    vars := {seq(seq(Uu||K[i,j],j=1..N),i=1..N), seq(Ee||K[i,i],i=
1..N)}
        minus {seq(Uu||K[i,i],i=1..N)};
    if N<9 then print(eqns||K=eqns) end if;    #####
    sols := mysolve(eqns,vars);
    #assign(sols);

```

```

U := subs(sols, Uu||K);
E := subs(sols, Ee||K);
printf("matrix %s\n", "E"||K);
if N<9 then print(factorMatrix(E)) end if;
T := eval(UC||K);
printf(`condition for the next U matrix`);
if N<9 then print(UC||K = 0) end if;
Ee||K := E;
T := subs([seq(U||i=Uu||i, i=0..K-1)], T);
T := subs(U||K = U, T);
T := subs(tr = LinearAlgebra:-Transpose, T);
T := subs(`&*` = LinearAlgebra:-MatrixMatrixMultiply, T);
T := eval(T);
eqns := normal(convert(T,set));
if N<9 then print(Eqns||K=eqns) end if;          #####
vars := {seq(U[i,i],i=1..N)};
print('vars'=vars);          #####
sols := mysolve(eqns,vars);
#assign(sols);
U := subs(sols, U);
printf("matrix %s\n", "U"||K);
if N<9 then print(factorMatrix(U)) end if;
Uu||K := U;
end do;
end proc;

```

Warning, (in AnHarmonic) environment variable `Order` declared as a global variable

We calculate and display  $H^{(1)}$ ,  $E^{(1)}$ ,  $U^{(1)}$ , then  $H^{(2)}$ ,  $E^{(2)}$ ,  $U^{(2)}$ ; we display also symbolic matrix equations. Like  $E^{(1)} = 0$ , all matrices  $E$  of other odd order are zero. Before executing this procedure, we activate the following special solver that greatly accelerates these calculations.

```

> mysolve := proc(eqns, unks)
    if type(eqns[1],`= `) then
        RETURN( solve( map(proc(x) lhs(x) - rhs(x) end, eqns) minus
{0}, unks ) )
    end if;
    map(proc(e,u)
        local x;
        if e=0 then
            RETURN()
        end if;
        x := indets(e) intersect(u);
        if nops(x)=1 then
            x := x[1];

```

```

        x = normal( -coeff(e,x,0)/coeff(e,x,1) )
    else
        ERROR(e, u);
    end if;
end, eqns, unks )
end proc:

```

The following test ensures that this procedure operates correctly.

```
> mysolve( {3*x=2, 4*y=b}, {x,y} );
```

$$\left\{ x = \frac{2}{3}, y = \frac{b}{4} \right\}$$

(38.6)

```
> AnHarmonic(2,6);
```

"Solving for the coefficient of",  $\lambda$

matrix H1

$$(k3 A^3) \&* \begin{bmatrix} 0 & 3 & 0 & \sqrt{2} \sqrt{3} & 0 & 0 \\ 3 & 0 & 6 \sqrt{2} & 0 & 2 \sqrt{2} \sqrt{3} & 0 \\ 0 & 6 \sqrt{2} & 0 & 9 \sqrt{3} & 0 & 2 \sqrt{3} \sqrt{5} \\ \sqrt{2} \sqrt{3} & 0 & 9 \sqrt{3} & 0 & 24 & 0 \\ 0 & 2 \sqrt{2} \sqrt{3} & 0 & 24 & 0 & 15 \sqrt{5} \\ 0 & 0 & 2 \sqrt{3} \sqrt{5} & 0 & 15 \sqrt{5} & 0 \end{bmatrix}$$

matrix equation to be solved

$$-E1 + H1 + U1 \&* H0 - (H0 \&* U1)$$

expanded matrix equation to be solved

$$\begin{aligned} & \left[ \left[ -e_{1,1}, 3 k3 A^3 + u_{1,2} \omega, 2 u_{1,3} \omega, k3 A^3 \sqrt{2} \sqrt{3} + 3 u_{1,4} \omega, 4 u_{1,5} \omega, 5 u_{1,6} \omega \right], \right. \\ & \left[ 3 k3 A^3 - u_{2,1} \omega, -e_{2,2}, 6 k3 A^3 \sqrt{2} + u_{2,3} \omega, 2 u_{2,4} \omega, 2 k3 A^3 \sqrt{2} \sqrt{3} + 3 u_{2,5} \omega, \right. \\ & \left. 4 u_{2,6} \omega \right], \\ & \left[ -2 u_{3,1} \omega, 6 k3 A^3 \sqrt{2} - u_{3,2} \omega, -e_{3,3}, 9 k3 A^3 \sqrt{3} + u_{3,4} \omega, 2 u_{3,5} \omega, 2 k3 A^3 \sqrt{3} \sqrt{5} \right. \\ & \left. + 3 u_{3,6} \omega \right], \\ & \left[ k3 A^3 \sqrt{2} \sqrt{3} - 3 u_{4,1} \omega, -2 u_{4,2} \omega, 9 k3 A^3 \sqrt{3} - u_{4,3} \omega, -e_{4,4}, 24 k3 A^3 + u_{4,5} \omega, \right. \\ & \left. 2 u_{4,6} \omega \right], \end{aligned}$$



$$\left[ -4 u_{5,1} \omega, 2 k3 A^3 \sqrt{2} \sqrt{3} - 3 u_{5,2} \omega, -2 u_{5,3} \omega, 24 k3 A^3 - u_{5,4} \omega, -e_{5,5}, 15 k3 A^3 \sqrt{5} \right. \\ \left. + u_{5,6} \omega \right],$$

$$\left[ -5 u_{6,1} \omega, -4 u_{6,2} \omega, 2 k3 A^3 \sqrt{3} \sqrt{5} - 3 u_{6,3} \omega, -2 u_{6,4} \omega, 15 k3 A^3 \sqrt{5} - u_{6,5} \omega, \right. \\ \left. -e_{6,6} \right] \Big] \Big]$$

$$eqns1 = \left\{ -e_{1,1}, -e_{2,2}, -e_{3,3}, -e_{4,4}, -e_{5,5}, -e_{6,6}, 2 u_{1,3} \omega, 4 u_{1,5} \omega, 5 u_{1,6} \omega, 2 u_{2,4} \omega, 4 u_{2,6} \omega, \right. \\ -2 u_{3,1} \omega, 2 u_{3,5} \omega, -2 u_{4,2} \omega, 2 u_{4,6} \omega, -4 u_{5,1} \omega, -2 u_{5,3} \omega, -5 u_{6,1} \omega, -4 u_{6,2} \omega, \\ -2 u_{6,4} \omega, 6 k3 A^3 \sqrt{2} + u_{2,3} \omega, 6 k3 A^3 \sqrt{2} - u_{3,2} \omega, 9 k3 A^3 \sqrt{3} + u_{3,4} \omega, 9 k3 A^3 \sqrt{3} \\ - u_{4,3} \omega, 15 k3 A^3 \sqrt{5} + u_{5,6} \omega, 15 k3 A^3 \sqrt{5} - u_{6,5} \omega, k3 A^3 \sqrt{2} \sqrt{3} + 3 u_{1,4} \omega, \\ k3 A^3 \sqrt{2} \sqrt{3} - 3 u_{4,1} \omega, 2 k3 A^3 \sqrt{2} \sqrt{3} + 3 u_{2,5} \omega, 2 k3 A^3 \sqrt{2} \sqrt{3} - 3 u_{5,2} \omega, \\ 2 k3 A^3 \sqrt{3} \sqrt{5} + 3 u_{3,6} \omega, 2 k3 A^3 \sqrt{3} \sqrt{5} - 3 u_{6,3} \omega, 3 k3 A^3 + u_{1,2} \omega, 3 k3 A^3 - u_{2,1} \omega, \\ \left. 24 k3 A^3 + u_{4,5} \omega, 24 k3 A^3 - u_{5,4} \omega \right\}$$

matrix E1

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

condition for the next U matrix

$$tr(UI) + UI = 0$$

$$Eqns1 = \{0, 2 u_{1,1}, 2 u_{2,2}, 2 u_{3,3}, 2 u_{4,4}, 2 u_{5,5}, 2 u_{6,6}\}$$

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}\}$$

matrix U1

$$\left( \frac{k3 A^3}{\omega} \right) \&^*$$

$$\begin{bmatrix} 0 & -3 & 0 & -\frac{\sqrt{2}\sqrt{3}}{3} & 0 & 0 \\ 3 & 0 & -6\sqrt{2} & 0 & -\frac{2\sqrt{2}\sqrt{3}}{3} & 0 \\ 0 & 6\sqrt{2} & 0 & -9\sqrt{3} & 0 & -\frac{2\sqrt{3}\sqrt{5}}{3} \\ \frac{\sqrt{2}\sqrt{3}}{3} & 0 & 9\sqrt{3} & 0 & -24 & 0 \\ 0 & \frac{2\sqrt{2}\sqrt{3}}{3} & 0 & 24 & 0 & -15\sqrt{5} \\ 0 & 0 & \frac{2\sqrt{3}\sqrt{5}}{3} & 0 & 15\sqrt{5} & 0 \end{bmatrix}$$

"Solving for the coefficient of",  $\lambda^2$

matrix H2

$$(k4 A^4) \&^* \begin{bmatrix} 3 & 0 & 6\sqrt{2} & 0 & 2\sqrt{2}\sqrt{3} & 0 \\ 0 & 15 & 0 & 10\sqrt{2}\sqrt{3} & 0 & 2\sqrt{2}\sqrt{3}\sqrt{5} \\ 6\sqrt{2} & 0 & 39 & 0 & 28\sqrt{3} & 0 \\ 0 & 10\sqrt{2}\sqrt{3} & 0 & 75 & 0 & 36\sqrt{5} \\ 2\sqrt{2}\sqrt{3} & 0 & 28\sqrt{3} & 0 & 123 & 0 \\ 0 & 2\sqrt{2}\sqrt{3}\sqrt{5} & 0 & 36\sqrt{5} & 0 & 183 \end{bmatrix}$$

matrix equation to be solved

$$-E2 + H2 + U2 \&^* H0 - (H0 \&^* U2) + U1 \&^* H1 - (E1 \&^* U1)$$

$$eqns2 = \left\{ u_{1,2} \omega, u_{2,3} \omega, u_{3,4} \omega, u_{4,5} \omega, u_{5,6} \omega, \right.$$

$$\frac{7 k^2 A^6 \sqrt{2} \sqrt{3} + 10 k 4 A^4 \sqrt{2} \sqrt{3} \omega - 2 u_{4,2} \omega^2}{\omega},$$

$$\frac{1145 k^2 A^6 + 183 k 4 A^4 \omega - e_{6,6} \omega}{\omega}, 3 u_{1,4} \omega, 5 u_{1,6} \omega, -u_{2,1} \omega, 3 u_{2,5} \omega, -u_{3,2} \omega,$$

$$3 u_{3,6} \omega, -3 u_{4,1} \omega, -u_{4,3} \omega, -3 u_{5,2} \omega, -u_{5,4} \omega, -5 u_{6,1} \omega, -3 u_{6,3} \omega, -u_{6,5} \omega,$$

$$-\frac{9 k^3 A^6 \sqrt{2} - 6 k^4 A^4 \sqrt{2} \omega + 2 u_{3,1} \omega^2}{\omega},$$

$$-\frac{27 k^3 A^6 \sqrt{2} - 6 k^4 A^4 \sqrt{2} \omega - 2 u_{1,3} \omega^2}{\omega},$$

$$\frac{2 \left( 37 k^3 A^6 \sqrt{3} + 14 k^4 A^4 \sqrt{3} \omega - u_{5,3} \omega^2 \right)}{\omega},$$

$$-\frac{2 \left( 121 k^3 A^6 \sqrt{3} - 14 k^4 A^4 \sqrt{3} \omega - u_{3,5} \omega^2 \right)}{\omega},$$

$$-\frac{2 \left( 153 k^3 A^6 \sqrt{5} - 18 k^4 A^4 \sqrt{5} \omega - u_{4,6} \omega^2 \right)}{\omega},$$

$$\frac{2 \left( 189 k^3 A^6 \sqrt{5} + 18 k^4 A^4 \sqrt{5} \omega - u_{6,4} \omega^2 \right)}{\omega},$$

$$-\frac{2 \left( 7 k^3 A^6 \sqrt{2} \sqrt{3} - k^4 A^4 \sqrt{2} \sqrt{3} \omega - 2 u_{1,5} \omega^2 \right)}{\omega},$$

$$\frac{2 \left( 13 k^3 A^6 \sqrt{2} \sqrt{3} + k^4 A^4 \sqrt{2} \sqrt{3} \omega - 2 u_{5,1} \omega^2 \right)}{\omega},$$

$$-\frac{67 k^3 A^6 \sqrt{2} \sqrt{3} - 10 k^4 A^4 \sqrt{2} \sqrt{3} \omega - 2 u_{2,4} \omega^2}{\omega},$$

$$-\frac{2 \left( 11 k^3 A^6 \sqrt{2} \sqrt{3} \sqrt{5} - k^4 A^4 \sqrt{2} \sqrt{3} \sqrt{5} \omega - 2 u_{2,6} \omega^2 \right)}{\omega},$$

$$\frac{2 \left( 17 k^3 A^6 \sqrt{2} \sqrt{3} \sqrt{5} + k^4 A^4 \sqrt{2} \sqrt{3} \sqrt{5} \omega - 2 u_{6,2} \omega^2 \right)}{\omega},$$

$$-\frac{11 k^3 A^6 - 3 k^4 A^4 \omega + e_{1,1} \omega}{\omega}, -\frac{71 k^3 A^6 - 15 k^4 A^4 \omega + e_{2,2} \omega}{\omega},$$

$$-\frac{191 k^3 A^6 - 39 k^4 A^4 \omega + e_{3,3} \omega}{\omega}, -\frac{331 k^3 A^6 - 75 k^4 A^4 \omega + e_{4,4} \omega}{\omega},$$

$$-\frac{541 k^3 A^6 - 123 k^4 A^4 \omega + e_{5,5} \omega}{\omega} \Bigg\}$$

matrix E2

$$\begin{aligned} & \left( \frac{A^4}{\omega} \right) \&^* \left[ \left[ -11 A^2 k^3 + 3 k^4 \omega, 0, 0, 0, 0, 0 \right], \right. \\ & \left[ 0, -71 A^2 k^3 + 15 k^4 \omega, 0, 0, 0, 0 \right], \\ & \left[ 0, 0, -191 A^2 k^3 + 39 k^4 \omega, 0, 0, 0 \right], \\ & \left[ 0, 0, 0, -331 A^2 k^3 + 75 k^4 \omega, 0, 0 \right], \\ & \left[ 0, 0, 0, 0, -541 A^2 k^3 + 123 k^4 \omega, 0 \right], \\ & \left. \left[ 0, 0, 0, 0, 0, 1145 A^2 k^3 + 183 k^4 \omega \right] \right] \end{aligned}$$

condition for the next U matrix

$$UI \&^* tr(UI) + tr(U2) + U2 = 0$$

$$\begin{aligned} Eqns2 = & \left\{ 0, \frac{29 k^3 A^6 + 6 u_{1,1} \omega^2}{3 \omega^2}, \frac{251 k^3 A^6 + 6 u_{2,2} \omega^2}{3 \omega^2}, \frac{965 k^3 A^6 + 6 u_{3,3} \omega^2}{3 \omega^2}, \right. \\ & \left. \frac{2459 k^3 A^6 + 6 u_{4,4} \omega^2}{3 \omega^2}, \frac{5111 k^3 A^6 + 6 u_{5,5} \omega^2}{3 \omega^2}, \frac{3395 k^3 A^6 + 6 u_{6,6} \omega^2}{3 \omega^2} \right\} \\ vars = & \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}\} \end{aligned}$$

matrix U2

$$\begin{aligned} & \left( \frac{A^4}{\omega^2} \right) \&^* \left[ \left[ -\frac{29 A^2 k^3}{6}, 0, \frac{3 \sqrt{2} (9 A^2 k^3 - 2 k^4 \omega)}{2}, 0, \frac{(7 A^2 k^3 - k^4 \omega) \sqrt{6}}{2}, 0 \right], \right. \\ & \left[ 0, -\frac{251 A^2 k^3}{6}, 0, \frac{(67 A^2 k^3 - 10 k^4 \omega) \sqrt{6}}{2}, 0, \frac{(11 A^2 k^3 - k^4 \omega) \sqrt{30}}{2} \right], \\ & \left[ -\frac{3 \sqrt{2} (3 A^2 k^3 - 2 k^4 \omega)}{2}, 0, -\frac{965 A^2 k^3}{6}, 0, \sqrt{3} (121 A^2 k^3 - 14 k^4 \omega), 0 \right], \\ & \left[ 0, \frac{(7 A^2 k^3 + 10 k^4 \omega) \sqrt{6}}{2}, 0, -\frac{2459 A^2 k^3}{6}, 0, 9 \sqrt{5} (17 A^2 k^3 - 2 k^4 \omega) \right], \\ & \left[ \frac{(13 A^2 k^3 + k^4 \omega) \sqrt{6}}{2}, 0, \sqrt{3} (37 A^2 k^3 + 14 k^4 \omega), 0, -\frac{5111 A^2 k^3}{6}, 0 \right], \\ & \left. \left[ 0, \frac{(17 A^2 k^3 + k^4 \omega) \sqrt{30}}{2}, 0, 9 \sqrt{5} (21 A^2 k^3 + 2 k^4 \omega), 0, -\frac{3395 A^2 k^3}{6} \right] \right] \end{aligned}$$

$$\left[ \left[ -\frac{29 k^3 A^6}{6 \omega^2}, 0, \frac{3 A^4 \sqrt{2} (9 A^2 k^3 - 2 k 4 \omega)}{2 \omega^2}, 0, \frac{A^4 \sqrt{2} \sqrt{3} (7 A^2 k^3 - k 4 \omega)}{2 \omega^2}, 0 \right], \right. \quad (38.7)$$

$$\left[ 0, -\frac{251 k^3 A^6}{6 \omega^2}, 0, \frac{A^4 \sqrt{2} \sqrt{3} (67 A^2 k^3 - 10 k 4 \omega)}{2 \omega^2}, 0, \right. \\ \left. \frac{A^4 \sqrt{2} \sqrt{3} \sqrt{5} (11 A^2 k^3 - k 4 \omega)}{2 \omega^2} \right],$$

$$\left[ -\frac{3 A^4 \sqrt{2} (3 A^2 k^3 - 2 k 4 \omega)}{2 \omega^2}, 0, -\frac{965 k^3 A^6}{6 \omega^2}, 0, \frac{A^4 \sqrt{3} (121 A^2 k^3 - 14 k 4 \omega)}{\omega^2}, 0 \right. \\ \left. \right],$$

$$\left[ 0, \frac{A^4 \sqrt{2} \sqrt{3} (7 A^2 k^3 + 10 k 4 \omega)}{2 \omega^2}, 0, -\frac{2459 k^3 A^6}{6 \omega^2}, 0, \right. \\ \left. \frac{9 A^4 \sqrt{5} (17 A^2 k^3 - 2 k 4 \omega)}{\omega^2} \right],$$

$$\left[ \frac{A^4 \sqrt{2} \sqrt{3} (13 A^2 k^3 + k 4 \omega)}{2 \omega^2}, 0, \frac{A^4 \sqrt{3} (37 A^2 k^3 + 14 k 4 \omega)}{\omega^2}, 0, -\frac{5111 k^3 A^6}{6 \omega^2}, 0 \right. \\ \left. \right],$$

$$\left[ 0, \frac{A^4 \sqrt{2} \sqrt{3} \sqrt{5} (17 A^2 k^3 + k 4 \omega)}{2 \omega^2}, 0, \frac{9 A^4 \sqrt{5} (21 A^2 k^3 + 2 k 4 \omega)}{\omega^2}, 0, \right. \\ \left. -\frac{3395 k^3 A^6}{6 \omega^2} \right] \Bigg]$$

```
> k4*A^4*Matrix([[3, 0, 6*2^(1/2), 0, 2*2^(1/2)*3^(1/2), 0], [0, 15,
0, 10*2^(1/2)*3^(1/2), 0,
2*2^(1/2)*3^(1/2)*5^(1/2)], [6*2^(1/2), 0, 39, 0, 28*3^(1/2), 0],
[0, 10*2^(1/2)*3^(1/2), 0,
75, 0, 36*5^(1/2)], [2*2^(1/2)*3^(1/2), 0, 28*3^(1/2), 0, 123, 0],
[0, 2*2^(1/2)*3^(1/2)*5^(1/2),
0, 36*5^(1/2), 0, 183]]); # same as matrix H2 above
```

$$\left[ \left[ 3 k 4 A^4, 0, 6 k 4 A^4 \sqrt{2}, 0, 2 k 4 A^4 \sqrt{2} \sqrt{3}, 0 \right], \right. \quad (38.8)$$

$$\left[ 0, 15 k 4 A^4, 0, 10 k 4 A^4 \sqrt{2} \sqrt{3}, 0, 2 k 4 A^4 \sqrt{2} \sqrt{3} \sqrt{5} \right],$$

$$\begin{aligned}
& [6 k4 A^4 \sqrt{2}, 0, 39 k4 A^4, 0, 28 k4 A^4 \sqrt{3}, 0], \\
& [0, 10 k4 A^4 \sqrt{2} \sqrt{3}, 0, 75 k4 A^4, 0, 36 k4 A^4 \sqrt{5}], \\
& [2 k4 A^4 \sqrt{2} \sqrt{3}, 0, 28 k4 A^4 \sqrt{3}, 0, 123 k4 A^4, 0], \\
& [0, 2 k4 A^4 \sqrt{2} \sqrt{3} \sqrt{5}, 0, 36 k4 A^4 \sqrt{5}, 0, 183 k4 A^4]]
\end{aligned}$$

To verify that all computations performed with procedure AnHarmonic are correct, such that we correctly diagonalize  $\mathbf{H}$  to  $O(\lambda^3)$ , we test that equation  $\mathbf{U} \mathbf{H} = \mathbf{E} \mathbf{U}$  to  $O(\lambda^3)$ .

```

> eqn := (1 + add(lambda^i*U||i,i=1..2)) &*
      add(lambda^i*H||i,i=0..2) =
      add(lambda^i*E||i,i=0..2) &* (1 +
      add(lambda^i*U||i,i=1..2));
eqn := (λ2 U2 + λ UI + 1) &* (λ2 H2 + λ HI + H0) = (λ2 E2 + λ EI + E0) &* (λ2 U2
      + λ UI + 1)

```

(38.9)

```

> K := 2:
Eqn := eval(subs([seq(U||i=Uu||i, i=0..K), seq(H||i=Hh||i, i=0..
K), seq(E||i=Ee||i, i=0..K), `&*&` = `.`], eqn)):
Eqn := lhs(Eqn) - rhs(Eqn);
Eqn := map(series, Eqn, lambda, K+1):
map(simplify, Eqn);

```

$$\begin{aligned}
Eqn := & \left[ \left( 1 - \frac{29 \lambda^2 k3^2 A^6}{6 \omega^2} \right) \left( 3 \lambda^2 k4 A^4 + \frac{\omega}{2} \right) - \frac{11 \lambda^2 k3^2 A^6}{\omega} \right. \\
& + \frac{18 \lambda^4 A^8 (9 A^2 k3^2 - 2 k4 \omega) k4}{\omega^2} + \frac{6 \lambda^4 A^8 (7 A^2 k3^2 - k4 \omega) k4}{\omega^2} - \left( \right. \\
& - \frac{\lambda^2 A^4 (11 A^2 k3^2 - 3 k4 \omega)}{\omega} + \frac{\omega}{2} \left. \right) \left( 1 - \frac{29 \lambda^2 k3^2 A^6}{6 \omega^2} \right), 3 \left( 1 \right. \\
& - \frac{29 \lambda^2 k3^2 A^6}{6 \omega^2} \left. \right) \lambda k3 A^3 - \frac{3 \lambda k3 A^3 \left( 15 \lambda^2 k4 A^4 + \frac{3 \omega}{2} \right)}{\omega} \\
& + \frac{18 \lambda^3 A^7 (9 A^2 k3^2 - 2 k4 \omega) k3}{\omega^2} - \frac{20 \lambda^3 k3 A^7 k4}{\omega} + \frac{6 \lambda^3 A^7 (7 A^2 k3^2 - k4 \omega) k3}{\omega^2}
\end{aligned}$$

$$\begin{aligned}
& + \frac{3 \left( -\frac{\lambda^2 A^4 (11 A^2 k^3 - 3 k^4 \omega)}{\omega} + \frac{\omega}{2} \right) \lambda k^3 A^3}{\omega}, 6 \left( 1 - \frac{29 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{2} \\
& - \frac{27 \lambda^2 k^3 A^6 \sqrt{2}}{\omega} + \frac{3 \lambda^2 A^4 \sqrt{2} (9 A^2 k^3 - 2 k^4 \omega) \left( 39 \lambda^2 k^4 A^4 + \frac{5 \omega}{2} \right)}{2 \omega^2} \\
& + \frac{42 \lambda^4 A^8 \sqrt{2} (7 A^2 k^3 - k^4 \omega) k^4}{\omega^2} \\
& - \frac{3 \left( -\frac{\lambda^2 A^4 (11 A^2 k^3 - 3 k^4 \omega)}{\omega} + \frac{\omega}{2} \right) \lambda^2 A^4 \sqrt{2} (9 A^2 k^3 - 2 k^4 \omega)}{2 \omega^2}, \left( 1 \right. \\
& \left. - \frac{29 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{2} \sqrt{3} - \frac{30 \lambda^3 k^3 A^7 k^4 \sqrt{2} \sqrt{3}}{\omega} \\
& + \frac{27 \lambda^3 A^7 \sqrt{2} (9 A^2 k^3 - 2 k^4 \omega) k^3 \sqrt{3}}{2 \omega^2} - \frac{\lambda k^3 A^3 \sqrt{2} \sqrt{3} \left( 75 \lambda^2 k^4 A^4 + \frac{7 \omega}{2} \right)}{3 \omega} \\
& + \frac{12 \lambda^3 A^7 \sqrt{2} \sqrt{3} (7 A^2 k^3 - k^4 \omega) k^3}{\omega^2} \\
& + \frac{\left( -\frac{\lambda^2 A^4 (11 A^2 k^3 - 3 k^4 \omega)}{\omega} + \frac{\omega}{2} \right) \lambda k^3 A^3 \sqrt{2} \sqrt{3}}{3 \omega}, 2 \left( 1 \right. \\
& \left. - \frac{29 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{2} \sqrt{3} - \frac{14 \lambda^2 k^3 A^6 \sqrt{2} \sqrt{3}}{\omega} \\
& + \frac{42 \lambda^4 A^8 \sqrt{2} (9 A^2 k^3 - 2 k^4 \omega) k^4 \sqrt{3}}{\omega^2}
\end{aligned}$$

$$\begin{aligned}
& + \frac{\lambda^2 A^4 \sqrt{2} \sqrt{3} (7 A^2 k^3 - k^4 \omega) \left( 123 \lambda^2 k^4 A^4 + \frac{9 \omega}{2} \right)}{2 \omega^2} \\
& - \frac{\left( -\frac{\lambda^2 A^4 (11 A^2 k^3 - 3 k^4 \omega)}{\omega} + \frac{\omega}{2} \right) \lambda^2 A^4 \sqrt{2} \sqrt{3} (7 A^2 k^3 - k^4 \omega)}{2 \omega^2}, \\
& - \frac{18 \lambda^3 k^3 A^7 k^4 \sqrt{2} \sqrt{3} \sqrt{5}}{\omega} + \frac{3 \lambda^3 A^7 \sqrt{2} (9 A^2 k^3 - 2 k^4 \omega) k^3 \sqrt{3} \sqrt{5}}{\omega^2} \\
& + \frac{15 \lambda^3 A^7 \sqrt{2} \sqrt{3} (7 A^2 k^3 - k^4 \omega) k^3 \sqrt{5}}{2 \omega^2} \Bigg], \\
& \left[ \frac{3 \lambda k^3 A^3 \left( 3 \lambda^2 k^4 A^4 + \frac{\omega}{2} \right)}{\omega} + 3 \left( 1 - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 - \frac{80 \lambda^3 k^3 A^7 k^4}{\omega} \right. \\
& + \frac{3 \lambda^3 A^7 (67 A^2 k^3 - 10 k^4 \omega) k^3}{\omega^2} \\
& - \frac{3 \left( -\frac{\lambda^2 A^4 (71 A^2 k^3 - 15 k^4 \omega)}{\omega} + \frac{3 \omega}{2} \right) \lambda k^3 A^3}{\omega}, - \frac{71 \lambda^2 k^3 A^6}{\omega} + \left( 1 \right. \\
& - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \Bigg) \left( 15 \lambda^2 k^4 A^4 + \frac{3 \omega}{2} \right) + \frac{30 \lambda^4 A^8 (67 A^2 k^3 - 10 k^4 \omega) k^4}{\omega^2} \\
& + \frac{30 \lambda^4 A^8 (11 A^2 k^3 - k^4 \omega) k^4}{\omega^2} - \left( -\frac{\lambda^2 A^4 (71 A^2 k^3 - 15 k^4 \omega)}{\omega} + \frac{3 \omega}{2} \right) \left( 1 \right. \\
& - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \Bigg), - \frac{38 \lambda^3 k^3 A^7 k^4 \sqrt{2}}{\omega} + 6 \left( 1 - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{2} \\
& - \frac{6 \lambda k^3 A^3 \sqrt{2} \left( 39 \lambda^2 k^4 A^4 + \frac{5 \omega}{2} \right)}{\omega} + \frac{27 \lambda^3 A^7 \sqrt{2} (67 A^2 k^3 - 10 k^4 \omega) k^3}{2 \omega^2}
\end{aligned}$$



$$\begin{aligned}
& + \frac{15 \lambda^3 A^7 \sqrt{2} (11 A^2 k^3 - k^4 \omega) k^3}{\omega^2} \\
& + \frac{6 \left( -\frac{\lambda^2 A^4 (71 A^2 k^3 - 15 k^4 \omega)}{\omega} + \frac{3 \omega}{2} \right) \lambda k^3 A^3 \sqrt{2}}{\omega}, - \frac{67 \lambda^2 k^3 A^6 \sqrt{2} \sqrt{3}}{\omega} \\
& + 10 \left( 1 - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{2} \sqrt{3} \\
& + \frac{\lambda^2 A^4 \sqrt{2} \sqrt{3} (67 A^2 k^3 - 10 k^4 \omega) \left( 75 \lambda^2 k^4 A^4 + \frac{7 \omega}{2} \right)}{2 \omega^2} \\
& + \frac{90 \lambda^4 A^8 \sqrt{2} \sqrt{3} (11 A^2 k^3 - k^4 \omega) k^4}{\omega^2} \\
& - \frac{\left( -\frac{\lambda^2 A^4 (71 A^2 k^3 - 15 k^4 \omega)}{\omega} + \frac{3 \omega}{2} \right) \lambda^2 A^4 \sqrt{2} \sqrt{3} (67 A^2 k^3 - 10 k^4 \omega)}{2 \omega^2}, \\
& - \frac{162 \lambda^3 k^3 A^7 k^4 \sqrt{2} \sqrt{3}}{\omega} + 2 \left( 1 - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{2} \sqrt{3} \\
& + \frac{12 \lambda^3 A^7 \sqrt{2} \sqrt{3} (67 A^2 k^3 - 10 k^4 \omega) k^3}{\omega^2} \\
& - \frac{2 \lambda k^3 A^3 \sqrt{2} \sqrt{3} \left( 123 \lambda^2 k^4 A^4 + \frac{9 \omega}{2} \right)}{3 \omega} \\
& + \frac{75 \lambda^3 A^7 \sqrt{2} \sqrt{3} (11 A^2 k^3 - k^4 \omega) k^3}{2 \omega^2}
\end{aligned}$$

$$\begin{aligned}
& + \frac{2 \left( -\frac{\lambda^2 A^4 (71 A^2 k^3 - 15 k^4 \omega)}{\omega} + \frac{3 \omega}{2} \right) \lambda k^3 A^3 \sqrt{2} \sqrt{3}}{3 \omega}, 2 \left( 1 \right. \\
& - \frac{251 \lambda^2 k^3 A^6}{6 \omega^2} \left. \right) \lambda^2 k^4 A^4 \sqrt{2} \sqrt{3} \sqrt{5} - \frac{22 \lambda^2 k^3 A^6 \sqrt{2} \sqrt{3} \sqrt{5}}{\omega} \\
& + \frac{18 \lambda^4 A^8 \sqrt{2} \sqrt{3} (67 A^2 k^3 - 10 k^4 \omega) k^4 \sqrt{5}}{\omega^2} \\
& + \frac{\lambda^2 A^4 \sqrt{2} \sqrt{3} \sqrt{5} (11 A^2 k^3 - k^4 \omega) \left( 183 \lambda^2 k^4 A^4 + \frac{11 \omega}{2} \right)}{2 \omega^2} \\
& - \frac{\left( -\frac{\lambda^2 A^4 (71 A^2 k^3 - 15 k^4 \omega)}{\omega} + \frac{3 \omega}{2} \right) \lambda^2 A^4 \sqrt{2} \sqrt{3} \sqrt{5} (11 A^2 k^3 - k^4 \omega)}{2 \omega^2} \left. \right], \\
& \left[ -\frac{3 \lambda^2 A^4 \sqrt{2} (3 A^2 k^3 - 2 k^4 \omega) \left( 3 \lambda^2 k^4 A^4 + \frac{\omega}{2} \right)}{2 \omega^2} - \frac{9 \lambda^2 k^3 A^6 \sqrt{2}}{\omega} + 6 \left( 1 \right. \right. \\
& - \frac{965 \lambda^2 k^3 A^6}{6 \omega^2} \left. \right) \lambda^2 k^4 A^4 \sqrt{2} + \frac{6 \lambda^4 A^8 (121 A^2 k^3 - 14 k^4 \omega) k^4 \sqrt{2}}{\omega^2} \\
& + \frac{3 \left( -\frac{\lambda^2 A^4 (191 A^2 k^3 - 39 k^4 \omega)}{\omega} + \frac{5 \omega}{2} \right) \lambda^2 A^4 \sqrt{2} (3 A^2 k^3 - 2 k^4 \omega)}{2 \omega^2}, \\
& - \frac{9 \lambda^3 A^7 \sqrt{2} (3 A^2 k^3 - 2 k^4 \omega) k^3}{2 \omega^2} + \frac{6 \lambda k^3 A^3 \sqrt{2} \left( 15 \lambda^2 k^4 A^4 + \frac{3 \omega}{2} \right)}{\omega} + 6 \left( 1 \right. \\
& - \frac{965 \lambda^2 k^3 A^6}{6 \omega^2} \left. \right) \lambda k^3 A^3 \sqrt{2} - \frac{290 \lambda^3 k^3 A^7 k^4 \sqrt{2}}{\omega}
\end{aligned}$$

$$\begin{aligned}
& + \frac{6 \lambda^3 A^7 (121 A^2 k^3 - 14 k^4 \omega) k^3 \sqrt{2}}{\omega^2} \\
& - \frac{6 \left( -\frac{\lambda^2 A^4 (191 A^2 k^3 - 39 k^4 \omega)}{\omega} + \frac{5 \omega}{2} \right) \lambda k^3 A^3 \sqrt{2}}{\omega}, \\
& - \frac{18 \lambda^4 A^8 (3 A^2 k^3 - 2 k^4 \omega) k^4}{\omega^2} - \frac{191 \lambda^2 k^3 A^6}{\omega} + \left( 1 - \frac{965 \lambda^2 k^3 A^6}{6 \omega^2} \right) \left( 39 \lambda^2 k^4 A^4 \right. \\
& + \left. \frac{5 \omega}{2} \right) + \frac{84 \lambda^4 A^8 (121 A^2 k^3 - 14 k^4 \omega) k^4}{\omega^2} - \left( -\frac{\lambda^2 A^4 (191 A^2 k^3 - 39 k^4 \omega)}{\omega} \right. \\
& + \left. \frac{5 \omega}{2} \right) \left( 1 - \frac{965 \lambda^2 k^3 A^6}{6 \omega^2} \right), - \frac{3 \lambda^3 A^7 (3 A^2 k^3 - 2 k^4 \omega) k^3 \sqrt{3}}{\omega^2} + 9 \left( 1 \right. \\
& - \left. \frac{965 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{3} - \frac{9 \lambda k^3 A^3 \sqrt{3} \left( 75 \lambda^2 k^4 A^4 + \frac{7 \omega}{2} \right)}{\omega} \\
& + \frac{24 \lambda^3 A^7 \sqrt{3} (121 A^2 k^3 - 14 k^4 \omega) k^3}{\omega^2} \\
& + \frac{9 \left( -\frac{\lambda^2 A^4 (191 A^2 k^3 - 39 k^4 \omega)}{\omega} + \frac{5 \omega}{2} \right) \lambda k^3 A^3 \sqrt{3}}{\omega}, \\
& - \frac{6 \lambda^4 A^8 (3 A^2 k^3 - 2 k^4 \omega) k^4 \sqrt{3}}{\omega^2} - \frac{242 \lambda^2 k^3 A^6 \sqrt{3}}{\omega} + 28 \left( 1 \right. \\
& - \left. \frac{965 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{3}
\end{aligned}$$

$$\begin{aligned}
& + \frac{\lambda^2 A^4 \sqrt{3} (121 A^2 k^3 - 14 k^4 \omega) \left(123 \lambda^2 k^4 A^4 + \frac{9 \omega}{2}\right)}{\omega^2} \\
& - \frac{\left(-\frac{\lambda^2 A^4 (191 A^2 k^3 - 39 k^4 \omega)}{\omega} + \frac{5 \omega}{2}\right) \lambda^2 A^4 \sqrt{3} (121 A^2 k^3 - 14 k^4 \omega)}{\omega^2}, \\
& - \frac{300 \lambda^3 k^3 A^7 k^4 \sqrt{3} \sqrt{5}}{\omega} + 2 \left(1 - \frac{965 \lambda^2 k^3^2 A^6}{6 \omega^2}\right) \lambda k^3 A^3 \sqrt{3} \sqrt{5} \\
& + \frac{15 \lambda^3 A^7 \sqrt{3} (121 A^2 k^3 - 14 k^4 \omega) k^3 \sqrt{5}}{\omega^2} \\
& - \frac{2 \lambda k^3 A^3 \sqrt{3} \sqrt{5} \left(183 \lambda^2 k^4 A^4 + \frac{11 \omega}{2}\right)}{3 \omega} \\
& + \frac{2 \left(-\frac{\lambda^2 A^4 (191 A^2 k^3 - 39 k^4 \omega)}{\omega} + \frac{5 \omega}{2}\right) \lambda k^3 A^3 \sqrt{3} \sqrt{5}}{3 \omega} \Bigg], \\
& \left[ \frac{\lambda k^3 A^3 \sqrt{2} \sqrt{3} \left(3 \lambda^2 k^4 A^4 + \frac{\omega}{2}\right)}{3 \omega} + \frac{3 \lambda^3 A^7 \sqrt{2} \sqrt{3} (7 A^2 k^3^2 + 10 k^4 \omega) k^3}{2 \omega^2} \right. \\
& + \frac{6 \lambda^3 k^3 A^7 k^4 \sqrt{2} \sqrt{3}}{\omega} + \left(1 - \frac{2459 \lambda^2 k^3^2 A^6}{6 \omega^2}\right) \lambda k^3 A^3 \sqrt{2} \sqrt{3} \\
& - \frac{\left(-\frac{\lambda^2 A^4 (331 A^2 k^3 - 75 k^4 \omega)}{\omega} + \frac{7 \omega}{2}\right) \lambda k^3 A^3 \sqrt{2} \sqrt{3}}{3 \omega}, \frac{7 \lambda^2 k^3^2 A^6 \sqrt{2} \sqrt{3}}{\omega} \\
& + \frac{\lambda^2 A^4 \sqrt{2} \sqrt{3} (7 A^2 k^3 + 10 k^4 \omega) \left(15 \lambda^2 k^4 A^4 + \frac{3 \omega}{2}\right)}{2 \omega^2} + 10 \left(1 \right.
\end{aligned}$$

$$\begin{aligned}
& - \frac{2459 \lambda^2 k^3 A^6}{6 \omega^2} \Bigg) \lambda^2 k^4 A^4 \sqrt{2} \sqrt{3} + \frac{90 \lambda^4 A^8 (17 A^2 k^3 - 2 k^4 \omega) k^4 \sqrt{2} \sqrt{3}}{\omega^2} \\
& - \frac{\left( - \frac{\lambda^2 A^4 (331 A^2 k^3 - 75 k^4 \omega)}{\omega} + \frac{7 \omega}{2} \right) \lambda^2 A^4 \sqrt{2} \sqrt{3} (7 A^2 k^3 + 10 k^4 \omega)}{2 \omega^2}, \\
& - \frac{668 \lambda^3 k^3 A^7 k^4 \sqrt{3}}{\omega} + \frac{6 \lambda^3 A^7 \sqrt{3} (7 A^2 k^3 + 10 k^4 \omega) k^3}{\omega^2} \\
& + \frac{9 \lambda k^3 A^3 \sqrt{3} \left( 39 \lambda^2 k^4 A^4 + \frac{5 \omega}{2} \right)}{\omega} + 9 \left( 1 - \frac{2459 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{3} \\
& + \frac{90 \lambda^3 A^7 (17 A^2 k^3 - 2 k^4 \omega) k^3 \sqrt{3}}{\omega^2} \\
& - \frac{9 \left( - \frac{\lambda^2 A^4 (331 A^2 k^3 - 75 k^4 \omega)}{\omega} + \frac{7 \omega}{2} \right) \lambda k^3 A^3 \sqrt{3}}{\omega}, - \frac{331 \lambda^2 k^3 A^6}{\omega} \\
& + \frac{30 \lambda^4 A^8 (7 A^2 k^3 + 10 k^4 \omega) k^4}{\omega^2} + \left( 1 - \frac{2459 \lambda^2 k^3 A^6}{6 \omega^2} \right) \left( 75 \lambda^2 k^4 A^4 + \frac{7 \omega}{2} \right) \\
& + \frac{1620 \lambda^4 A^8 (17 A^2 k^3 - 2 k^4 \omega) k^4}{\omega^2} - \left( - \frac{\lambda^2 A^4 (331 A^2 k^3 - 75 k^4 \omega)}{\omega} + \frac{7 \omega}{2} \right) \left( 1 \right. \\
& \left. - \frac{2459 \lambda^2 k^3 A^6}{6 \omega^2} \right), \frac{760 \lambda^3 k^3 A^7 k^4}{\omega} + \frac{6 \lambda^3 A^7 (7 A^2 k^3 + 10 k^4 \omega) k^3}{\omega^2} + 24 \left( 1 \right. \\
& \left. - \frac{2459 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 - \frac{24 \lambda k^3 A^3 \left( 123 \lambda^2 k^4 A^4 + \frac{9 \omega}{2} \right)}{\omega}
\end{aligned}$$

$$\begin{aligned}
& + \frac{675 \lambda^3 A^7 (17 A^2 k^3 - 2 k^4 \omega) k^3}{\omega^2} \\
& + \frac{24 \left( -\frac{\lambda^2 A^4 (331 A^2 k^3 - 75 k^4 \omega)}{\omega} + \frac{7 \omega}{2} \right) \lambda k^3 A^3}{\omega}, \\
& \frac{6 \lambda^4 A^8 (7 A^2 k^3 + 10 k^4 \omega) k^4 \sqrt{5}}{\omega^2} - \frac{306 \lambda^2 k^3 A^6 \sqrt{5}}{\omega} + 36 \left( 1 \right. \\
& \left. - \frac{2459 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{5} \\
& + \frac{9 \lambda^2 A^4 \sqrt{5} (17 A^2 k^3 - 2 k^4 \omega) \left( 183 \lambda^2 k^4 A^4 + \frac{11 \omega}{2} \right)}{\omega^2} \\
& - \frac{9 \left( -\frac{\lambda^2 A^4 (331 A^2 k^3 - 75 k^4 \omega)}{\omega} + \frac{7 \omega}{2} \right) \lambda^2 A^4 \sqrt{5} (17 A^2 k^3 - 2 k^4 \omega)}{\omega^2} \Bigg], \\
& \left[ \frac{\lambda^2 A^4 \sqrt{2} \sqrt{3} (13 A^2 k^3 + k^4 \omega) \left( 3 \lambda^2 k^4 A^4 + \frac{\omega}{2} \right)}{2 \omega^2} + \frac{26 \lambda^2 k^3 A^6 \sqrt{2} \sqrt{3}}{\omega} \right. \\
& + \frac{6 \lambda^4 A^8 \sqrt{3} (37 A^2 k^3 + 14 k^4 \omega) k^4 \sqrt{2}}{\omega^2} + 2 \left( 1 \right. \\
& \left. - \frac{5111 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{2} \sqrt{3} \\
& \left. - \frac{\left( -\frac{\lambda^2 A^4 (541 A^2 k^3 - 123 k^4 \omega)}{\omega} + \frac{9 \omega}{2} \right) \lambda^2 A^4 \sqrt{2} \sqrt{3} (13 A^2 k^3 + k^4 \omega)}{2 \omega^2} \right],
\end{aligned}$$

$$\begin{aligned}
& \frac{3 \lambda^3 A^7 \sqrt{2} \sqrt{3} (13 A^2 k^3 + k^4 \omega) k^3}{2 \omega^2} + \frac{2 \lambda k^3 A^3 \sqrt{2} \sqrt{3} \left(15 \lambda^2 k^4 A^4 + \frac{3 \omega}{2}\right)}{3 \omega} \\
& + \frac{6 \lambda^3 A^7 \sqrt{3} (37 A^2 k^3 + 14 k^4 \omega) k^3 \sqrt{2}}{\omega^2} + \frac{90 \lambda^3 k^3 A^7 k^4 \sqrt{2} \sqrt{3}}{\omega} + 2 \left(1 \right. \\
& \left. - \frac{5111 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{2} \sqrt{3} \\
& - \frac{2 \left( - \frac{\lambda^2 A^4 (541 A^2 k^3 - 123 k^4 \omega)}{\omega} + \frac{9 \omega}{2} \right) \lambda k^3 A^3 \sqrt{2} \sqrt{3}}{3 \omega},
\end{aligned}$$

$$\begin{aligned}
& \frac{6 \lambda^4 A^8 \sqrt{3} (13 A^2 k^3 + k^4 \omega) k^4}{\omega^2} + \frac{74 \lambda^2 k^3 A^6 \sqrt{3}}{\omega} \\
& + \frac{\lambda^2 A^4 \sqrt{3} (37 A^2 k^3 + 14 k^4 \omega) \left(39 \lambda^2 k^4 A^4 + \frac{5 \omega}{2}\right)}{\omega^2} + 28 \left(1 \right. \\
& \left. - \frac{5111 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k^4 A^4 \sqrt{3} \\
& - \frac{\left( - \frac{\lambda^2 A^4 (541 A^2 k^3 - 123 k^4 \omega)}{\omega} + \frac{9 \omega}{2} \right) \lambda^2 A^4 \sqrt{3} (37 A^2 k^3 + 14 k^4 \omega)}{\omega^2},
\end{aligned}$$

$$\begin{aligned}
& \frac{3 \lambda^3 A^7 (13 A^2 k^3 + k^4 \omega) k^3}{\omega^2} - \frac{2660 \lambda^3 k^3 A^7 k^4}{\omega} \\
& + \frac{27 \lambda^3 A^7 (37 A^2 k^3 + 14 k^4 \omega) k^3}{\omega^2} + \frac{24 \lambda k^3 A^3 \left(75 \lambda^2 k^4 A^4 + \frac{7 \omega}{2}\right)}{\omega} + 24 \left(1 \right.
\end{aligned}$$

$$- \frac{5111 \lambda^2 k^3 A^6}{6 \omega^2} \Bigg) \lambda k^3 A^3 - \frac{24 \left( -\frac{\lambda^2 A^4 (541 A^2 k^3^2 - 123 k^4 \omega)}{\omega} + \frac{9 \omega}{2} \right) \lambda k^3 A^3}{\omega},$$

$$\frac{6 \lambda^4 A^8 (13 A^2 k^3^2 + k^4 \omega) k^4}{\omega^2} - \frac{541 \lambda^2 k^3^2 A^6}{\omega} + \frac{84 \lambda^4 A^8 (37 A^2 k^3^2 + 14 k^4 \omega) k^4}{\omega^2}$$

$$+ \left( 1 - \frac{5111 \lambda^2 k^3^2 A^6}{6 \omega^2} \right) \left( 123 \lambda^2 k^4 A^4 + \frac{9 \omega}{2} \right) - \left( -\frac{\lambda^2 A^4 (541 A^2 k^3^2 - 123 k^4 \omega)}{\omega} \right.$$

$$+ \frac{9 \omega}{2} \Bigg) \left( 1 - \frac{5111 \lambda^2 k^3^2 A^6}{6 \omega^2} \right), \frac{872 \lambda^3 k^3 A^7 k^4 \sqrt{5}}{\omega}$$

$$+ \frac{6 \lambda^3 A^7 (37 A^2 k^3^2 + 14 k^4 \omega) k^3 \sqrt{5}}{\omega^2} + 15 \left( 1 - \frac{5111 \lambda^2 k^3^2 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{5}$$

$$- \frac{15 \lambda k^3 A^3 \sqrt{5} \left( 183 \lambda^2 k^4 A^4 + \frac{11 \omega}{2} \right)}{\omega}$$

$$+ \frac{15 \left( -\frac{\lambda^2 A^4 (541 A^2 k^3^2 - 123 k^4 \omega)}{\omega} + \frac{9 \omega}{2} \right) \lambda k^3 A^3 \sqrt{5}}{\omega} \Bigg],$$

$$\left[ \frac{3 \lambda^3 A^7 \sqrt{2} \sqrt{3} \sqrt{5} (17 A^2 k^3^2 + k^4 \omega) k^3}{2 \omega^2} + \frac{34 \lambda^3 k^3 A^7 k^4 \sqrt{2} \sqrt{3} \sqrt{5}}{\omega} \right.$$

$$+ \frac{9 \lambda^3 A^7 \sqrt{5} (21 A^2 k^3^2 + 2 k^4 \omega) k^3 \sqrt{2} \sqrt{3}}{\omega^2},$$

$$\frac{\lambda^2 A^4 \sqrt{2} \sqrt{3} \sqrt{5} (17 A^2 k^3^2 + k^4 \omega) \left( 15 \lambda^2 k^4 A^4 + \frac{3 \omega}{2} \right)}{2 \omega^2}$$



$$\begin{aligned}
& + \frac{34 \lambda^2 k^3 A^6 \sqrt{2} \sqrt{3} \sqrt{5}}{\omega} + \frac{90 \lambda^4 A^8 \sqrt{5} (21 A^2 k^3 + 2 k 4 \omega) k 4 \sqrt{2} \sqrt{3}}{\omega^2} + 2 \left( 1 \right. \\
& \left. - \frac{3395 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda^2 k 4 A^4 \sqrt{2} \sqrt{3} \sqrt{5} \\
& - \frac{1}{2 \omega^2} \left( \left( \frac{\lambda^2 A^4 (1145 A^2 k^3 + 183 k 4 \omega)}{\omega} \right. \right. \\
& \left. \left. + \frac{11 \omega}{2} \right) \lambda^2 A^4 \sqrt{2} \sqrt{3} \sqrt{5} (17 A^2 k^3 + k 4 \omega) \right), \\
& \frac{6 \lambda^3 A^7 \sqrt{3} \sqrt{5} (17 A^2 k^3 + k 4 \omega) k 3}{\omega^2} + \frac{2 \lambda k 3 A^3 \sqrt{3} \sqrt{5} \left( 39 \lambda^2 k 4 A^4 + \frac{5 \omega}{2} \right)}{3 \omega} \\
& + \frac{81 \lambda^3 A^7 \sqrt{5} (21 A^2 k^3 + 2 k 4 \omega) k 3 \sqrt{3}}{\omega^2} + \frac{420 \lambda^3 k 3 A^7 k 4 \sqrt{3} \sqrt{5}}{\omega} + 2 \left( 1 \right. \\
& \left. - \frac{3395 \lambda^2 k^3 A^6}{6 \omega^2} \right) \lambda k 3 A^3 \sqrt{3} \sqrt{5} \\
& - \frac{2 \left( \frac{\lambda^2 A^4 (1145 A^2 k^3 + 183 k 4 \omega)}{\omega} + \frac{11 \omega}{2} \right) \lambda k 3 A^3 \sqrt{3} \sqrt{5}}{3 \omega}, \\
& \frac{30 \lambda^4 A^8 \sqrt{5} (17 A^2 k^3 + k 4 \omega) k 4}{\omega^2} + \frac{378 \lambda^2 k^3 A^6 \sqrt{5}}{\omega} \\
& + \frac{9 \lambda^2 A^4 \sqrt{5} (21 A^2 k^3 + 2 k 4 \omega) \left( 75 \lambda^2 k 4 A^4 + \frac{7 \omega}{2} \right)}{\omega^2} + 36 \left( 1 \right.
\end{aligned}$$

$$\begin{aligned}
& - \frac{3395 \lambda^2 k^3 A^6}{6 \omega^2} \Bigg) \lambda^2 k^4 A^4 \sqrt{5} \\
& - \frac{9 \left( \frac{\lambda^2 A^4 (1145 A^2 k^3^2 + 183 k^4 \omega)}{\omega} + \frac{11 \omega}{2} \right) \lambda^2 A^4 \sqrt{5} (21 A^2 k^3^2 + 2 k^4 \omega)}{\omega^2}, \\
& \frac{6 \lambda^3 A^7 \sqrt{5} (17 A^2 k^3^2 + k^4 \omega) k^3}{\omega^2} + \frac{56 \lambda^3 k^3 A^7 k^4 \sqrt{5}}{\omega} \\
& + \frac{216 \lambda^3 A^7 \sqrt{5} (21 A^2 k^3^2 + 2 k^4 \omega) k^3}{\omega^2} + \frac{15 \lambda k^3 A^3 \sqrt{5} \left( 123 \lambda^2 k^4 A^4 + \frac{9 \omega}{2} \right)}{\omega} \\
& + 15 \left( 1 - \frac{3395 \lambda^2 k^3^2 A^6}{6 \omega^2} \right) \lambda k^3 A^3 \sqrt{5} \\
& - \frac{15 \left( \frac{\lambda^2 A^4 (1145 A^2 k^3^2 + 183 k^4 \omega)}{\omega} + \frac{11 \omega}{2} \right) \lambda k^3 A^3 \sqrt{5}}{\omega}, \\
& \frac{30 \lambda^4 A^8 (17 A^2 k^3^2 + k^4 \omega) k^4}{\omega^2} + \frac{1145 \lambda^2 k^3^2 A^6}{\omega} \\
& + \frac{1620 \lambda^4 A^8 (21 A^2 k^3^2 + 2 k^4 \omega) k^4}{\omega^2} + \left( 1 - \frac{3395 \lambda^2 k^3^2 A^6}{6 \omega^2} \right) \left( 183 \lambda^2 k^4 A^4 \right. \\
& \left. + \frac{11 \omega}{2} \right) - \left( \frac{\lambda^2 A^4 (1145 A^2 k^3^2 + 183 k^4 \omega)}{\omega} + \frac{11 \omega}{2} \right) \left( 1 - \frac{3395 \lambda^2 k^3^2 A^6}{6 \omega^2} \right) \Bigg] \Bigg] \\
& \left[ \begin{array}{cccccc}
o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) \\
o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) \\
o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) \\
o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) \\
o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) \\
o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4) & o(\lambda^3) & o(\lambda^4)
\end{array} \right]
\end{aligned}
\tag{38.10}$$

We proceed to examine a contribution to energy of second order, namely matrix

**> mE2 := map(expand, Ee2);**

$$mE2 := \begin{bmatrix} \left[ -\frac{11 k^3 A^6}{\omega} + 3 k4 A^4, 0, 0, 0, 0, 0 \right], \\ \left[ 0, -\frac{71 k^3 A^6}{\omega} + 15 k4 A^4, 0, 0, 0, 0 \right], \\ \left[ 0, 0, -\frac{191 k^3 A^6}{\omega} + 39 k4 A^4, 0, 0, 0 \right], \\ \left[ 0, 0, 0, -\frac{331 k^3 A^6}{\omega} + 75 k4 A^4, 0, 0 \right], \\ \left[ 0, 0, 0, 0, -\frac{541 k^3 A^6}{\omega} + 123 k4 A^4, 0 \right], \\ \left[ 0, 0, 0, 0, 0, \frac{1145 k^3 A^6}{\omega} + 183 k4 A^4 \right] \end{bmatrix} \quad (38.11)$$

Because we truncate matrices **H**, not all entries in matrices **E** and **U** are correct: in particular, only the first three diagonal entries in  $E^{(2)}$  are correct. We compare our results with those of T. Y. Wu in *Quantum Mechanics* (World Scientific, Singapore, 1985), who used the following definition for **H**.

$$H = \frac{p^2}{2\mu} + \frac{k_1 x^2}{2!} + \frac{k_2 x^3}{3!} + \frac{k_3 x^4}{4!} + \dots$$

**> W2 := SubMatrix(mE2,1..3,1..3);**

$$W2 := \begin{bmatrix} -\frac{11 k^3 A^6}{\omega} + 3 k4 A^4 & 0 & 0 \\ 0 & -\frac{71 k^3 A^6}{\omega} + 15 k4 A^4 & 0 \\ 0 & 0 & -\frac{191 k^3 A^6}{\omega} + 39 k4 A^4 \end{bmatrix} \quad (38.12)$$

**> interp([0,1,2], [W2[1,1],W2[2,2],W2[3,3]], v);**

$$-\frac{A^4 (30 A^2 k^3 - 6 k4 \omega) v^2}{\omega} - \frac{A^4 (30 A^2 k^3 - 6 k4 \omega) v}{\omega} - \frac{A^4 (11 A^2 k^3 - 3 k4 \omega)}{\omega} \quad (38.13)$$

**> map(collect, series(%, v=-1/2), A);**

$$-\frac{7 k^3 A^6}{2 \omega} + \frac{3 k4 A^4}{2} + \left( -\frac{30 k^3 A^6}{\omega} + 6 k4 A^4 \right) \left( v + \frac{1}{2} \right)^2 \quad (38.14)$$

**> factor(algsb(A^4=Be/4,%));**

(38.15)

$$- \frac{Be \left( 30 A^2 k^3 v^2 + 30 A^2 k^3 v + 11 A^2 k^3 - 6 k4 \omega v^2 - 6 k4 \omega v - 3 k4 \omega \right)}{4 \omega} \quad (38.15)$$

**> simplify(subs(omega=A^2\*4,%),symbolic);**

$$- \frac{15 \left( \left( k^3 - \frac{4 k4}{5} \right) v^2 + \left( k^3 - \frac{4 k4}{5} \right) v + \frac{11 k^3}{30} - \frac{2 k4}{5} \right) Be}{8} \quad (38.16)$$

**> factor(series(expand(%),n=-1/2,3));**

$$- \frac{Be \left( 30 k^3 v^2 + 30 k^3 v - 24 k4 v^2 + 11 k^3 - 24 k4 v - 12 k4 \right)}{16} \quad (38.17)$$

With  $E^{(0)} = \omega_0 \left( v + \frac{1}{2} \right)$ , we convert our results for  $E^{(2)}$  to conform to Wu's notation.

**> W2 := subs(k3=k2/3!, k4=k3/4!, omega=omega[0]\*h,  
SubMatrix(mE2,1..3,1..3));**

$$W2 := \begin{bmatrix} -\frac{11 k^2 A^6}{36 \omega_0 h} + \frac{k^3 A^4}{8} & 0 & 0 \\ 0 & -\frac{71 k^2 A^6}{36 \omega_0 h} + \frac{5 k^3 A^4}{8} & 0 \\ 0 & 0 & -\frac{191 k^2 A^6}{36 \omega_0 h} + \frac{13 k^3 A^4}{8} \end{bmatrix} \quad (38.18)$$

These diagonal entries are consistent with equation (II-140) in Wu's book. The correction to energy of the harmonic oscillator in Wu's equation we obtain by interpolation from three values in the above matrix. We obtain

**> interp([0,1,2], [W2[1,1],W2[2,2],W2[3,3]], n);**

$$- \frac{A^4 \left( 60 k^2 A^2 - 18 k^3 \omega_0 h \right) n^2}{72 \omega_0 h} - \frac{A^4 \left( 60 k^2 A^2 - 18 k^3 \omega_0 h \right) n}{72 \omega_0 h} - \frac{A^4 \left( 22 k^2 A^2 - 9 k^3 \omega_0 h \right)}{72 \omega_0 h} \quad (38.19)$$

Two alternative ways to write this expression are as a polynomial in  $A$  or in  $n + \frac{1}{2}$  with  $n$  as vibrational quantum number.

**> collect(%, A, factor);**

$$- \frac{k^2 \left( 30 n^2 + 30 n + 11 \right) A^6}{36 \omega_0 h} + \frac{k^3 \left( 2 n^2 + 2 n + 1 \right) A^4}{8} \quad (38.20)$$

**> map(collect, series(%, n=-1/2), A);**

$$-\frac{7 k^2 A^6}{72 \omega_0 h} + \frac{k^3 A^4}{16} + \left( -\frac{5 k^2 A^6}{6 \omega_0 h} + \frac{k^3 A^4}{4} \right) \left( n + \frac{1}{2} \right)^2 \quad (38.21)$$

Corrections to greater order are obtained on running procedure AnHarmonic with matrices of sufficient rank. Five statements, as given below beginning with "AnHarmonic(4,10):" for instance, suffice to generate corrections of a given order; the duration of calculation increases exponentially with order (according to this, or any alternative, approach).

We comment here on computations. With regard to construction of  $H^{(K)}$  for  $K > 0$ , when we first computed these matrices, we used  $H_{i,j}^{(1)} = k_3 \left( \sum_{i,j} x_{m,i} x_{i,j} x_{j,n} \right)$  and  $H_{i,j}^{(2)} = k_4 \left( \sum_{i,j} x_{m,i} x_{i,j} x_{j,k} x_{k,n} \right)$  et cetera. This procedure yields an algorithm to compute  $H^{(K)}$  of which the running time is exponential in  $K$ . An algorithm based on computing matrix power  $x^K$  is superior, and is sufficiently quick that there is little point in using formulae for bands of  $H^{(K)}$ . The linear system of equations that is constructed and solved is a diagonal system, but, because formulae involve several square roots of small integers, *Maple* runs much more slowly than if coefficients were simple integers: a reason is that *Maple* is careful to determine algebraic relations between square roots, e.g.  $\sqrt{6} - \sqrt{2} \sqrt{3} = 0$ . For our calculations here, if one has no objection to see  $\sqrt{2}$ ,  $\sqrt{3}$  and  $\sqrt{6}$  in an answer, one can accelerate calculations ten or more times if one solves equations *blindly*; we devised for this purpose our own solver presented above as **mysolve**.

Succeeding calculations require progressively increasing duration and memory. The first argument in each call to AnHarmonic indicates the perturbative order of a calculation, and the second argument specifies the rank of matrices involved in a calculation; this rank must increase exponentially with order to achieve accurate results. We calculate correction terms to fourth order,

**> AnHarmonic(4, 10):**

"Solving for the coefficient of",  $\lambda$

```
matrix H1
matrix equation to be solved
expanded matrix equation to be solved
matrix E1
condition for the next U matrix
vars = {u1,1, u2,2, u3,3, u4,4, u5,5, u6,6, u7,7, u8,8, u9,9, u10,10}
matrix U1
```

"Solving for the coefficient of",  $\lambda^2$

```
matrix H2
matrix equation to be solved
matrix E2
condition for the next U matrix
vars = {u1,1, u2,2, u3,3, u4,4, u5,5, u6,6, u7,7, u8,8, u9,9, u10,10}
matrix U2
```

"Solving for the coefficient of",  $\lambda^3$

```

matrix H3
matrix equation to be solved
matrix E3
condition for the next U matrix

```

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}\}$$

```
matrix U3
```

"Solving for the coefficient of",  $\lambda^4$

```

matrix H4
matrix equation to be solved
matrix E4
condition for the next U matrix

```

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}\}$$

```
matrix U4
```

```
> factormatrix(SubMatrix(Ee4,1..4, 1..4));
```

$$\left(\frac{A^6}{\omega^3}\right) \&* \left[ \begin{aligned} &[-930 A^6 k^3 \omega^4 + 684 A^4 k^3 \omega^4 - 130 A^2 k^3 k^5 \omega^2 - 42 A^2 k^4 \omega^2 + 15 k^6 \omega^3, 0, \\ &0, 0], \\ &[0, -11250 A^6 k^3 \omega^4 + 7452 A^4 k^3 \omega^4 - 1230 A^2 k^3 k^5 \omega^2 - 330 A^2 k^4 \omega^2 + 105 k^6 \omega^3, \\ &0, 0], \\ &[0, 0, -46950 A^6 k^3 \omega^4 + 30420 A^4 k^3 \omega^4 - 4850 A^2 k^3 k^5 \omega^2 - 1230 A^2 k^4 \omega^2 \\ &+ 375 k^6 \omega^3, 0], \\ &[0, 0, 0, -124950 A^6 k^3 \omega^4 + 80388 A^4 k^3 \omega^4 - 12670 A^2 k^3 k^5 \omega^2 - 3150 A^2 k^4 \omega^2 \\ &+ 945 k^6 \omega^3] \end{aligned} \right] \quad (38.22)$$

```
> interp([0,1,2,3], [seq(Ee4[i,i], i=1..4)], n):
```

```
> collect(%, [A,k3,k4,k5,k6,omega], factor);
```

$$\begin{aligned} & - \frac{30 (2n+1) (47n^2 + 47n + 31) k^3 A^{12}}{\omega^3} \\ & + \frac{36 (2n+1) (25n^2 + 25n + 19) k^4 k^3 A^{10}}{\omega^2} + \left( \right. \\ & - \frac{10 (2n+1) (14n^2 + 14n + 13) k^5 k^3}{\omega} - \frac{2 (2n+1) (17n^2 + 17n + 21) k^4 \omega^2}{\omega} \left. \right) A^8 \\ & + 5 (2n+1) (2n^2 + 2n + 3) k^6 A^6 \end{aligned} \quad (38.23)$$

```
> evaln( Ee4[n,n] ) = map(collect, taylor(%, n=-1/2, 5), A, factor)
;
```

$$Ee4_{n,n} = \left( -\frac{1155 k^3 A^{12}}{\omega^3} + \frac{918 k^3 A^{10} k^4}{\omega^2} - \frac{(190 k^5 k^3 + 67 k^4^2) A^8}{\omega} + 25 k^6 A^6 \right) \left( n + \frac{1}{2} \right) + \left( -\frac{2820 k^3 A^{12}}{\omega^3} + \frac{1800 k^3 A^{10} k^4}{\omega^2} - \frac{4 (70 k^5 k^3 + 17 k^4^2) A^8}{\omega} + 20 k^6 A^6 \right) \left( n + \frac{1}{2} \right)^3 \quad (38.24)$$

sixth order,

```
> AnHarmonic(6, 18):
```

"Solving for the coefficient of",  $\lambda$

```
matrix H1
```

```
matrix equation to be solved
```

```
expanded matrix equation to be solved
```

```
matrix E1
```

```
condition for the next U matrix
```

```
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,  
u16, 16, u17, 17, u18, 18}
```

```
matrix U1
```

"Solving for the coefficient of",  $\lambda^2$

```
matrix H2
```

```
matrix equation to be solved
```

```
matrix E2
```

```
condition for the next U matrix
```

```
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,  
u16, 16, u17, 17, u18, 18}
```

```
matrix U2
```

"Solving for the coefficient of",  $\lambda^3$

```
matrix H3
```

```
matrix equation to be solved
```

```
matrix E3
```

```
condition for the next U matrix
```

```
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,  
u16, 16, u17, 17, u18, 18}
```

```
matrix U3
```

"Solving for the coefficient of",  $\lambda^4$

```
matrix H4
matrix equation to be solved
matrix E4
condition for the next U matrix
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,
        u16, 16, u17, 17, u18, 18}
matrix U4
```

"Solving for the coefficient of",  $\lambda^5$

```
matrix H5
matrix equation to be solved
matrix E5
condition for the next U matrix
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,
        u16, 16, u17, 17, u18, 18}
matrix U5
```

"Solving for the coefficient of",  $\lambda^6$

```
matrix H6
matrix equation to be solved
matrix E6
condition for the next U matrix
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,
        u16, 16, u17, 17, u18, 18}
matrix U6
```

```
> interp([0,1,2,3,4],[seq(Ee6[i,i],i=1..5)],n):
```

```
> evaln( Ee6[n,n] ) = map(collect, taylor(%,n=-1/2, 5), A, factor);
```

$$Ee6_{n,n} = -\frac{101479 k^3 A^{18}}{4 \omega^5} + \frac{131817 k^3 k4 A^{16}}{4 \omega^4} - \frac{k^3 (29554 k3 k5 + 40261 k4^2) A^{14}}{4 \omega^3} \quad (38.25)$$

$$+ \frac{(6055 k^3 k6 + 11334 k3 k4 k5 + 1539 k4^3) A^{12}}{4 \omega^2}$$

$$- \frac{3 (770 k3 k7 + 630 k4 k6 + 369 k5^2) A^{10}}{8 \omega} + \frac{315 k8 A^8}{8} + \left( -\frac{418110 k^3 A^{18}}{\omega^5} \right)$$



$$\begin{aligned}
& + \frac{479970 k3^4 k4 A^{16}}{\omega^4} - \frac{6 k3^2 (15910 k3 k5 + 20671 k4^2) A^{14}}{\omega^3} \\
& + \frac{6 (2845 k3^2 k6 + 4890 k3 k4 k5 + 569 k4^3) A^{12}}{\omega^2} \\
& - \frac{5 (546 k3 k7 + 354 k4 k6 + 217 k5^2) A^{10}}{\omega} + 245 k8 A^8 \left( n + \frac{1}{2} \right)^2 + \left( \right. \\
& - \frac{463020 k3^6 A^{18}}{\omega^5} + \frac{465300 k3^4 k4 A^{16}}{\omega^4} - \frac{60 k3^2 (1302 k3 k5 + 1663 k4^2) A^{14}}{\omega^3} \\
& + \frac{60 (181 k3^2 k6 + 322 k3 k4 k5 + 25 k4^3) A^{12}}{\omega^2} \\
& \left. - \frac{30 (42 k3 k7 + 22 k4 k6 + 21 k5^2) A^{10}}{\omega} + 70 k8 A^8 \right) \left( n + \frac{1}{2} \right)^4
\end{aligned}$$

and eighth order; the order of the matrix increases correspondingly.

**> AnHarmonic(8, 28):**

"Solving for the coefficient of",  $\lambda$

```
matrix H1
matrix equation to be solved
expanded matrix equation to be solved
matrix E1
condition for the next U matrix
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,
        u16, 16, u17, 17, u18, 18, u19, 19, u20, 20, u21, 21, u22, 22, u23, 23, u24, 24, u25, 25, u26, 26, u27, 27, u28, 28}
matrix U1
```

"Solving for the coefficient of",  $\lambda^2$

```
matrix H2
matrix equation to be solved
matrix E2
condition for the next U matrix
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,
        u16, 16, u17, 17, u18, 18, u19, 19, u20, 20, u21, 21, u22, 22, u23, 23, u24, 24, u25, 25, u26, 26, u27, 27, u28, 28}
matrix U2
```

"Solving for the coefficient of",  $\lambda^3$

```
matrix H3
```

matrix equation to be solved

matrix E3

condition for the next U matrix

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}, u_{11,11}, u_{12,12}, u_{13,13}, u_{14,14}, u_{15,15}, \\ u_{16,16}, u_{17,17}, u_{18,18}, u_{19,19}, u_{20,20}, u_{21,21}, u_{22,22}, u_{23,23}, u_{24,24}, u_{25,25}, u_{26,26}, u_{27,27}, u_{28,28}\}$$

matrix U3

"Solving for the coefficient of",  $\lambda^4$

matrix H4

matrix equation to be solved

matrix E4

condition for the next U matrix

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}, u_{11,11}, u_{12,12}, u_{13,13}, u_{14,14}, u_{15,15}, \\ u_{16,16}, u_{17,17}, u_{18,18}, u_{19,19}, u_{20,20}, u_{21,21}, u_{22,22}, u_{23,23}, u_{24,24}, u_{25,25}, u_{26,26}, u_{27,27}, u_{28,28}\}$$

matrix U4

"Solving for the coefficient of",  $\lambda^5$

matrix H5

matrix equation to be solved

matrix E5

condition for the next U matrix

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}, u_{11,11}, u_{12,12}, u_{13,13}, u_{14,14}, u_{15,15}, \\ u_{16,16}, u_{17,17}, u_{18,18}, u_{19,19}, u_{20,20}, u_{21,21}, u_{22,22}, u_{23,23}, u_{24,24}, u_{25,25}, u_{26,26}, u_{27,27}, u_{28,28}\}$$

matrix U5

"Solving for the coefficient of",  $\lambda^6$

matrix H6

matrix equation to be solved

matrix E6

condition for the next U matrix

$$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}, u_{11,11}, u_{12,12}, u_{13,13}, u_{14,14}, u_{15,15}, \\ u_{16,16}, u_{17,17}, u_{18,18}, u_{19,19}, u_{20,20}, u_{21,21}, u_{22,22}, u_{23,23}, u_{24,24}, u_{25,25}, u_{26,26}, u_{27,27}, u_{28,28}\}$$

matrix U6

"Solving for the coefficient of",  $\lambda^7$

matrix H7

matrix equation to be solved

matrix E7

condition for the next U matrix

```
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,  
u16, 16, u17, 17, u18, 18, u19, 19, u20, 20, u21, 21, u22, 22, u23, 23, u24, 24, u25, 25, u26, 26, u27, 27, u28, 28}
```

```
matrix U7
```

"Solving for the coefficient of",  $\lambda^8$

```
matrix H8
```

```
matrix equation to be solved
```

```
matrix E8
```

```
condition for the next U matrix
```

```
vars = {u1, 1, u2, 2, u3, 3, u4, 4, u5, 5, u6, 6, u7, 7, u8, 8, u9, 9, u10, 10, u11, 11, u12, 12, u13, 13, u14, 14, u15, 15,  
u16, 16, u17, 17, u18, 18, u19, 19, u20, 20, u21, 21, u22, 22, u23, 23, u24, 24, u25, 25, u26, 26, u27, 27, u28, 28}
```

```
matrix U8
```

```
> interp([0,1,2,3,4,5],[seq(Ee8[i,i],i=1..6)],n):
```

```
> evaln( Ee8[n,n] ) = map(collect, taylor(%n=-1/2, 6), A, factor);
```

$$Ee8_{n,n} = \left( -\frac{129443349 k^3 A^{24}}{4 \omega^7} + \frac{53574549 k^3 k_4 A^{22}}{\omega^6} \right. \quad (38.26)$$

$$- \frac{3 k^3 (7690522 k_3 k_5 + 17666725 k_4^2) A^{20}}{2 \omega^5}$$

$$+ \frac{3 k^3 (1595083 k^2 k_6 + 5805700 k_3 k_4 k_5 + 2606190 k_4^3) A^{18}}{2 \omega^4}$$

$$- \frac{1}{4 \omega^3} ( (1930488 k^3 k_7 + 4987188 k^2 k_4 k_6 + 2529360 k^2 k_5^2 + 4477660 k_3 k_4^2 k_5$$

$$+ 305141 k_4^4) A^{16} )$$

$$+ \frac{1}{2 \omega^2} ( (177506 k^2 k_8 + 298956 k_3 k_4 k_7 + 290834 k_3 k_5 k_6 + 117281 k_4^2 k_6$$

$$+ 129462 k_4 k_5^2) A^{14} ) - \frac{(56154 k_3 k_9 + 42084 k_4 k_8 + 44058 k_5 k_7 + 19277 k_6^2) A^{12}}{4 \omega}$$

$$+ \frac{5607 k_{10} A^{10}}{4} \Bigg) \left( n + \frac{1}{2} \right) + \left( -\frac{154601370 k^3 A^{24}}{\omega^7} + \frac{231728040 k^3 k_4 A^{22}}{\omega^6} \right.$$

$$\left. - \frac{60 k^3 (750326 k_3 k_5 + 1695241 k_4^2) A^{20}}{\omega^5} \right)$$

$$\begin{aligned}
& + \frac{60 k3^2 (137821 k3^2 k6 + 493980 k3 k4 k5 + 213046 k4^3) A^{18}}{\omega^4} \\
& - \frac{1}{\omega^3} (10 (145656 k3^3 k7 + 361836 k3^2 k4 k6 + 187040 k3^2 k5^2 + 313860 k3 k4^2 k5 \\
& + 17833 k4^4) A^{16}) \\
& + \frac{1}{\omega^2} (20 (11186 k3^2 k8 + 18060 k3 k4 k7 + 17706 k3 k5 k6 + 5911 k4^2 k6 \\
& + 7518 k4 k5^2) A^{14}) - \frac{10 (2814 k3 k9 + 1764 k4 k8 + 2142 k5 k7 + 829 k6^2) A^{12}}{\omega} \\
& + 1890 k10 A^{10} \Bigg) \left( n + \frac{1}{2} \right)^3 + \left( - \frac{95872644 k3^8 A^{24}}{\omega^7} + \frac{130619664 k3^6 k4 A^{22}}{\omega^6} \right. \\
& - \frac{504 k3^4 (44578 k3 k5 + 101325 k4^2) A^{20}}{\omega^5} \\
& + \frac{2520 k3^2 (1371 k3^2 k6 + 5188 k3 k4 k5 + 2150 k4^3) A^{18}}{\omega^4} \\
& - \frac{84 (5880 k3^3 k7 + 15300 k3^2 k4 k6 + 8720 k3^2 k5^2 + 13580 k3 k4^2 k5 + 509 k4^4) A^{16}}{\omega^3} \\
& + \frac{168 (354 k3^2 k8 + 588 k3 k4 k7 + 658 k3 k5 k6 + 149 k4^2 k6 + 294 k4 k5^2) A^{14}}{\omega^2} \\
& \left. - \frac{12 (462 k3 k9 + 252 k4 k8 + 462 k5 k7 + 131 k6^2) A^{12}}{\omega} + 252 k10 A^{10} \right) \left( n + \frac{1}{2} \right)^5
\end{aligned}$$

For tenth order we obtain these results.

**> AnHarmonic(10, 72):**

"Solving for the coefficient of",  $\lambda$

matrix H1

matrix equation to be solved

expanded matrix equation to be solved

matrix E1

condition for the next U matrix

$vars = \{u_{1,1}, u_{2,2}, u_{3,3}, u_{4,4}, u_{5,5}, u_{6,6}, u_{7,7}, u_{8,8}, u_{9,9}, u_{10,10}, u_{11,11}, u_{12,12}, u_{13,13}, u_{14,14}, u_{15,15},$

$u_{16,16}, u_{17,17}, u_{18,18}, u_{19,19}, u_{20,20}, u_{21,21}, u_{22,22}, u_{23,23}, u_{24,24}, u_{25,25}, u_{26,26}, u_{27,27}, u_{28,28},$

$$\begin{aligned} &u_{29, 29}, u_{30, 30}, u_{31, 31}, u_{32, 32}, u_{33, 33}, u_{34, 34}, u_{35, 35}, u_{36, 36}, u_{37, 37}, u_{38, 38}, u_{39, 39}, u_{40, 40}, u_{41, 41}, \\ &u_{42, 42}, u_{43, 43}, u_{44, 44}, u_{45, 45}, u_{46, 46}, u_{47, 47}, u_{48, 48}, u_{49, 49}, u_{50, 50}, u_{51, 51}, u_{52, 52}, u_{53, 53}, u_{54, 54}, \\ &u_{55, 55}, u_{56, 56}, u_{57, 57}, u_{58, 58}, u_{59, 59}, u_{60, 60}, u_{61, 61}, u_{62, 62}, u_{63, 63}, u_{64, 64}, u_{65, 65}, u_{66, 66}, u_{67, 67}, \\ &u_{68, 68}, u_{69, 69}, u_{70, 70}, u_{71, 71}, u_{72, 72} \} \end{aligned}$$

matrix U1

"Solving for the coefficient of",  $\lambda^2$

matrix H2

matrix equation to be solved

matrix E2

condition for the next U matrix

$$\begin{aligned} vars = \{ &u_{1, 1}, u_{2, 2}, u_{3, 3}, u_{4, 4}, u_{5, 5}, u_{6, 6}, u_{7, 7}, u_{8, 8}, u_{9, 9}, u_{10, 10}, u_{11, 11}, u_{12, 12}, u_{13, 13}, u_{14, 14}, u_{15, 15}, \\ &u_{16, 16}, u_{17, 17}, u_{18, 18}, u_{19, 19}, u_{20, 20}, u_{21, 21}, u_{22, 22}, u_{23, 23}, u_{24, 24}, u_{25, 25}, u_{26, 26}, u_{27, 27}, u_{28, 28}, \\ &u_{29, 29}, u_{30, 30}, u_{31, 31}, u_{32, 32}, u_{33, 33}, u_{34, 34}, u_{35, 35}, u_{36, 36}, u_{37, 37}, u_{38, 38}, u_{39, 39}, u_{40, 40}, u_{41, 41}, \\ &u_{42, 42}, u_{43, 43}, u_{44, 44}, u_{45, 45}, u_{46, 46}, u_{47, 47}, u_{48, 48}, u_{49, 49}, u_{50, 50}, u_{51, 51}, u_{52, 52}, u_{53, 53}, u_{54, 54}, \\ &u_{55, 55}, u_{56, 56}, u_{57, 57}, u_{58, 58}, u_{59, 59}, u_{60, 60}, u_{61, 61}, u_{62, 62}, u_{63, 63}, u_{64, 64}, u_{65, 65}, u_{66, 66}, u_{67, 67}, \\ &u_{68, 68}, u_{69, 69}, u_{70, 70}, u_{71, 71}, u_{72, 72} \} \end{aligned}$$

matrix U2

"Solving for the coefficient of",  $\lambda^3$

matrix H3

matrix equation to be solved

matrix E3

condition for the next U matrix

$$\begin{aligned} vars = \{ &u_{1, 1}, u_{2, 2}, u_{3, 3}, u_{4, 4}, u_{5, 5}, u_{6, 6}, u_{7, 7}, u_{8, 8}, u_{9, 9}, u_{10, 10}, u_{11, 11}, u_{12, 12}, u_{13, 13}, u_{14, 14}, u_{15, 15}, \\ &u_{16, 16}, u_{17, 17}, u_{18, 18}, u_{19, 19}, u_{20, 20}, u_{21, 21}, u_{22, 22}, u_{23, 23}, u_{24, 24}, u_{25, 25}, u_{26, 26}, u_{27, 27}, u_{28, 28}, \\ &u_{29, 29}, u_{30, 30}, u_{31, 31}, u_{32, 32}, u_{33, 33}, u_{34, 34}, u_{35, 35}, u_{36, 36}, u_{37, 37}, u_{38, 38}, u_{39, 39}, u_{40, 40}, u_{41, 41}, \\ &u_{42, 42}, u_{43, 43}, u_{44, 44}, u_{45, 45}, u_{46, 46}, u_{47, 47}, u_{48, 48}, u_{49, 49}, u_{50, 50}, u_{51, 51}, u_{52, 52}, u_{53, 53}, u_{54, 54}, \\ &u_{55, 55}, u_{56, 56}, u_{57, 57}, u_{58, 58}, u_{59, 59}, u_{60, 60}, u_{61, 61}, u_{62, 62}, u_{63, 63}, u_{64, 64}, u_{65, 65}, u_{66, 66}, u_{67, 67}, \\ &u_{68, 68}, u_{69, 69}, u_{70, 70}, u_{71, 71}, u_{72, 72} \} \end{aligned}$$

matrix U3

"Solving for the coefficient of",  $\lambda^4$

```

matrix H4
matrix equation to be solved
matrix E4
condition for the next U matrix
vars = {u_1, 1, u_2, 2, u_3, 3, u_4, 4, u_5, 5, u_6, 6, u_7, 7, u_8, 8, u_9, 9, u_10, 10, u_11, 11, u_12, 12, u_13, 13, u_14, 14, u_15, 15,
        u_16, 16, u_17, 17, u_18, 18, u_19, 19, u_20, 20, u_21, 21, u_22, 22, u_23, 23, u_24, 24, u_25, 25, u_26, 26, u_27, 27, u_28, 28,
        u_29, 29, u_30, 30, u_31, 31, u_32, 32, u_33, 33, u_34, 34, u_35, 35, u_36, 36, u_37, 37, u_38, 38, u_39, 39, u_40, 40, u_41, 41,
        u_42, 42, u_43, 43, u_44, 44, u_45, 45, u_46, 46, u_47, 47, u_48, 48, u_49, 49, u_50, 50, u_51, 51, u_52, 52, u_53, 53, u_54, 54,
        u_55, 55, u_56, 56, u_57, 57, u_58, 58, u_59, 59, u_60, 60, u_61, 61, u_62, 62, u_63, 63, u_64, 64, u_65, 65, u_66, 66, u_67, 67,
        u_68, 68, u_69, 69, u_70, 70, u_71, 71, u_72, 72}
matrix U4

```

"Solving for the coefficient of",  $\lambda^5$

```

matrix H5
matrix equation to be solved
matrix E5
condition for the next U matrix
vars = {u_1, 1, u_2, 2, u_3, 3, u_4, 4, u_5, 5, u_6, 6, u_7, 7, u_8, 8, u_9, 9, u_10, 10, u_11, 11, u_12, 12, u_13, 13, u_14, 14, u_15, 15,
        u_16, 16, u_17, 17, u_18, 18, u_19, 19, u_20, 20, u_21, 21, u_22, 22, u_23, 23, u_24, 24, u_25, 25, u_26, 26, u_27, 27, u_28, 28,
        u_29, 29, u_30, 30, u_31, 31, u_32, 32, u_33, 33, u_34, 34, u_35, 35, u_36, 36, u_37, 37, u_38, 38, u_39, 39, u_40, 40, u_41, 41,
        u_42, 42, u_43, 43, u_44, 44, u_45, 45, u_46, 46, u_47, 47, u_48, 48, u_49, 49, u_50, 50, u_51, 51, u_52, 52, u_53, 53, u_54, 54,
        u_55, 55, u_56, 56, u_57, 57, u_58, 58, u_59, 59, u_60, 60, u_61, 61, u_62, 62, u_63, 63, u_64, 64, u_65, 65, u_66, 66, u_67, 67,
        u_68, 68, u_69, 69, u_70, 70, u_71, 71, u_72, 72}
matrix U5

```

"Solving for the coefficient of",  $\lambda^6$

```

matrix H6
matrix equation to be solved
matrix E6
condition for the next U matrix
vars = {u_1, 1, u_2, 2, u_3, 3, u_4, 4, u_5, 5, u_6, 6, u_7, 7, u_8, 8, u_9, 9, u_10, 10, u_11, 11, u_12, 12, u_13, 13, u_14, 14, u_15, 15,
        u_16, 16, u_17, 17, u_18, 18, u_19, 19, u_20, 20, u_21, 21, u_22, 22, u_23, 23, u_24, 24, u_25, 25, u_26, 26, u_27, 27, u_28, 28,
        u_29, 29, u_30, 30, u_31, 31, u_32, 32, u_33, 33, u_34, 34, u_35, 35, u_36, 36, u_37, 37, u_38, 38, u_39, 39, u_40, 40, u_41, 41,
        u_42, 42, u_43, 43, u_44, 44, u_45, 45, u_46, 46, u_47, 47, u_48, 48, u_49, 49, u_50, 50, u_51, 51, u_52, 52, u_53, 53, u_54, 54,

```

$$u_{55, 55}, u_{56, 56}, u_{57, 57}, u_{58, 58}, u_{59, 59}, u_{60, 60}, u_{61, 61}, u_{62, 62}, u_{63, 63}, u_{64, 64}, u_{65, 65}, u_{66, 66}, u_{67, 67},$$

$$u_{68, 68}, u_{69, 69}, u_{70, 70}, u_{71, 71}, u_{72, 72} \}$$

matrix U6

"Solving for the coefficient of",  $\lambda^7$

matrix H7

matrix equation to be solved

matrix E7

condition for the next U matrix

$$vars = \{u_{1, 1}, u_{2, 2}, u_{3, 3}, u_{4, 4}, u_{5, 5}, u_{6, 6}, u_{7, 7}, u_{8, 8}, u_{9, 9}, u_{10, 10}, u_{11, 11}, u_{12, 12}, u_{13, 13}, u_{14, 14}, u_{15, 15},$$

$$u_{16, 16}, u_{17, 17}, u_{18, 18}, u_{19, 19}, u_{20, 20}, u_{21, 21}, u_{22, 22}, u_{23, 23}, u_{24, 24}, u_{25, 25}, u_{26, 26}, u_{27, 27}, u_{28, 28},$$

$$u_{29, 29}, u_{30, 30}, u_{31, 31}, u_{32, 32}, u_{33, 33}, u_{34, 34}, u_{35, 35}, u_{36, 36}, u_{37, 37}, u_{38, 38}, u_{39, 39}, u_{40, 40}, u_{41, 41},$$

$$u_{42, 42}, u_{43, 43}, u_{44, 44}, u_{45, 45}, u_{46, 46}, u_{47, 47}, u_{48, 48}, u_{49, 49}, u_{50, 50}, u_{51, 51}, u_{52, 52}, u_{53, 53}, u_{54, 54},$$

$$u_{55, 55}, u_{56, 56}, u_{57, 57}, u_{58, 58}, u_{59, 59}, u_{60, 60}, u_{61, 61}, u_{62, 62}, u_{63, 63}, u_{64, 64}, u_{65, 65}, u_{66, 66}, u_{67, 67},$$

$$u_{68, 68}, u_{69, 69}, u_{70, 70}, u_{71, 71}, u_{72, 72} \}$$

matrix U7

"Solving for the coefficient of",  $\lambda^8$

matrix H8

matrix equation to be solved

matrix E8

condition for the next U matrix

$$vars = \{u_{1, 1}, u_{2, 2}, u_{3, 3}, u_{4, 4}, u_{5, 5}, u_{6, 6}, u_{7, 7}, u_{8, 8}, u_{9, 9}, u_{10, 10}, u_{11, 11}, u_{12, 12}, u_{13, 13}, u_{14, 14}, u_{15, 15},$$

$$u_{16, 16}, u_{17, 17}, u_{18, 18}, u_{19, 19}, u_{20, 20}, u_{21, 21}, u_{22, 22}, u_{23, 23}, u_{24, 24}, u_{25, 25}, u_{26, 26}, u_{27, 27}, u_{28, 28},$$

$$u_{29, 29}, u_{30, 30}, u_{31, 31}, u_{32, 32}, u_{33, 33}, u_{34, 34}, u_{35, 35}, u_{36, 36}, u_{37, 37}, u_{38, 38}, u_{39, 39}, u_{40, 40}, u_{41, 41},$$

$$u_{42, 42}, u_{43, 43}, u_{44, 44}, u_{45, 45}, u_{46, 46}, u_{47, 47}, u_{48, 48}, u_{49, 49}, u_{50, 50}, u_{51, 51}, u_{52, 52}, u_{53, 53}, u_{54, 54},$$

$$u_{55, 55}, u_{56, 56}, u_{57, 57}, u_{58, 58}, u_{59, 59}, u_{60, 60}, u_{61, 61}, u_{62, 62}, u_{63, 63}, u_{64, 64}, u_{65, 65}, u_{66, 66}, u_{67, 67},$$

$$u_{68, 68}, u_{69, 69}, u_{70, 70}, u_{71, 71}, u_{72, 72} \}$$

matrix U8

"Solving for the coefficient of",  $\lambda^9$

matrix H9

matrix equation to be solved

matrix E9

condition for the next U matrix

```
vars = {u_1, 1, u_2, 2, u_3, 3, u_4, 4, u_5, 5, u_6, 6, u_7, 7, u_8, 8, u_9, 9, u_10, 10, u_11, 11, u_12, 12, u_13, 13, u_14, 14, u_15, 15,
        u_16, 16, u_17, 17, u_18, 18, u_19, 19, u_20, 20, u_21, 21, u_22, 22, u_23, 23, u_24, 24, u_25, 25, u_26, 26, u_27, 27, u_28, 28,
        u_29, 29, u_30, 30, u_31, 31, u_32, 32, u_33, 33, u_34, 34, u_35, 35, u_36, 36, u_37, 37, u_38, 38, u_39, 39, u_40, 40, u_41, 41,
        u_42, 42, u_43, 43, u_44, 44, u_45, 45, u_46, 46, u_47, 47, u_48, 48, u_49, 49, u_50, 50, u_51, 51, u_52, 52, u_53, 53, u_54, 54,
        u_55, 55, u_56, 56, u_57, 57, u_58, 58, u_59, 59, u_60, 60, u_61, 61, u_62, 62, u_63, 63, u_64, 64, u_65, 65, u_66, 66, u_67, 67,
        u_68, 68, u_69, 69, u_70, 70, u_71, 71, u_72, 72}
```

```
matrix U9
```

"Solving for the coefficient of",  $\lambda^{10}$

```
matrix H10
```

```
matrix equation to be solved
```

```
matrix E10
```

```
condition for the next U matrix
```

```
vars = {u_1, 1, u_2, 2, u_3, 3, u_4, 4, u_5, 5, u_6, 6, u_7, 7, u_8, 8, u_9, 9, u_10, 10, u_11, 11, u_12, 12, u_13, 13, u_14, 14, u_15, 15,
        u_16, 16, u_17, 17, u_18, 18, u_19, 19, u_20, 20, u_21, 21, u_22, 22, u_23, 23, u_24, 24, u_25, 25, u_26, 26, u_27, 27, u_28, 28,
        u_29, 29, u_30, 30, u_31, 31, u_32, 32, u_33, 33, u_34, 34, u_35, 35, u_36, 36, u_37, 37, u_38, 38, u_39, 39, u_40, 40, u_41, 41,
        u_42, 42, u_43, 43, u_44, 44, u_45, 45, u_46, 46, u_47, 47, u_48, 48, u_49, 49, u_50, 50, u_51, 51, u_52, 52, u_53, 53, u_54, 54,
        u_55, 55, u_56, 56, u_57, 57, u_58, 58, u_59, 59, u_60, 60, u_61, 61, u_62, 62, u_63, 63, u_64, 64, u_65, 65, u_66, 66, u_67, 67,
        u_68, 68, u_69, 69, u_70, 70, u_71, 71, u_72, 72}
```

```
matrix U10
```

```
> interp([0,1,2,3,4,5,6],[seq(Ee10[i,i],i=1..7)],n):
```

```
> evaln( Ee10[n,n] ) = map(collect, taylor(%,n=-1/2,7), A, factor);
```

$$Ee10_{n,n} = -\frac{2375536317 k^3 A^{30}}{2 \omega^9} + \frac{5112354429 k^3 k^4 A^{28}}{2 \omega^8} \quad (38.27)$$

$$- \frac{k^6 (570170440 k^3 k^5 + 1875235809 k^4^2) A^{26}}{\omega^7}$$

$$+ \frac{k^4 (125451228 k^3 k^2 k^6 + 697320300 k^3 k^4 k^5 + 542138237 k^4^3) A^{24}}{\omega^6}$$

$$- \frac{1}{2 \omega^5} (k^3^2 (54858006 k^3 k^7 + 245446860 k^3^2 k^4 k^6 + 121918445 k^3^2 k^5^2$$



$$\begin{aligned}
& + 453292880 k_3 k_4^2 k_5 + 104283313 k_4^4) A^{22}) + \frac{1}{2 \omega^4} ( (11623829 k_3^4 k_8 \\
& + 40733788 k_3^3 k_4 k_7 + 39214848 k_3^3 k_5 k_6 + 54140744 k_3^2 k_4^2 k_6 + 54388854 k_3^2 k_4 k_5^2 \\
& + 33066120 k_3 k_4^3 k_5 + 1456569 k_4^5) A^{20}) - \frac{1}{2 \omega^3} ( (2336663 k_3^3 k_9 \\
& + 5991174 k_3^2 k_4 k_8 + 5703723 k_3^2 k_5 k_7 + 2729425 k_3^2 k_6^2 + 5188782 k_3 k_4^2 k_7 \\
& + 10091532 k_3 k_4 k_5 k_6 + 1709370 k_3 k_5^3 + 1470420 k_4^3 k_6 + 2301381 k_4^2 k_5^2) \\
& A^{18}) + \frac{1}{4 \omega^2} ( 3 ( 282975 k_{10} k_3^2 + 477792 k_3 k_4 k_9 + 449358 k_3 k_5 k_8 \\
& + 420200 k_3 k_6 k_7 + 194670 k_4^2 k_8 + 386544 k_4 k_5 k_7 + 179550 k_4 k_6^2 + 191160 k_5^2 k_6) \\
& A^{16}) - \frac{9 ( 46200 k_{10} k_4 + 57750 k_{11} k_3 + 45318 k_5 k_9 + 39900 k_6 k_8 + 20075 k_7^2) A^{14}}{16 \omega} \\
& + \frac{51975 k_{12} A^{12}}{16} + \left( - \frac{26541790065 k_3^{10} A^{30}}{\omega^9} + \frac{53237904993 k_3^8 k_4 A^{28}}{\omega^8} \right. \\
& - \frac{6 k_3^6 ( 1853896870 k_3 k_5 + 6007627359 k_4^2) A^{26}}{\omega^7} \\
& + \frac{6 k_3^4 ( 379992501 k_3^2 k_6 + 2073384570 k_3 k_4 k_5 + 1580214947 k_4^3) A^{24}}{\omega^6} \\
& - \frac{1}{\omega^5} ( 3 k_3^2 ( 153794592 k_3^3 k_7 + 670871478 k_3^2 k_4 k_6 + 333289220 k_3^2 k_5^2 \\
& + 1210044260 k_3 k_4^2 k_5 + 269873047 k_4^4) A^{22}) + \frac{1}{\omega^4} ( 3 ( 29671040 k_3^4 k_8 \\
& + 101516128 k_3^3 k_4 k_7 + 97475340 k_3^3 k_5 k_6 + 129658238 k_3^2 k_4^2 k_6 \\
& + 130951020 k_3^2 k_4 k_5^2 + 76740540 k_3 k_4^3 k_5 + 3105983 k_4^5) A^{20}) \\
& - \frac{1}{\omega^3} ( 3 ( 5373242 k_3^3 k_9 + 13220088 k_3^2 k_4 k_8 + 12733770 k_3^2 k_5 k_7 + 6056107 k_3^2 k_6^2 \\
& + 11023824 k_3 k_4^2 k_7 + 21314964 k_3 k_4 k_5 k_6 + 3613960 k_3 k_5^3 + 2839538 k_4^3 k_6
\end{aligned}$$

$$\begin{aligned}
& + 4678032 k^4 k^5 A^{18}) + \frac{1}{\omega^2} (3 (860895 k^{10} k^3 + 1365588 k^3 k^4 k^9 \\
& + 1290310 k^3 k^5 k^8 + 1223964 k^3 k^6 k^7 + 506016 k^4 k^2 k^8 + 1056244 k^4 k^5 k^7 \\
& + 463623 k^4 k^6 k^2 + 510070 k^5 k^2 k^6) A^{16}) \\
& - \frac{21 (45040 k^{10} k^4 + 63954 k^{11} k^3 + 45426 k^5 k^9 + 39004 k^6 k^8 + 21161 k^7 k^2) A^{14}}{4 \omega} \\
& + \frac{101409 k^{12} A^{12}}{4} \Bigg) \left( n + \frac{1}{2} \right)^2 + \left( - \frac{57626387280 k^3 k^{10} A^{30}}{\omega^9} \right. \\
& + \frac{106553134800 k^3 k^8 k^4 A^{28}}{\omega^8} - \frac{238560 k^3 k^6 (85455 k^3 k^5 + 275707 k^4 k^2) A^{26}}{\omega^7} \\
& + \frac{1680 k^3 k^4 (2232271 k^3 k^2 k^6 + 12280770 k^3 k^4 k^5 + 9214130 k^4 k^3) A^{24}}{\omega^6} \\
& - \frac{1}{\omega^5} (840 k^3 k^2 (804342 k^3 k^3 k^7 + 3509190 k^3 k^2 k^4 k^6 + 1781705 k^3 k^2 k^5 k^2 \\
& + 6338700 k^3 k^4 k^2 k^5 + 1352338 k^4 k^4) A^{22}) + \frac{1}{\omega^4} (120 (947667 k^3 k^4 k^8 \\
& + 3252004 k^3 k^3 k^4 k^7 + 3178444 k^3 k^3 k^5 k^6 + 4058582 k^3 k^2 k^4 k^2 k^6 + 4280262 k^3 k^2 k^4 k^5 k^2 \\
& + 2358580 k^3 k^4 k^3 k^5 + 78302 k^4 k^5) A^{20}) - \frac{1}{\omega^3} (40 (440097 k^3 k^3 k^9 \\
& + 1072806 k^3 k^2 k^4 k^8 + 1075557 k^3 k^2 k^5 k^7 + 499206 k^3 k^2 k^6 k^2 + 870198 k^3 k^4 k^2 k^7 \\
& + 1744728 k^3 k^4 k^5 k^6 + 314930 k^3 k^5 k^3 + 189594 k^4 k^3 k^6 + 373849 k^4 k^2 k^5 k^2) A^{18}) \\
& + \frac{1}{\omega^2} (20 (116235 k^{10} k^3 k^2 + 180936 k^3 k^4 k^9 + 180726 k^3 k^5 k^8 + 167664 k^3 k^6 k^7 \\
& + 57106 k^4 k^2 k^8 + 142968 k^4 k^5 k^7 + 54636 k^4 k^6 k^2 + 73220 k^5 k^2 k^6) A^{16})
\end{aligned}$$

$$\begin{aligned}
& - \frac{35 (4200 k10 k4 + 6798 k11 k3 + 5214 k5 k9 + 3868 k6 k8 + 2343 k7^2) A^{14}}{\omega} \\
& + 12705 k12 A^{12} \left( n + \frac{1}{2} \right)^4 + \left( - \frac{22598568720 k3^{10} A^{30}}{\omega^9} + \frac{38797354512 k3^8 k4 A^{28}}{\omega^8} \right. \\
& - \frac{672 k3^6 (10043890 k3 k5 + 32742281 k4^2) A^{26}}{\omega^7} \\
& + \frac{672 k3^4 (1607327 k3^2 k6 + 9312030 k3 k4 k5 + 6934565 k4^3) A^{24}}{\omega^6} \\
& - \frac{1}{5} (336 k3^2 (492744 k3^3 k7 + 2282130 k3^2 k4 k6 + 1231160 k3^2 k5^2 \\
& + 4295340 k3 k4^2 k5 + 868465 k4^4) A^{22}) + \frac{1}{4} (336 (68940 k3^4 k8 \\
& + 253360 k3^3 k4 k7 + 268900 k3^3 k5 k6 + 323450 k3^2 k4^2 k6 + 375980 k3^2 k4 k5^2 \\
& + 191060 k3 k4^3 k5 + 4169 k4^5) A^{20}) - \frac{1}{3} (336 (8690 k3^3 k9 + 22416 k3^2 k4 k8 \\
& + 25650 k3^2 k5 k7 + 11725 k3^2 k6^2 + 18552 k3 k4^2 k7 + 41612 k3 k4 k5 k6 + 8480 k3 k5^3 \\
& + 3046 k4^3 k6 + 9276 k4^2 k5^2) A^{18}) + \frac{1}{2} (112 (2745 k10 k3^2 + 4356 k3 k4 k9 \\
& + 5210 k3 k5 k8 + 4860 k3 k6 k7 + 1156 k4^2 k8 + 4356 k4 k5 k7 + 1203 k4 k6^2 \\
& + 2430 k5^2 k6) A^{16}) \\
& - \frac{28 (480 k10 k4 + 858 k11 k3 + 858 k5 k9 + 508 k6 k8 + 429 k7^2) A^{14}}{\omega} \\
& + 924 k12 A^{12} \left( n + \frac{1}{2} \right)^6
\end{aligned}$$

This calculation can be pursued to higher order with appropriate modification of the latter three commands.

#### *e1.43 exercise*

For a formula for potential energy of an anharmonic oscillator of Dunham's form, i.e.

$V(x) = a_0 x^2 \left( 1 + \sum_{j=1} a_j x^j \right)$ , in which  $V(x) = a_0 x^2$  is the limiting form for the canonical harmonic oscillator and additional terms  $a_0 a_j x^{j+2}$  represent the corrections to take into account anharmonic behaviour, convert the preceding derivation so that the results of the energies are expressed only in terms of coefficients  $a_j$ ,  $j = 0, 1, 2, \dots$  according to the selected order of perturbation theory. Take  $a_0 = \frac{B_e}{g^2}$

in which  $g = \frac{2 B_e}{\omega_e}$  with equilibrium rotational parameter  $B_e$  and equilibrium vibrational parameter  $\omega_e$

so that expressions for the energies of various orders involve  $g$  to various powers and coefficients  $a_j$  with  $j > 0$ .

#### ***e1.44 exercise***

Within wave mechanics, a system described with hamiltonian  $H$  that supports only two states is describable with an amplitude function of form  $\psi = c_1 \phi_1 + c_2 \phi_2$ .

- Assuming that  $H$  and coefficients  $c_1$  and  $c_2$  are real and that  $\phi_1$  and  $\phi_2$  form a complete orthonormal set, derive equations for the exact energies of this system in terms of matrix elements of  $H$ .
- With  $H^{(0)} \phi_j = E_j^{(0)} \phi_j$ , let  $H = H^{(0)} + H^{(1)}$  and compare the results of non-degenerate and degenerate perturbation theories.

#### ***e1.45 exercise***

For an anharmonic oscillator having quadratic and other terms of only even power, the hamiltonian has this form.

$$H = \frac{p^2}{2\mu} + \frac{k_e q^2}{2} + \epsilon q^l$$

Replacing  $k_e$  with  $4\pi^2 \mu v_0^2$  to obtain

$$H = \frac{p^2}{2\mu} + 2\pi^2 \mu v_0^2 q^2 + \epsilon q^l,$$

with Dirac's operators, evaluate the shifts of the energies from those of a canonical linear harmonic oscillator with perturbation theory, for which  $H$  is divided into  $H_0$  and  $H_1$ , for

- $l = 4$  and
- $l = 6$ ;

take  $H_0 = h v_0 \left( b a + \frac{1}{2} \right)$ , containing creation operator  $b$  and destruction operator  $a$ , with the same value of parameter  $v_0$ , assuming that quartic term  $H_1 = \epsilon q^4$  or sextic term  $H_1 = \epsilon q^6$  is small.

#### ***e1.46 exercise***

With the Schroedinger equation in one dimension as

$$-\left( \frac{d^2}{dx^2} \psi(x) \right) + V(x) \psi(x) = E \psi(x)$$

in which  $V \rightarrow \frac{8\pi^2 m V}{h^2}$  and  $E \rightarrow \frac{8\pi^2 m E}{h^2}$  are reduced variables, in a Hilbert space  $L_2(\mathbf{R})$  such that an

integral of formula or function  $y(x)$  as  $\int_{-\infty}^{\infty} |y(x)|^2 dx < \infty$ ,

i) show that, for  $V(x) = p^2 x^6 - 3 x^2$  and  $p > 0$ ,  $\psi(x) = e^{-p x^4}$  is a solution and find the eigenvalue; plot  $V(x)$  and  $\psi(x)$  for varied values of  $p$ ;

ii) show that, for  $V(x) = p^2 x^6 + 2 p q x^4 + (q^2 - 3 p) x^2$ ,  $\psi(x) = e^{-\frac{p x^4}{4} - \frac{q x^2}{2}}$  is a solution and find the eigenvalue; plot  $V(x)$  and  $\psi(x)$  for varied values of  $p$  and  $q$ , both positive and negative.

#### e1.47 exercise, particle on a ring

For a particle of mass  $\mu$  confined to a ring of radius  $R$  such that  $V=0$  on the ring and  $V \rightarrow \infty$  elsewhere, calculate the amplitude functions and energies of the stationary states according to wave mechanics. This result is applicable also to a rigid body with moment of inertia  $I_z$  rotating freely in plane  $xy$ , with that moment  $\mu R^2$  replacing mass  $\mu$ .

#### e1.48 exercise

For this amplitude function of a particle of mass  $\mu$  in one spatial dimension,

$$\psi(x) = c \left( \frac{x}{x_0} \right)^n e^{-\frac{x}{x_0}}$$

in which  $c$  and  $n$  are constant parameters and  $x_0 > 0$ , calculate the potential energy  $V(x)$  and energy  $E$  for which this amplitude function is an eigenfunction.

#### e1.49 exercise

For a symmetric function of potential energy attributed to Rosen and Morse,  $V(x) = -12 \operatorname{sech}(x)^2$ , show that  $\psi_0(x) = \operatorname{sech}(x)^3$ ,  $\psi_1(x) = \operatorname{sech}(x)^2 \tanh(x)$  and  $\psi_3(x) = \operatorname{sech}(x) (5 \tanh(x)^2 - 1)$  are

solutions of Schroedinger's equation in which  $m = \frac{h^2}{8 \pi^2}$ , and find the corresponding energies of these

three discrete states in terms of the same quantity. Plot the given amplitude functions at their energies with the curve for potential energy, and observe the number of nodes in these amplitude functions.

### 1.46 anharmonic oscillator according to Dirac operators

#### > restart:

After executing all procedures in section 1.241 and all commands in section 1.242, for the anharmonic oscillator we apply, according to perturbation theory, as the exact result of order zero of perturbation this energy of the canonical linear harmonic oscillator.

```
> `H^o *`|n>` = factor(H &@ ket(n));
```

$$H^o |n\rangle = H \&@ ket(n) \quad (46.1)$$

```
> E0 := n -> (n+1/2)*h*nu[0];
```

$$E0 := n \mapsto \left( n + \frac{1}{2} \right) \cdot h \cdot \nu_0 \quad (46.2)$$

We take as our hamiltonian for the anharmonic oscillator hamiltonian  $H^o$  of the canonical linear harmonic oscillator with two further terms in  $H''$  containing coefficients  $a_1$  and  $a_2$  to indicate the extent of the perturbation and parameter  $\lambda$  to reflect the order of smallness of those coefficients:

$$H = H^o + H'' = H^o + h \nu_0 a_1 \lambda q^3 + h \nu_0 a_2 \lambda^2 q^4$$

We recall also operators  $a$  and  $a^\dagger$ , represented as  $a$  to decrease the population of a state by one unit and  $b$  to increase the population of a state by one unit, for the same reasons as before, with these properties.

$$\begin{aligned} > \text{'a |n>' = a \&@ ket(n);} \\ & \qquad a |n> = a \&@ ket(n) \end{aligned} \quad (46.3)$$

$$\begin{aligned} > \text{'b |n-1>' = b \&@ ket(n-1);} \\ & \qquad b |n-1> = b \&@ ket(n-1) \end{aligned} \quad (46.4)$$

As before, coordinate  $q$  for displacement is expressed in terms of a sum of  $a$  and  $b$  as

$$\begin{aligned} > q; \\ & \qquad q \end{aligned} \quad (46.5)$$

We apply a simplified form.

$$\begin{aligned} > q := a + b; \\ & \qquad q := a + b \end{aligned} \quad (46.6)$$

We proceed to evaluate matrix elements of  $q$  to various powers.

$$\begin{aligned} > \text{'< m | q | n >' = bracket3(m, q, n);} \\ & \qquad \langle m | q | n \rangle = \text{braket3}(m, a + b, n) \end{aligned} \quad (46.7)$$

$$\begin{aligned} > \text{convert(\%, Krondelta);} \\ & \text{Error, unrecognized conversion: Krondelta} \\ > \text{'< m | q^2 | n >' = bracket3(m, q^2, n);} \\ & \qquad \langle m | q^2 | n \rangle = \text{braket3}(m, (a + b) \&^2, n) \end{aligned} \quad (46.8)$$

$$\begin{aligned} > \text{'< m | q^2 | n >' = convert(rhs(\%), Krondelta);} \\ & \text{Error, unrecognized conversion: Krondelta} \\ > \text{'< m | q^3 | n >' = bracket3(m, q^3, n);} \\ & \qquad \langle m | q^3 | n \rangle = \text{braket3}(m, (a + b) \&^3, n) \end{aligned} \quad (46.9)$$

$$\begin{aligned} > \text{'< m | q^3 | n >' = convert(rhs(\%), Krondelta);} \\ & \text{Error, unrecognized conversion: Krondelta} \\ > \text{'< m | q^4 | n >' = bracket3(m, q^4, n);} \\ & \qquad \langle m | q^4 | n \rangle = \text{braket3}(m, (a + b) \&^4, n) \end{aligned} \quad (46.10)$$

$$\begin{aligned} > \text{'< m | q^4 | n >' = convert(rhs(\%), Krondelta);} \\ & \text{Error, unrecognized conversion: Krondelta} \end{aligned}$$

For eigenvalues  $E_n$  and eigenvectors  $|n\rangle$  of perturbed hamiltonian  $H$  specified above, only approximate values are practicable, according to perturbation theory. We apply a system of equations as follows,

$$\begin{aligned} \frac{d}{d\lambda} E_n(\lambda) &= \langle n(\lambda) | \frac{\partial}{\partial \lambda} (H) | n(\lambda) \rangle \\ \frac{d}{d\lambda} E_n(\lambda) &= \sum_{m < n} \frac{\langle m(\lambda) | \left( \frac{\partial}{\partial \lambda} (H) \right) | n(\lambda) \rangle}{E_n(\lambda) - E_m(\lambda)} \langle n(\lambda) | \end{aligned}$$

with

$$\frac{\partial}{\partial \lambda} (H) = h v_0 a_1 q^3 + 2 h v_0 a_2 \lambda q^4$$

We show these calculations.

$$> \text{'H'} := h \nu_0 a_1 \lambda^2 q^4 + h \nu_0 a_2 \lambda q^3; \quad H' := h \nu_0 a_2 \lambda^2 q^4 + h \nu_0 a_1 \lambda q^3 \quad (46.11)$$

$$> \text{Diff}(\text{'H'}, \lambda) = \text{diff}(\%, \lambda); \quad \frac{\partial}{\partial \lambda} (H') = 2 h \lambda (a + b)^4 a_2 \nu_0 + h (a + b)^3 a_1 \nu_0 \quad (46.12)$$

Assuming that

$$E_n(\lambda) = E_n^0 + \sum_{j=1}^{\infty} \lambda^j E_{n,j}$$

and

$$|n(\lambda)\rangle = |n\rangle + \sum_{j=1}^{\infty} \lambda^j |n_j\rangle$$

in which  $E_n(\lambda)$  and  $|n_j\rangle$  are the corresponding corrections, we express the equations of the system in a form

$$E_{n,1} + 2 \lambda E_{n,2} + \dots = h \nu_0 \langle n(\lambda) | a_1 q^3 + 2 a_2 \lambda q^4 + \dots | n(\lambda) \rangle$$

$$|n_1\rangle + 2 \lambda |n_2\rangle + \dots = h \nu_0 \sum_{m < n} \frac{\langle m(\lambda) | (a_1 q^3 + 2 a_2 \lambda q^4) | n(\lambda) \rangle}{E_n(\lambda) - E_m(\lambda)} |m(\lambda)\rangle$$

For the corrections of first order, we set  $\lambda=0$  in these equations to obtain

$$E_{n,1} = h \nu_0 a_1 \langle n | q^3 | n \rangle,$$

which evaluates to

$$> E1(n) := h \nu_0 a_1 \text{braket3}(n, q^3, n); \quad E1(n) := h \nu_0 a_1 \text{braket3}(n, (a + b)^3, n) \quad (46.13)$$

and with  $\lambda=0$  the correction of first order to  $|n\rangle$  is

$$|n_1\rangle = h \nu_0 a_1 \sum_{m < n} \frac{\langle m(\lambda) | q^3 | n(\lambda) \rangle}{E_n^0 - E_m^0} |m\rangle$$

$$> \text{ket}(n[1]) = h \nu_0 a_1 \text{braket3}(m, q^3, n) / (E0(n) - E0(m));$$

$$\text{ket}(n_1) = \frac{h \nu_0 a_1 \text{braket3}(m, (a + b)^3, n)}{\left(n + \frac{1}{2}\right) h \nu_0 - \left(m + \frac{1}{2}\right) h \nu_0} \quad (46.14)$$

> expand(convert(%, Krondelta));

Error, unrecognized conversion: Krondelta

> ket(n[1]) = eval(rhs(%), m=n+1)\*ket(n+1) + eval(rhs(%), m=n+3)\*ket(n+3) + eval(rhs(%), m=n-1)\*ket(n-1) + eval(rhs(%), m=n-3)\*ket(n-3);

$$\text{ket}(n_1) = \frac{h \nu_0 a_1 \text{braket3}(n+1, (a + b)^3, n) \text{ket}(n+1)}{\left(n + \frac{1}{2}\right) h \nu_0 - \left(n + \frac{3}{2}\right) h \nu_0} \quad (46.15)$$

$$\begin{aligned}
& + \frac{h v_0 a_1 \text{braket3}(n+3, (a+b) \wedge 3, n) \text{ket}(n+3)}{\left(n + \frac{1}{2}\right) h v_0 - \left(n + \frac{7}{2}\right) h v_0} \\
& + \frac{h v_0 a_1 \text{braket3}(n-1, (a+b) \wedge 3, n) \text{ket}(n-1)}{\left(n + \frac{1}{2}\right) h v_0 - \left(n - \frac{1}{2}\right) h v_0} \\
& + \frac{h v_0 a_1 \text{braket3}(n-3, (a+b) \wedge 3, n) \text{ket}(n-3)}{\left(n + \frac{1}{2}\right) h v_0 - \left(n - \frac{5}{2}\right) h v_0}
\end{aligned}$$

**> ket(n[1]) = simplify(rhs(%));**

$$\begin{aligned}
\text{ket}(n_1) = & -\frac{1}{3} \left( a_1 (3 \text{braket3}(n+1, (a+b) \wedge 3, n) \text{ket}(n+1) + \text{braket3}(n+3, (a+b) \wedge 3, n) \text{ket}(n+3) \right. \\
& \left. - 3 \text{braket3}(n-1, (a+b) \wedge 3, n) \text{ket}(n-1) - \text{braket3}(n-3, (a+b) \wedge 3, n) \text{ket}(n-3) \right)
\end{aligned} \quad (46.16)$$

To obtain the corrections of second order, we differentiate the equations of the system with respect to  $\lambda$ , and then set  $\lambda$  equal to zero.

**> sys2 := E1(n) + 2\*lambda\*E2(n) = braket3(n(lambda), a[1]\*qq&^3 + 2\*a[2]\*lambda\*qq&^4, n(lambda));**

$$\begin{aligned}
\text{sys2} := & h v_0 a_1 \text{braket3}(n, (a+b) \wedge 3, n) + 2 \lambda E2(n) = \text{braket3}(n(\lambda), a_1 q q \wedge^3 \\
& + 2 a_2 \lambda q q \wedge^4, n(\lambda))
\end{aligned} \quad (46.17)$$

**> diff(sys2, lambda);**

$$\begin{aligned}
2 E2(n) = & D_1(\text{braket3})(n(\lambda), a_1 q q \wedge^3 + 2 a_2 \lambda q q \wedge^4, n(\lambda)) \left( \frac{d}{d\lambda} n(\lambda) \right) \\
& + 2 D_2(\text{braket3})(n(\lambda), a_1 q q \wedge^3 + 2 a_2 \lambda q q \wedge^4, n(\lambda)) a_2 q q \wedge^4 \\
& + D_3(\text{braket3})(n(\lambda), a_1 q q \wedge^3 + 2 a_2 \lambda q q \wedge^4, n(\lambda)) \left( \frac{d}{d\lambda} n(\lambda) \right)
\end{aligned} \quad (46.18)$$

As a result

$$E_{n,2} = \frac{1}{2} h v_0 (< n_1 | q^3 | n > + < n | q^3 | n_1 >) + h v_0 a_2 < n | q^4 | n >$$

and

$$\begin{aligned}
| n_2 > = & \frac{1}{2} h v_0 a_1 \sum_{n < > m} \frac{< m_1 | q^3 | n > + < m | q^3 | n_1 >}{E_{n,0} - E_{m,0}} | m > + \frac{1}{2} h v_0 a_1 \\
& \sum_{m < > n} \frac{< m | q^3 | n >}{E_{n,0} - E_{m,0}} | m_1 > + h v_0 a_2 \sum_{m < > n} \frac{< m | q^4 | n >}{E_{n,0} - E_{m,0}} | m >
\end{aligned}$$

For  $E_{n,2}$  we have



$$E_{n,2} = -h \nu_0 a_1^2 (30 n^2 + 30 n + 11) + h \nu_0 a_2 (6 n^2 + 6 n + 3)$$

Correction  $|n_2\rangle$  represents an expansion with respect to vectors  $|n-k\rangle$  and  $|n+k\rangle$ , in which  $k=0, 2, 4, 6$ .

Before one adds terms containing  $q^5, q^6, \dots$  to the hamiltonian, a calculation of corrections of greater order, beginning with power  $j=3$  of  $\lambda$ , has no meaning. The principal problem of the theory of anharmonicity involves the investigation of this hamiltonian,

$$H = H^0 + h \nu_0 \sum_{j>0} \lambda^j a_j q^{j+2}$$

in which  $a_j$  serve as anharmonic coefficients.

As an exercise, complete the coding of statements to add the terms of second order above, and proceed to add terms of third and fourth order, i.e. involving  $a_3 q^5$  and  $a_4 q^6$ , seeking a generalization that might extend the calculation to greater orders. For correctness the results can be compared with the corresponding calculation with matrix mechanics in section 1.47.

### 1.47 anharmonic oscillator according to wave mechanics with Morse's function for potential energy

**> restart;**

P. M. Morse [Physical Review, **34**, 57 - 64, 1929] produced the first treatment with wave mechanics to predict bound states of finite number, with a function to model the potential energy of a diatomic molecule of this form,

$$V(x) = D_e (1 - e^{-\alpha x})^2$$

in which  $D_e$  denotes energy in excess of that necessary for dissociation, independent variable  $x =$

$\frac{R - R_e}{R_e}$  is a reduced displacement variable with instantaneous  $R$  and equilibrium  $R_e$  internuclear

separations and  $\alpha$  is a parameter related to the coefficient for restoring force for a small displacement from equilibrium; that condition occurs when  $R = R_e$ , so that  $x = 0$  and  $V(x) = 0$ . We define the formula for potential energy,

**> VM := De\*(1-exp(-alpha\*x))^2;**

$$VM := De (1 - e^{-\alpha x})^2 \quad (47.1)$$

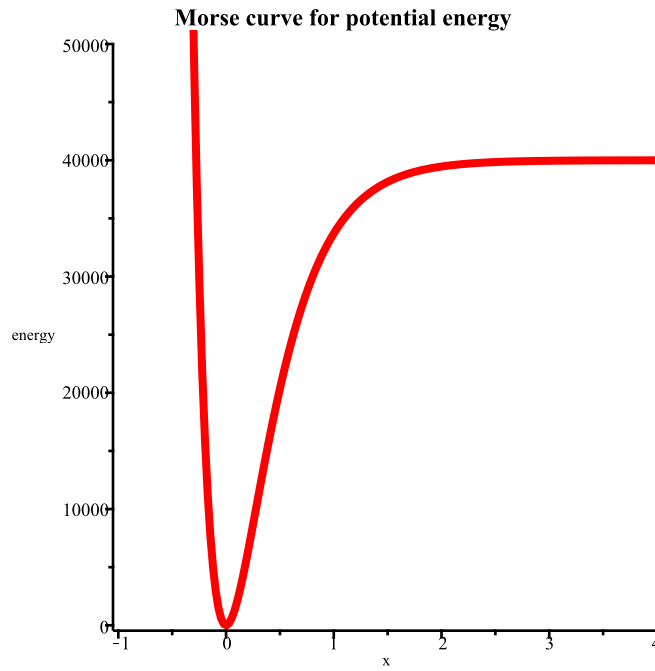
and thereby define the zero of energy of the system.

**> Eval(VM, x=0) = eval(VM, x=0);**

$$De (1 - e^{-\alpha x})^2 \Big|_{x=0} = 0 \quad (47.2)$$

With appropriate values of parameters, we plot this formula.

```
> plot(eval(VM, [De=40000, alpha=2.5]), x=-1..4, 0..50000,
      thickness=3,
      axes=frame, title="Morse curve for potential energy",
      titlefont=[TIMES,BOLD,14], labels=["x","energy"], colour=red);
```



According to that plot, parameter  $D_e$  represents the difference of energy between the energy at the asymptote for large  $x$  and the energy at the minimum of the curve. When we expand that Morse function,

$$\begin{aligned} &> \text{'taylor'(VM, x=0, 5) = taylor(VM, x=0, 5);} \\ &\quad \text{taylor}\left(De \left(1 - e^{-\alpha x}\right)^2, x=0, 5\right) = De \alpha^2 x^2 - De \alpha^3 x^3 + \frac{7}{12} De \alpha^4 x^4 + O(x^5) \end{aligned} \quad (47.3)$$

the leading term has  $D_e \alpha^2$  as coefficient of displacement variable to the second power; in the limit of a small displacement, that coefficient would be proportional to  $\frac{1}{2} k$  for a canonical linear harmonic oscillator.

The temporally independent Schroedinger equation is hence expressed as

$$-\frac{h \left( \frac{d^2}{dx^2} \psi(x) \right)}{8 \pi^2 \mu} + D_e \left( 1 - e^{-\alpha x} \right)^2 \psi(x) = E \psi(x) .$$

With this potential energy and taking  $D_e$  and  $E$  to have wavenumber unit, which requires for consistency multiplication of the first term by  $h c$ , Schroedinger's temporally independent equation becomes

$$\begin{aligned} &> \text{deq} := -h^2 'c' / (8 * \text{Pi}^2 'c' * h' * \mu * R[e]^2) * \text{diff}(\text{psi}(x), x\$2) + \\ &\quad \text{VM} * \text{psi}(x) = E * \text{psi}(x); \\ &\quad \text{deq} := -\frac{h^2 'c' \left( \frac{d^2}{dx^2} \psi(x) \right)}{8 \pi^2 'c' h' \mu R_e^2} + De \left( 1 - e^{-\alpha x} \right)^2 \psi(x) = E \psi(x) \end{aligned} \quad (47.4)$$

Substituting

$$h c B_e = \frac{h^2 c}{8 \pi^2 h c \mu R_e^2} \text{ for the coefficient of the second derivative of } \psi(x) \text{ with respect to}$$

$x$  and assuming all  $B_e$ ,  $D_e$  and  $E$  to be expressed in wavenumber units, we convert Schroedinger's equation into this form,

$$\begin{aligned} & \text{> deq} := -B_e \text{diff}(\psi(x), x^2) + V_m \psi(x) = E \psi(x); \\ & \text{deq} := -B_e \left( \frac{d^2}{dx^2} \psi(x) \right) + D_e (1 - e^{-\alpha x})^2 \psi(x) = E \psi(x) \end{aligned} \quad (47.5)$$

and seek a solution.

$$\begin{aligned} & \text{> sol} := \text{dsolve}(\text{deq}, \psi(x)); \\ & \text{sol} := \psi(x) = \_C1 e^{\frac{\alpha x}{2}} \text{WhittakerM} \left( \frac{\sqrt{D_e}}{\alpha \sqrt{B_e}}, \frac{\sqrt{D_e - E}}{\alpha \sqrt{B_e}}, \frac{2 \sqrt{D_e} e^{-\alpha x}}{\alpha \sqrt{B_e}} \right) \\ & + \_C2 e^{\frac{\alpha x}{2}} \text{WhittakerW} \left( \frac{\sqrt{D_e}}{\alpha \sqrt{B_e}}, \frac{\sqrt{D_e - E}}{\alpha \sqrt{B_e}}, \frac{2 \sqrt{D_e} e^{-\alpha x}}{\alpha \sqrt{B_e}} \right) \end{aligned} \quad (47.6)$$

As Whittaker W functions are not well behaved, we eliminate them and work with Whittaker M functions.

$$\begin{aligned} & \text{> sol} := \text{eval}(\text{sol}, \_C2=0); \\ & \text{sol} := \psi(x) = \_C1 e^{\frac{\alpha x}{2}} \text{WhittakerM} \left( \frac{\sqrt{D_e}}{\alpha \sqrt{B_e}}, \frac{\sqrt{D_e - E}}{\alpha \sqrt{B_e}}, \frac{2 \sqrt{D_e} e^{-\alpha x}}{\alpha \sqrt{B_e}} \right) \end{aligned} \quad (47.7)$$

Because other functions are preferable to WhittakerM functions, such as hypergeometric or KummerM or Laguerre functions, we undertake these conversions.

$$\begin{aligned} & \text{> solh} := \text{convert}(\text{sol}, \text{hypergeom}); \\ & \text{solh} := \psi(x) \end{aligned} \quad (47.8)$$

$$\begin{aligned} & = \frac{1}{\frac{\sqrt{D_e}}{e^{\alpha \sqrt{B_e} e^{\alpha x}}}} \left( \_C1 e^{\frac{\alpha x}{2}} \left( \frac{2 \sqrt{D_e}}{\alpha \sqrt{B_e} e^{\alpha x}} \right)^{\frac{\alpha \sqrt{B_e} + 2 \sqrt{D_e - E}}{2 \alpha \sqrt{B_e}}} \text{hypergeom} \left( \left[ \frac{1}{2 \alpha \sqrt{B_e}} (\alpha \right. \right. \right. \\ & \left. \left. \left. \sqrt{B_e} - 2 \sqrt{D_e} + 2 \sqrt{D_e - E} \right) \right], \left[ \frac{\alpha \sqrt{B_e} + 2 \sqrt{D_e - E}}{\alpha \sqrt{B_e}} \right], \frac{2 \sqrt{D_e}}{\alpha \sqrt{B_e} e^{\alpha x}} \right) \right) \end{aligned}$$

$$\begin{aligned} & \text{> soll} := \text{convert}(\text{sol}, \text{Laguerre}); \\ & \text{soll} := \psi(x) = \left( \_C1 e^{\frac{\alpha x}{2}} \left( \frac{2 \sqrt{D_e}}{\alpha \sqrt{B_e} e^{\alpha x}} \right)^{\frac{\alpha \sqrt{B_e} + 2 \sqrt{D_e - E}}{2 \alpha \sqrt{B_e}}} \text{LaguerreL} \left( \right. \right. \end{aligned} \quad (47.9)$$

$$\left. -\frac{\alpha\sqrt{Be} - 2\sqrt{De} + 2\sqrt{De-E}}{2\alpha\sqrt{Be}}, \frac{\alpha\sqrt{Be} + 2\sqrt{De-E}}{\alpha\sqrt{Be}} - 1, \frac{2\sqrt{De}}{\alpha\sqrt{Be} e^{\alpha x}} \right)$$

$$\left( \left( \frac{\frac{2\sqrt{De-E}}{\sqrt{Be}} + \frac{\alpha\sqrt{Be} + 2\sqrt{De}}{\sqrt{Be}} - 2\alpha}{2\alpha} - \frac{\alpha\sqrt{Be} - 2\sqrt{De} + 2\sqrt{De-E}}{2\alpha\sqrt{Be}} \right) e^{\frac{\sqrt{De}}{\alpha\sqrt{Be}} e^{\alpha x}} \right)$$

Is that formula containing either hypergeometric or Laguerre functions an acceptable solution?

```
> odetest(solh, deq);
```

$$0 \quad (47.10)$$

```
> odetest(soll, deq);
```

$$0 \quad (47.11)$$

As the solution containing hypergeometric functions appears more compact than that containing Laguerre functions, we proceed with the former. We extract the arguments of the hypergeometric formula.

```
> arg1 := expand(op(op(1, indets(solh, 'specfunc(anything,
hypergeom)')[1])));
```

$$arg1 := \frac{1}{2} + \frac{\sqrt{De-E}}{\alpha\sqrt{Be}} - \frac{\sqrt{De}}{\alpha\sqrt{Be}} \quad (47.12)$$

```
> arg2 := expand(op(op(2, indets(solh, 'specfunc(anything,
hypergeom)')[1])));
```

$$arg2 := 1 + \frac{2\sqrt{De-E}}{\alpha\sqrt{Be}} \quad (47.13)$$

```
> arg3 := op(3, indets(solh, 'specfunc(anything,
hypergeom)')[1]);
```

$$arg3 := \frac{2\sqrt{De}}{\alpha\sqrt{Be} e^{\alpha x}} \quad (47.14)$$

For bound states of the Morse oscillator for which  $E < D_e$ , a hypergeometric series must terminate, which requires the first argument of hypergeom to be a negative integer or zero; we accordingly set that first argument to be equal to  $-v$ , solve for  $E$  as  $E_v$  and collect in powers of  $v$ .

```
> Ev := collect(solve(arg1 = -v, E), v);
```

$$Ev := -v^2 \alpha^2 Be + (-Be \alpha^2 + 2\alpha\sqrt{Be}\sqrt{De})v - \frac{Be \alpha^2}{4} + \alpha\sqrt{Be}\sqrt{De} \quad (47.15)$$

We make a Taylor expansion of that energy in  $v + \frac{1}{2}$ ,

```
> Ev := taylor(Ev, v=-1/2, 5);
```

$$E_v := 2 \alpha \sqrt{B_e} \sqrt{D_e} \left( \frac{1}{2} + v \right) - B_e \alpha^2 \left( \frac{1}{2} + v \right)^2 \quad (47.16)$$

which eliminates the term independent of  $v + \frac{1}{2}$ . The coefficient of  $v + \frac{1}{2}$  has the dimension of a

vibrational wavenumber that we write as  $\omega$ ; we denote the coefficient of  $\left( v + \frac{1}{2} \right)^2$  by  $\beta$ , such that

both  $\omega$  and  $\beta$  have wavenumber unit. The presence of the second term indicates that the Morse oscillator is anharmonic -- the interval of energy between adjacent states is not constant, but decreases as quantum number  $v$  increases.

```
> Ev := subs(2*sqrt(Be)*sqrt(De)*alpha=omega, alpha^2*Be=beta, Ev);
```

$$E_v := \omega \left( \frac{1}{2} + v \right) - \beta \left( \frac{1}{2} + v \right)^2 \quad (47.17)$$

For  $v = 0$  that denotes the state of least accessible energy, there is a residual energy,

```
> `residual energy` = eval(Ev, v=0);
```

$$\text{residual energy} = \frac{\omega}{2} - \frac{\beta}{4} \quad (47.18)$$

that represents the difference between  $D_e$  and the dissociation energy, both expressed in wavenumber unit.

```
> `dissociation energy` = De - eval(Ev, v=0);
```

$$\text{dissociation energy} = D_e - \frac{\omega}{2} + \frac{\beta}{4} \quad (47.19)$$

With  $E_v$  in the above form, we find relations between the coefficients therein and the parameters in the preceding expression, first for  $\alpha$  in terms of  $\omega$ ,  $B_e$  and  $D_e$ .

```
> alpha^2 = solve(omega = 2*alpha*Be^(1/2)*De^(1/2), alpha)^2;
```

$$\alpha^2 = \frac{\omega^2}{4 B_e D_e} \quad (47.20)$$

```
> alpha = simplify(sqrt(rhs(%)), symbolic);
```

$$\alpha = \frac{\omega}{2 \sqrt{B_e} \sqrt{D_e}} \quad (47.21)$$

On that basis, we express  $D_e$  in terms of  $\omega$  and  $\beta$ , with  $\omega = 2 \sqrt{D_e} \alpha \sqrt{B_e}$  as the coefficient of  $v + \frac{1}{2}$

and  $\beta = \alpha^2 B_e$  as the coefficient of  $\left( v + \frac{1}{2} \right)^2$ ,

```
> De = solve(beta/Be = 1/4*omega^2/Be/De, De);
```

$$De = \frac{\omega^2}{4\beta} \quad (47.22)$$

and another formula for  $\alpha$  in terms of  $\beta$  and  $B_e$ .

```
> alpha = simplify(op({op(map(abs, [solve(beta = -alpha^2*Be, alpha)
1]))}))
assuming positive;
```

$$\alpha = \frac{\sqrt{\beta}}{\sqrt{Be}} \quad (47.23)$$

As the first argument of **hypergeom** contains within it the second argument, we define that second argument,  $1 + \frac{2\sqrt{De-E}}{\alpha\sqrt{Be}}$ , in terms of  $v$  as  $k - 2v$ , from which we obtain, on substituting the result for  $v$  from the first argument of **hypergeom**;

```
> k = simplify(arg2 - 2*arg1, symbolic);
```

$$k = \frac{2\sqrt{De}}{\alpha\sqrt{Be}} \quad (47.24)$$

from the results for  $\alpha$  and  $D_e$  above, we obtain a relation for  $k$  in terms of  $\omega$  and  $\beta$ ,

```
> k = simplify(subs(alpha = 1/2*omega/Be^(1/2)/De^(1/2), De = 1/4*
omega^2/beta, rhs(%)), symbolic);
```

$$k = \frac{\omega}{\beta} \quad (47.25)$$

and hence in terms of  $\omega$  and  $D_e$ .

```
> k = subs(beta = omega^2/(4*De), omega/beta);
```

$$k = \frac{4De}{\omega} \quad (47.26)$$

The difference of energy between the energies of two adjacent states is

```
> Delta*E[v] = simplify(eval(Ev, v=n+1) - eval(Ev, v=n));
```

$$\Delta E_v = \left( \omega \left( \frac{3}{2} + n \right) - \beta \left( \frac{3}{2} + n \right)^2 \right) - \left( \omega \left( \frac{1}{2} + n \right) - \beta \left( \frac{1}{2} + n \right)^2 \right) \quad (47.27)$$

That value becomes zero at the energy of dissociation,

```
> v[D] = expand(solve(rhs(%), n));
```

$$v_D = -1 + \frac{\omega}{2\beta} \quad (47.28)$$

which indicates that the number of vibrational states, numbering from  $v = 0$ , is finite and equal to  $-1 + \frac{k}{2}$ , or approximately equal to  $\frac{1}{2} k$ ;  $k$  has hence the significance of twice the number of vibrational states.

When we define the third argument of **hypergeom** as  $z = \frac{2\sqrt{De}}{\alpha\sqrt{Be}} e^{\alpha x} = k e^{-\alpha x}$ , the solution becomes

expressed compactly as

```
> solh := psi(x) = _C1*exp(1/2*alpha*x)*z^(k/2-v)*hypergeom([-v],
[k-2*v],z)*exp(-z/2);
```

$$solh := \psi(x) = _C1 e^{\frac{\alpha x}{2}} z^{\frac{k}{2} - v} \text{hypergeom}([-v], [k - 2v], z) e^{-\frac{z}{2}} \quad (47.29)$$

When we express multiplicand  $e^{\frac{\alpha x}{2}}$  as  $\frac{z^{\frac{1}{2}}}{k}$  and combine that term in  $z$  with  $z^{\frac{k}{2} - v}$  and replace  $_C1$  with  $_Ch$ , we obtain

```
> solh := psi(x) = _Ch/k*exp(-z/2)*z^(k/2-v-1/2)*hypergeom([-v],
[k-2*v],z);
```

$$solh := \psi(x) = \frac{_Ch e^{-\frac{z}{2}} z^{\frac{k}{2} - v - \frac{1}{2}} \text{hypergeom}([-v], [k - 2v], z)}{k} \quad (47.30)$$

When we apply the same transformations to the solution containing the Laguerre functions, we obtain this form.

```
> soll := psi(x) = _C1*z^(k/2-v-1/2)*LaguerreL(v,k-2*v-1,z)*exp(-
z/2)/(k*binomial(k+v-1,v));
```

$$soll := \psi(x) = \frac{_C1 z^{\frac{k}{2} - v - \frac{1}{2}} \text{LaguerreL}(v, k - 2v - 1, z) e^{-\frac{z}{2}}}{k \binom{k + v - 1}{v}} \quad (47.31)$$

In the solution containing hypergeometric functions, we substitute for  $_Ch$  expression

$\sqrt{\frac{\alpha \Gamma(k - v)}{v! \Gamma(k - 2v - 1) \Gamma(k - 2v)}}$  as normalising factor, with  $k$  in the preceding denominator absorbed

into that normalising factor and  $(-1)^v$  to adjust the phase; the result, in terms of  $z$ , becomes

```
> solh := psi(x) = (-1)^v*(alpha*GAMMA(k-v)/(v!*GAMMA(k-2*v-1)*GAMMA
(k-2*v)))^(1/2)
```

```
*exp(-z/2)*z^(k/2-v-1/2)*hypergeom([-v],[k-2*v],
z);
```

$$solh := \psi(x) = (-1)^v \sqrt{\frac{\alpha \Gamma(k - v)}{v! \Gamma(k - 2v - 1) \Gamma(k - 2v)}} e^{-\frac{z}{2}} z^{\frac{k}{2} - v - \frac{1}{2}} \text{hypergeom}([-v], [k - 2v], z) \quad (47.32)$$

To make  $x$  the explicit variable in the right side, we replace  $z$  by  $k e^{-\alpha x}$  to obtain the ultimate expression for the Morse amplitude functions in hypergeometric form.

```
> solh := subs(z=k*exp(-alpha*x), solh);
```

$$solh := \psi(x) \quad (47.33)$$

$$= (-1)^v \sqrt{\frac{\alpha \Gamma(k-v)}{v! \Gamma(k-2v-1) \Gamma(k-2v)}} e^{-\frac{k e^{-\alpha x}}{2}} (k e^{-\alpha x})^{\frac{k}{2} - v - \frac{1}{2}} \text{hypergeom}([$$

$$-v], [k-2v], k e^{-\alpha x})$$

```
> solh := psi(x) = (-1)^v*(alpha*GAMMA(k-v)/v!/GAMMA(k-2*v-1)/GAMMA
(k-2*v))^(1/2)
*exp(-1/2*k*exp(-alpha*x))*(k*exp(-alpha*x))^(1/2*
k-v-1/2)
*hypergeom([-v],[k-2*v],k*exp(-alpha*x));
```

*solh* :=  $\psi(x)$  (47.34)

$$= (-1)^v \sqrt{\frac{\alpha \Gamma(k-v)}{v! \Gamma(k-2v-1) \Gamma(k-2v)}} e^{-\frac{k e^{-\alpha x}}{2}} (k e^{-\alpha x})^{\frac{k}{2} - v - \frac{1}{2}} \text{hypergeom}([$$

$$-v], [k-2v], k e^{-\alpha x})$$

We test the normalisation. As the domain of  $R$  is  $0.. \infty$ , the domain of  $x$  is  $-1.. \infty$ ; as  $\psi(x)$  contains prospectively numerically large magnitudes but has a finite amplitude over only a small domain about  $x = 0$ , as implied in the above plot of the potential energy and confirmed in the succeeding plots of  $\psi(x)$ , we safely abbreviate the domain of integration to less than  $-1.. \infty$  to obtain rapidly accurate integrations; for our numerical integrations we assume typical values,  $k = 30.5$  and  $\alpha = 2.5$ , for the parameters.

```
> Int(eval(rhs(solh), [k=30.5, v=j, alpha=2.5]))^2, x=-1..infinity) =
```

```
seq((evalf[12](Int(unapply(simplify(eval(rhs(solh), [k=30.5, v=j,
alpha=2.5]))^2, x), -1..infinity))), j=0..5);
```

$$\int_{-1}^{\infty} \frac{1}{j! \Gamma(29.5 - 2j) \Gamma(30.5 - 2j)} \left( 2.500000000 ((-1)^j)^2 \Gamma(30.5 \right.$$

$$\left. - j) \left( e^{-15.25000000 e^{-2.5x}} \right)^2 \left( (30.5 e^{-2.5x})^{14.75000000 - j} \right)^2 \text{hypergeom}([-j], [30.5 \right.$$

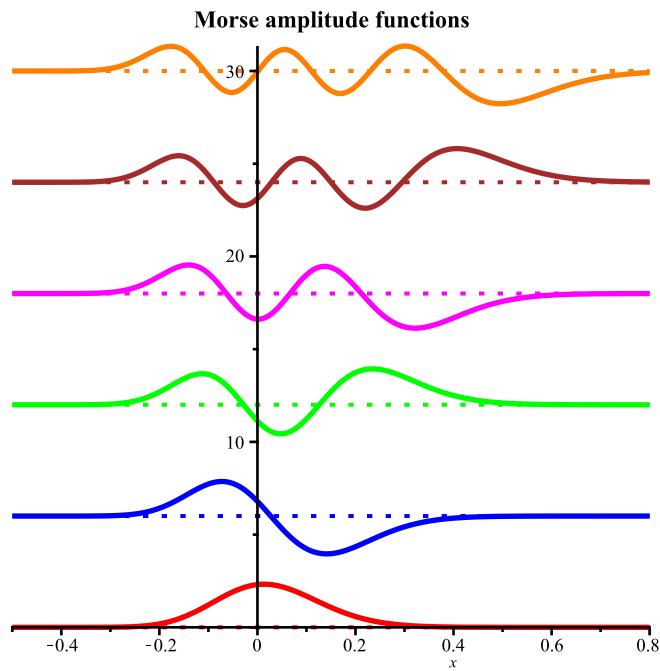
$$\left. - 2j], 30.5 e^{-2.5x} \right)^2 \Big) dx = (0.999999999985, 1.000000000000, 0.999999999987,$$

$$0.999999999996, 1.000000000000, 0.999999999996)$$

The amplitude functions are clearly normalised. We plot the amplitude functions for the Morse function for potential energy for states with energy less than the dissociation energy, displaced vertically upward with increasing  $v$  for clarity,

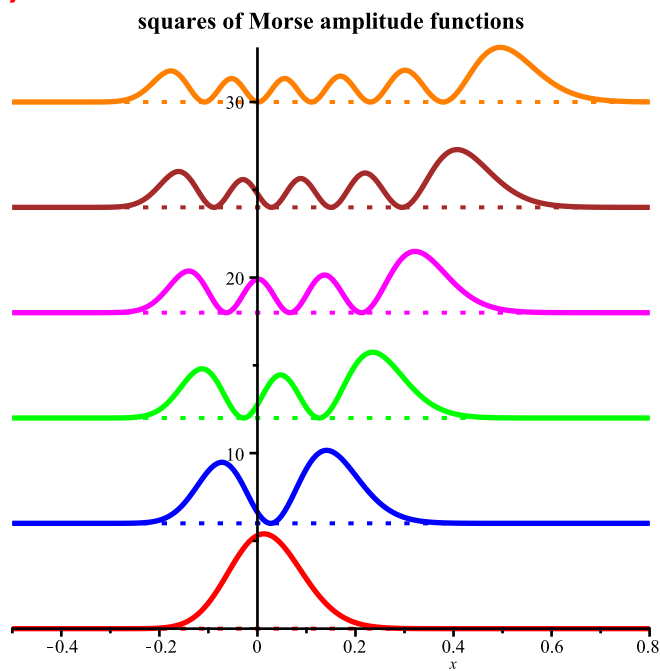
```
> plot([seq(eval(rhs(solh), [k=30.5, v=j, alpha=2.5]))+6*j, j=0..5),
seq(6*j, j=0..5)], x=-0.5..0.8, linestyle=[1$6, 2$6],
thickness=[2$6, 1$6], colour=[red, blue, green, magenta, brown,
coral],
title="Morse amplitude functions", titlefont=[TIMES, BOLD, 14]
);
```





and the squares of these correctly normalised amplitude functions.

```
> plot([seq(eval(rhs(solh), [k=30.5, v=j, alpha=2.5])^2+6*j, j=0.
.5),
      seq(6*j,j=0..5)], x=-0.5..0.8, linestyle=[1$6,2$6],
      thickness=[2$6,1$6], colour=[red,blue,green,magenta,brown,
coral],
      title="squares of Morse amplitude functions", titlefont=
[TIMES,BOLD,14]);
```



We convert our solution in terms of hypergeom into LaguerreL functions,

> convert(solh, LaguerreL);

$\Psi(x)$  (47.36)

$$= \frac{1}{\binom{k-v-1}{v}} \left( (-1)^v \sqrt{\frac{\alpha \Gamma(k-v)}{v! \Gamma(k-2v-1) \Gamma(k-2v)}} e^{-\frac{ke^{-\alpha x}}{2}} (ke^{-\alpha x})^{\frac{k}{2} - v - \frac{1}{2}} \right. \\ \left. \text{LaguerreL}\left(v, k-2v-1, \frac{k}{e^{\alpha x}}\right) \right)$$

and test their normalisation.

> Int(eval(rhs(%), [k=30.5, v=j, alpha=2.5])^2, x=-1..infinity) =  
seq((evalf[12](Int(unapply(simplify(eval(rhs(%), [k=30.5, v=j,  
alpha=2.5]))^2, x), -1..infinity))), j=0..5);

$$\int_{-1}^{\infty} \frac{1}{j! \Gamma(29.5-2j) \Gamma(30.5-2j) \binom{29.5-j}{j}^2} \left( 2.500000000 ((-1)^j)^2 \Gamma(30.5-2j) \left( e^{-15.25000000 e^{-2.5x}} \right)^2 \left( (30.5 e^{-2.5x})^{14.75000000-j} \right)^2 \text{LaguerreL}\left(j, 29.5-2j, \frac{30.5}{e^{2.5x}}\right)^2 \right) dx = (0.999999999985, 1.000000000001, 0.999999999987, 0.999999999990, 1.000000000000, 0.999999999996)$$
 (47.37)

These functions are also clearly normalised. The result of this test indicates that we can employ either **hypergeom** or **LaguerreL** functions for the Morse oscillator.

With parameters selected to be  $D_e = 40,000 \text{ cm}^{-1}$ ,  $B_e = 10 \text{ cm}^{-1}$  and  $\alpha = 2.5$ , comparable with values of parameters for HCl, such that the number of vibrational states is

> k/2 - 1 = evalf[3](eval(2/alpha/Be^(1/2)\*De^(1/2), [De=40000,  
alpha=2.5, Be=10])/2-1);

$$\frac{k}{2} - 1 = 24.3$$
 (47.38)

we calculate the term values/ $\text{cm}^{-1}$  of the vibrational states for  $0 \leq v \leq 23$  as

> seq(evalf[6](eval(2\*sqrt(Be)\*sqrt(De)\*alpha\*(j+1/2)-Be\*alpha^2\*(j+1/2)^2, [De=40000, alpha=2.5, Be=10])), j=0..23);  
1565.52, 4602.80, 7515.08, 10302.4, 12964.7, 15501.9, 17914.2, 20201.5, 22363.8, 24401.1, (47.39)  
26313.3, 28100.6, 29762.9, 31300.2, 32712.5, 33999.7, 35162.0, 36199.3, 37111.6,  
37898.9, 38561.1, 39098.4, 39510.7, 39798.0

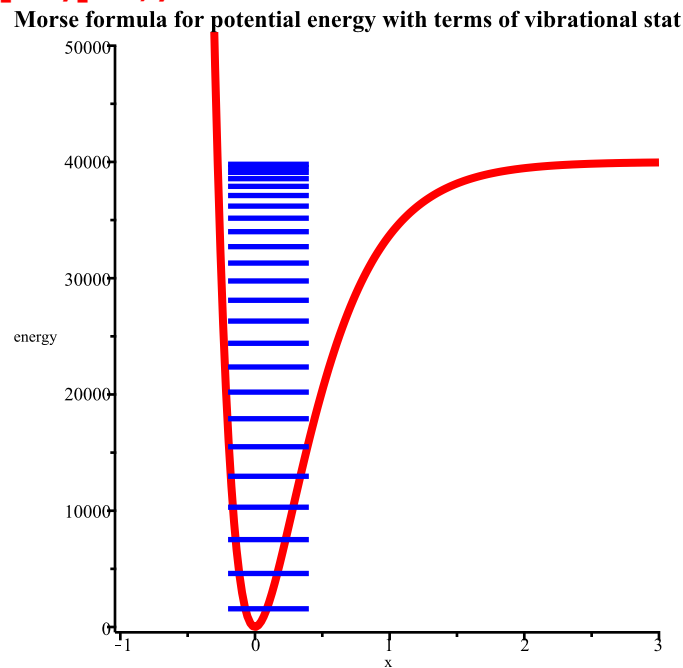
and plot the curve for potential energy according to the Morse function with these vibrational terms.

> pm1 := plot(eval(VM, [De=40000, alpha=2.5]), x=-1..3, 0..50000,

```

thickness=3,
    axes=frame, title="Morse formula for potential energy with
terms of vibrational states",
    titlefont=[TIMES,BOLD,14], labels=["x","energy"], colour=red):
pM2 := plot([seq(eval(2*sqrt(Be)*sqrt(De)*alpha*(j+1/2)-Be*
alpha^2*(j+1/2)^2, [De=40000, alpha=2.5, Be=10]), j=0..23)],
    x=-0.2..0.4, colour=[blue$24], thickness=[2$24]):
> plots[display](pM1,pM2);

```



We evaluate some matrix elements  $\langle v | x | 0 \rangle = \int_{-1}^{\infty} \psi(v, x) x \psi(0, x) dx$  of  $x$  that would govern the intensities of transitions from the vibrational ground state for which  $v = 0$  to vibrationally excited states with  $1 \leq v \leq 5$ .

```

> ` $\langle v | x | 0 \rangle` = seq(evalf(Int(simplify(eval(rhs(solh), [k=30.5, v=j,
alpha=2.5])))*x
    *simplify(eval(rhs(solh), [k=30.5, v=0, alpha=2.5])),
    x=-1..20)), j=1..5);
<math>\langle v | x | 0 \rangle = (-0.07360062091, -0.009728814927, -0.002134094243, -0.0006181146181, (47.40)
    -0.0002171008805)$ 
```

The magnitude of  $\langle 1 | x | 0 \rangle = \int_{-1}^{\infty} \psi(1, x) x \psi(0, x) dx$  is similar to that calculated for other oscillators, such as for the linear harmonic oscillators in sections 1.31 and 1.32, but the magnitudes of matrix elements for states with  $v > 1$  decrease more slowly than for other oscillators, such as the Davidson oscillator in section 1.32.

Because  $\frac{R}{R_e} = 1 + x$ , we calculate expectation values  $\langle v | (1 + x)^{-2} | v \rangle$  that are related to

rotational parameters  $B_v$ , proportional to  $\langle v | \frac{1}{R^2} | v \rangle$ .

```
> lv := [seq(evalf(Int(simplify(eval(rhs(solh), [k=30.5, v=j, alpha=
2.5]))^2/(1+x)^2), x=-1..10)), j=0..5)];
lv := [0.9762940078, 0.9282925648, 0.8794446025, 0.8296739393, 0.7788861297,
0.7269626792]
```

(47.41)

We apply polynomial interpolation to those values,

```
> pv := CurveFitting[PolynomialInterpolation]([seq(j, j=0..5)], lv,
v);
pv := -4.820916667 × 10-8 v5 - 2.789041666 × 10-7 v4 - 9.818279167 × 10-6 v3
- 0.0003911293458 v2 - 0.04760016826 v + 0.9762940078
```

(47.42)

and form a series in  $v + \frac{1}{2}$ , which as product of  $B_e$  becomes a formula for  $B_v$

```
> B[v] = B[e]*(taylor(pv, v=-1/2, 6));
B_v = B_e (0.9999975210 - 0.04721627824 (1/2 + v) - 0.0003767600218 (1/2 + v)2
- 9.380993750 × 10-6 (1/2 + v)3 - 1.583812499 × 10-7 (1/2 + v)4 - 4.820916667
× 10-8 (1/2 + v)5)
```

(47.43)

This result shows that rotational parameter  $B_v$  decreases gradually with increasing  $v$  in a manner comparable with experimental values. Although the analogous expansion for vibrational energies, above, requires only two terms -- up to  $\left(v + \frac{1}{2}\right)^2$ , this expansion for  $B_v$  appears to require as many terms as data to fit.

Our solution, with wave mechanics, of the energies of vibrational and rotational states and matrix elements according to Morse's formula for potential energy exhibits similarities with the properties of real molecules:

- there is a finite limit of the energy of bound states, at energy  $D_e$  relative to a zero of energy for  $V_M = 0$  at  $x = 0$  or  $R = R_e$ ;
- the bound states number finitely;
- the vibrational energies are anharmonic and tend to converge with increasing vibrational quantum number  $v$ , but the vibrational state of greatest energy has a finite limit as  $v_D$  at or just below the dissociation limit;
- the rotational parameters are consistent with a non-rigid rotor and decrease with increasing vibrational quantum number  $v$ ;
- two terms in an expansion of the vibrational energy in  $v + \frac{1}{2}$  represent the vibrational energies

exactly; the magnitude of the coefficient of  $\left(v + \frac{1}{2}\right)^2$ , called  $\beta$  above but generally named  $\omega_e x_e$  in the spectrometric literature, is much smaller than the coefficient of  $v + \frac{1}{2}$ , called  $\omega$  here, such that

their ratio is  $\frac{\omega}{\beta} = k$  and

- the magnitudes of vibrational matrix elements of  $x$  for transitions from the vibrational ground state with  $v = 0$  to vibrationally excited states with  $v > 0$  decrease with increasing  $v$ .

Although these features are somewhat realistic for a stable diatomic molecule in its electronic ground state that has vibrational states both of finite number, unless it dissociates into ions, and tending to converge toward a limit  $D_e$ , the expansion of  $E_v$  as a function of  $v + \frac{1}{2}$  continues beyond the quadratic term, even though the magnitude of the coefficient of  $\left(v + \frac{1}{2}\right)^3$  is much smaller than the magnitude of the coefficient of  $\left(v + \frac{1}{2}\right)^2$ , which is in turn much smaller than the magnitude of the coefficient of  $v + \frac{1}{2}$ . The magnitudes of the matrix elements

$$\langle v | x | 0 \rangle = \int_{-1}^{\infty} \psi(v, x) x \psi(0, x) dx$$

for  $v > 0$  decrease less rapidly with increasing  $v$  than for typical diatomic molecules. The parameters  $\alpha$ ,  $\omega$ ,  $D_e$ ,  $\beta$ ,  $k$  of a real molecule are inconsistent with the relations between these parameters of this model function, as derived above. For a real, electrically neutral and stable, diatomic molecule, the potential energy varies as  $R^{-n}$  at moderately large internuclear distance,  $R \gg R_e$ , with  $n = 5$  or  $6$  typically, depending on the electronic states of the electrically neutral atoms after dissociation, not according to  $e^{-R}$  as compelled according to the Morse formula. At the other extreme of molecular existence -- the united atom as  $x \rightarrow -1$  or  $R \rightarrow 0$ , the inaccurate representation of the actual potential energy, for which  $\frac{1}{R} \rightarrow +\infty$ , instead of  $V(-1) \sim 12 D_e$ , is less important for bound states. For these reasons, one is advised to regard the Morse oscillator as a topic for an exercise in wave mechanics, rather than as a viable model of a diatomic molecule, for which more practical procedures are presented in chapter 13.

Other formulae for potential energy that involve exponential functions in various forms might also be susceptible to algebraic solution, but they, like other model formulae with few parameters, have no particular chemical or physical interest.

## 1.48 Liouville transformation

> **restart:**

A [Lie](#) algebra is an algebraic structure that was introduced into mathematics to enable a study of the concept of an [infinitesimal transformation](#) that is a limiting form of a small transformation. The realization of Lie algebra  $SO(1,2)$  by means of [differential operators](#) of second order is applicable to

various problems in quantum mechanics, either in one dimension or separable in many dimensions [Algebraic Methods in Quantum Chemistry and Physics, F. M. Fernandez and E. A. Castro, CRC Press, Boca Raton, FL USA, 1996, pp. 248 -- 254]. Through an appropriate transformation of both [independent](#) and [dependent variables](#) according to a *Liouville transformation*, one might convert one such [eigenvalue](#) problem into another. This transformation connects eigenvalue problems that one solves exactly by means of a method of Lie algebra, and enables a comparison of methods of Lie algebra and factorization [Am. J. Physics, 40, 1459, 1972]. This material is kindly provided by Professor F. M. Fernandez; some labels **B.** beside *Maple* commands or statements pertain to those equations in appendix B of the specified book.

With this Liouville transformation one converts a [differential equation](#) of [second order](#) of form

$$\frac{d^2}{dr^2} \Psi(r) + Q(r) \Psi(r) = 0$$

into another such equation through a definition of a new independent variable,

$$x = x(r),$$

such that  $x(r)$  has an [inverse](#) transformation  $r(x)$ , and a new dependent variable.

$$F(x) = \frac{\Psi(r(x))}{u(x)}$$

The resulting differential equation for  $F(x)$  lacks  $\frac{d}{dx} F(x)$  if  $u(x)^2$  is proportional to  $\frac{d}{dx} r(x)$ ;

function  $u(x)$  that satisfies this equation is free from [branch points](#) if  $\frac{d}{dx} r(x)$  be positive for all values of  $x$ . For simplicity, we choose arbitrarily

$$u(x) = \sqrt{\frac{d}{dx} r(x)}, \quad \frac{d}{dx} r(x) \geq 0.$$

We begin by differentiating  $\Phi(x) = \Psi(r(x))$  with respect to  $x$ ,

**> eq1 := diff(Phi(x) = psi(r(x)), x);**

$$eq1 := \frac{d}{dx} \Phi(x) = D(\Psi)(r(x)) \left( \frac{d}{dx} r(x) \right) \quad (48.1)$$

and solve for  $\frac{d}{dx} \Psi(r(x))$  for subsequent use.

**> c1 := solve(eq1, D(psi)(r(x)));**

$$c1 := \frac{\frac{d}{dx} \Phi(x)}{\frac{d}{dx} r(x)} \quad (48.2)$$

**> eq3 := diff(Phi(x) = psi(r(x)), x\$2);**

$$eq3 := \frac{d^2}{dx^2} \Phi(x) = D^{(2)}(\Psi)(r(x)) \left( \frac{d}{dx} r(x) \right)^2 + D(\Psi)(r(x)) \left( \frac{d^2}{dx^2} r(x) \right) \quad (48.3)$$

We extract the coefficient of  $\frac{d^2}{dx^2} r(x)$ ,

**> d1 := op(1, op(2, [op(rhs(eq3))]));**

$$d1 := D(\psi)(r(x)) \quad (48.4)$$

and substitute for that quantity in the preceding result the value of  $\frac{d}{dx} \psi(r(x))$ .

**> eq4 := subs(d1 = c1, eq3);**

$$eq4 := \frac{d^2}{dx^2} \Phi(x) = D^{(2)}(\psi)(r(x)) \left( \frac{d}{dx} r(x) \right)^2 + \frac{\left( \frac{d}{dx} \Phi(x) \right) \left( \frac{d^2}{dx^2} r(x) \right)}{\frac{d}{dx} r(x)} \quad (48.5)$$

As a test, we form the second derivative of  $\Phi(x) = u(x) F(x)$ ,

**> eq5 := diff(Phi(x) = u(x)\*F(x), x\$2);**

$$eq5 := \frac{d^2}{dx^2} \Phi(x) = \left( \frac{d^2}{dx^2} u(x) \right) F(x) + 2 \left( \frac{d}{dx} u(x) \right) \left( \frac{d}{dx} F(x) \right) + u(x) \left( \frac{d^2}{dx^2} F(x) \right) \quad (48.6)$$

before substituting this relation into the preceding result.

**> eq6 := expand(subs(Phi(x)=u(x)\*F(x), eq4));**

$$\begin{aligned} eq6 := & \left( \frac{d^2}{dx^2} u(x) \right) F(x) + 2 \left( \frac{d}{dx} u(x) \right) \left( \frac{d}{dx} F(x) \right) + u(x) \left( \frac{d^2}{dx^2} F(x) \right) \\ & = D^{(2)}(\psi)(r(x)) \left( \frac{d}{dx} r(x) \right)^2 + \frac{\left( \frac{d^2}{dx^2} r(x) \right) \left( \frac{d}{dx} u(x) \right) F(x)}{\frac{d}{dx} r(x)} \\ & + \frac{\left( \frac{d^2}{dx^2} r(x) \right) u(x) \left( \frac{d}{dx} F(x) \right)}{\frac{d}{dx} r(x)} \end{aligned} \quad (48.7)$$

We undertake some manipulations to express the result in a recognizable form.

**> eq7 := lhs(eq6) - rhs(eq6) = 0;**

$$\begin{aligned} eq7 := & \left( \frac{d^2}{dx^2} u(x) \right) F(x) + 2 \left( \frac{d}{dx} u(x) \right) \left( \frac{d}{dx} F(x) \right) + u(x) \left( \frac{d^2}{dx^2} F(x) \right) \\ & - D^{(2)}(\psi)(r(x)) \left( \frac{d}{dx} r(x) \right)^2 - \frac{\left( \frac{d^2}{dx^2} r(x) \right) \left( \frac{d}{dx} u(x) \right) F(x)}{\frac{d}{dx} r(x)} \\ & - \frac{\left( \frac{d^2}{dx^2} r(x) \right) u(x) \left( \frac{d}{dx} F(x) \right)}{\frac{d}{dx} r(x)} = 0 \end{aligned} \quad (48.8)$$

**> eq8 := collect(eq7, [diff(F(x),x,x), diff(F(x),x), F(x)]);**

$$eq8 := u(x) \left( \frac{d^2}{dx^2} F(x) \right) + \left( 2 \frac{d}{dx} u(x) - \frac{\left( \frac{d^2}{dx^2} r(x) \right) u(x)}{\frac{d}{dx} r(x)} \right) \left( \frac{d}{dx} F(x) \right) + \left( \frac{d^2}{dx^2} u(x) - \frac{\left( \frac{d^2}{dx^2} r(x) \right) \left( \frac{d}{dx} u(x) \right)}{\frac{d}{dx} r(x)} \right) F(x) - D^{(2)}(\psi)(r(x)) \left( \frac{d}{dx} r(x) \right)^2 = 0 \quad (48.9)$$

We extract the coefficient of  $\frac{d}{dx} F(x)$ ,

**> d2 := op(1, op(2, [op(lhs(eq8))]));**

$$d2 := 2 \frac{d}{dx} u(x) - \frac{\left( \frac{d^2}{dx^2} r(x) \right) u(x)}{\frac{d}{dx} r(x)} \quad (48.10)$$

and solve for  $u(x)$ ,

**> eq8b := dsolve(d2, u(x));**

$$eq8b := u(x) = \_C1 \sqrt{\frac{d}{dx} r(x)} \quad (48.11)$$

and for  $r(x)$ .

**> eq8c := dsolve(d2, r(x));**

$$eq8c := r(x) = \_C1 + \left( \int u(x)^2 dx \right) \_C2 \quad (48.12)$$

We substitute that value of  $u(x)$  into a preceding result.

**> eq9 := expand(subs(eval(eq8b, \\_C1=1), eq8));**

$$eq9 := \sqrt{\frac{d}{dx} r(x)} \left( \frac{d^2}{dx^2} F(x) \right) - \frac{3 F(x) \left( \frac{d^2}{dx^2} r(x) \right)^2}{4 \left( \frac{d}{dx} r(x) \right)^{3/2}} + \frac{F(x) \left( \frac{d^3}{dx^3} r(x) \right)}{2 \sqrt{\frac{d}{dx} r(x)}} - D^{(2)}(\psi)(r(x)) \left( \frac{d}{dx} r(x) \right)^2 = 0 \quad (48.13)$$

We extract the coefficient of  $\left( \frac{d}{dx} r(x) \right)^2$ ,

**> d3 := op(2, op(4, [op(lhs(eq9))]));**

$$d3 := D^{(2)}(\psi)(r(x)) \quad (48.14)$$

and equate it to  $Q F(x) u(x)$ .



**> eq9b := subs(d3 = -Q\*F(x)\*u(x), eq9);**

$$\begin{aligned} eq9b := & \sqrt{\frac{d}{dx} r(x)} \left( \frac{d^2}{dx^2} F(x) \right) - \frac{3 F(x) \left( \frac{d^2}{dx^2} r(x) \right)^2}{4 \left( \frac{d}{dx} r(x) \right)^{3/2}} + \frac{F(x) \left( \frac{d^3}{dx^3} r(x) \right)}{2 \sqrt{\frac{d}{dx} r(x)}} \\ & + Q F(x) u(x) \left( \frac{d}{dx} r(x) \right)^2 = 0 \end{aligned} \quad (48.15)$$

We substitute the value of  $r(x)$  deduced above into the latter equation.

**> eq9c := expand(subs(eval(eq8c, [\_C1=0, \_C2=1]), eq9b));**

$$\begin{aligned} eq9c := & \sqrt{u(x)^2} \left( \frac{d^2}{dx^2} F(x) \right) - \frac{3 F(x) u(x)^2 \left( \frac{d}{dx} u(x) \right)^2}{(u(x)^2)^{3/2}} + \frac{F(x) \left( \frac{d}{dx} u(x) \right)^2}{\sqrt{u(x)^2}} \\ & + \frac{F(x) \left( \frac{d^2}{dx^2} u(x) \right) u(x)}{\sqrt{u(x)^2}} + Q F(x) u(x)^5 = 0 \end{aligned} \quad (48.16)$$

and undertake some manipulation to present results in a convenient form.

**> eq10 := expand(simplify(eq9c, symbolic));**

$$\begin{aligned} eq10 := & u(x) \left( \frac{d^2}{dx^2} F(x) \right) - \frac{2 F(x) \left( \frac{d}{dx} u(x) \right)^2}{u(x)} + \left( \frac{d^2}{dx^2} u(x) \right) F(x) + Q F(x) u(x)^5 \\ & = 0 \end{aligned} \quad (48.17)$$

**> eq10b := expand(eq10/u(x));**

$$eq10b := \frac{d^2}{dx^2} F(x) - \frac{2 F(x) \left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} + \frac{\left( \frac{d^2}{dx^2} u(x) \right) F(x)}{u(x)} + u(x)^4 Q F(x) = 0 \quad (48.18)$$

**> eq10c := collect(eq10b, [diff(F(x), x\$2), F(x)]); # equivalent to B4**

$$eq10c := \frac{d^2}{dx^2} F(x) + \left( -\frac{2 \left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} + \frac{\frac{d^2}{dx^2} u(x)}{u(x)} + u(x)^4 Q \right) F(x) = 0 \quad (48.19)$$

To confirm this result we undertake some differentiations,

**> c2 := diff(diff(u(x), x)/u(x), x);**

$$c2 := \frac{\frac{d^2}{dx^2} u(x)}{u(x)} - \frac{\left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} \quad (48.20)$$

```
> eq11 := (Diff(Diff(u(x),x)/u(x),x)*F(x)
- (diff(diff(u(x),x)/u(x),x))*F(x)) = 0;
```

$$eq11 := \left( \frac{d}{dx} \left( \frac{\frac{d}{dx} u(x)}{u(x)} \right) \right) F(x) - \left( \frac{\frac{d^2}{dx^2} u(x)}{u(x)} - \frac{\left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} \right) F(x) = 0 \quad (48.21)$$

```
> eq11b := expand(eq10c + eq11);
```

$$eq11b := \frac{d^2}{dx^2} F(x) - \frac{F(x) \left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} + u(x)^4 Q F(x) + \left( \frac{d}{dx} \left( \frac{\frac{d}{dx} u(x)}{u(x)} \right) \right) F(x) = 0 \quad (48.22)$$

so to generate the result in a known form.

```
> eq12 := collect(eq11b, [diff(F(x),x$2), F(x)]); # B4
```

$$eq12 := \frac{d^2}{dx^2} F(x) + \left( -\frac{\left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} + u(x)^4 Q + \frac{d}{dx} \left( \frac{\frac{d}{dx} u(x)}{u(x)} \right) \right) F(x) = 0 \quad (48.23)$$

Because

$$\int \psi(r)^2 dr = \int u(x)^2 F(x)^2 \left( \frac{d}{dx} r(x) \right) dx = \int F(x)^2 \left( \frac{d}{dx} r(x) \right)^2 dx,$$

if  $\psi(r)$  be normalised,  $F(x)$  becomes also normalised with the [metric](#)

$$d\sigma = \left( \frac{d}{dx} r(x) \right)^2 dx = u(x)^4 dx$$

We apply this transformation to the general coulombic problem, with reduced quantities such that  $\frac{h}{2\pi} = m_e = 1$ , for which the coulombic potential energy of electrostatic attraction,  $-\frac{2B}{r}$ , between an electron and an atomic nucleus is  $V(r) = -\frac{2B}{r}$  with  $B > 0$ , and with a centrifugal distortion,  $+\frac{A}{r^2}$ , of the coulombic attraction related to angular momentum,

```
> eq13 := subs(Q = 2*Ec - A/r^2 + 2*B/r, eq10c);
```

$$eq13 := \frac{d^2}{dx^2} F(x) + \left( -\frac{2 \left( \frac{d}{dx} u(x) \right)^2}{u(x)^2} + \frac{\frac{d^2}{dx^2} u(x)}{u(x)} + u(x)^4 \left( 2Ec - \frac{A}{r^2} + \frac{2B}{r} \right) \right) F(x) = 0 \quad (48.24)$$

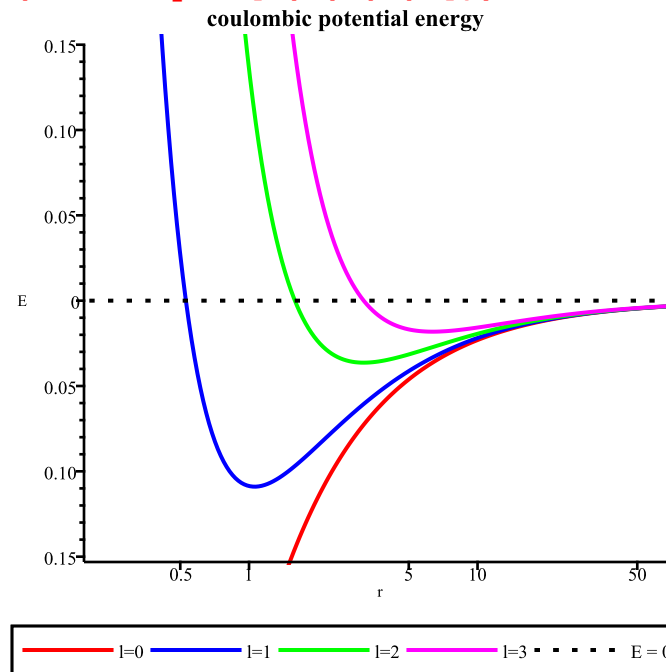
so that the discrete spectrum has energy values  $E_{n,l} = -\frac{B^2}{2n^2}$  with  $n = l + m - 1$ ,  $l = \sqrt{A + \frac{1}{4}} - \frac{1}{2}$  and  $m = 0, 1, \dots, \leq n - l - 1$ . This coulombic potential energy supports bound states provided that

$A \geq -\frac{1}{4}$ . With an appropriate scaling of energy and distance between electron and atomic nucleus and a logarithmic scale on the abscissal axis, we plot this coulombic potential energy for  $l=0, 1, 2, 3$ .

```
> evalf(-1.602e-19^2/(4*Pi*8.854187815e-12*r/1.0e-10)+
(6.62606957e-34/(2*Pi))^2/(2*5.4857990946e-4*1.660538821e-27*
r^2/1.0e-20));
```

$$-\frac{2.306568886 \times 10^{-38}}{r} + \frac{6.104264152 \times 10^{-59}}{r^2} \quad (48.25)$$

```
> plots[semilogplot]([seq(-0.2307/r + 0.06104/r^2*l*(l+1), l=0..3),
0],
r=0.2..70, -0.15..0.15, colour=[red,blue,green,magenta,
black],
title="coulombic potential energy", titlefont=[TIMES,BOLD,
14],
legend=["l=0","l=1","l=2","l=3","E = 0"], labels=["r", "E"],
axes=frame, linestyle=[1,1,1,1,2]);
```



In these reduced units the minima of these curves for the H atom are

```
> seq(solve(diff(eval(-0.2307/r + 0.06104/r^2*l*(l+1)),r)=0, r), l=
1..3);
```

$$1.058344170, 3.175032510, 6.350065020 \quad (48.26)$$

so equal to  $r=2 a_0$  for  $l=1$ ,  $r=6 a_0$  for  $l=2$  and  $r=12 a_0$  for  $l=3$ , or  $l(l+1) a_0$  in general. The H atom is treated at length in section 1.53.

For a transformation of independent variable  $r(x) = x(r)^v$  or  $x(r) = r(x)^{\frac{1}{v}}$ , the condition for  $u(x)$  is

> eq13b := u(x) = sqrt(diff(x^nu,x));

$$eq13b := u(x) = \sqrt{\frac{x^v v}{x}} \quad (48.27)$$

When we make this substitution into the preceding general result, we obtain

> eq13c := collect(expand(simplify(subs(eq13b, eq12),  
symbolic)), [diff(F(x),x\$2), F(x)]); # B8

$$eq13c := \frac{d^2}{dx^2} F(x) + \left( \frac{(x^v)^2 v^2 Q}{x^2} - \frac{v^2}{4 x^2} + \frac{1}{4 x^2} \right) F(x) = 0 \quad (48.28)$$

For a particular case  $v = 2$  so that  $r(x) = x(r)^2$  and  $u(x) = \sqrt{\frac{d}{dx} r(x)}$ , we obtain

> eq14a := r = x^2;

$$eq14a := r = x^2 \quad (48.29)$$

> eq14b := u(x) = sqrt(diff(rhs(eq14a),x));

$$eq14b := u(x) = \sqrt{2} \sqrt{x} \quad (48.30)$$

> eq14c := expand(simplify(subs(eq14a, eq14b, eq13), symbolic));

$$eq14c := 8 x^2 Ec F(x) + 8 B F(x) - \frac{3 F(x)}{4 x^2} + \frac{d^2}{dx^2} F(x) - \frac{4 A F(x)}{x^2} = 0 \quad (48.31)$$

> eq14 := collect(eq14c, [diff(F(x),x\$2), F(x),x]); # B11

$$eq14 := \frac{d^2}{dx^2} F(x) + \left( 8 x^2 Ec + 8 B + \frac{-\frac{3}{4} - 4 A}{x^2} \right) F(x) = 0 \quad (48.32)$$

> Q^HO = op(1, op(2, [op(lhs(eq14))]));

$$Q^{HO} = 8 x^2 Ec + 8 B + \frac{-\frac{3}{4} - 4 A}{x^2} \quad (48.33)$$

which resembles the eigenvalue equation for a canonical linear harmonic oscillator, treated in section 1.23, for which  $V(x) = \omega^2 x^2$ , with frequency  $\omega$ , angular momentum  $L$  and energy  $E^{HO}$  given by

$$\omega^2 = -8 Ec, \quad L(L+1) = 4 A + \frac{3}{4}, \quad E^{HO} = 4 B$$

A calculation with these relations and the corresponding ones above for the general coulombic problem yields the eigenvalues of that canonical harmonic oscillator as

$$E^{HO} = \omega \left( 2 m + L + \frac{3}{2} \right)$$

and the corresponding eigenfunctions are

$$F(x) = \psi(x)^{HO} = \frac{1}{\sqrt{2 x}} \psi(x^2)^c$$

The metric for the canonical harmonic oscillator is  $d\sigma = 4 x^2 dx$ .

A transformation  $r(x) = e^{-ax}$  with  $a > 0$  and  $-\infty < x < \infty$ ,

**> eq15a := r = exp(-a\*x);**

$$eq15a := r = e^{-ax} \quad (48.34)$$

**> eq15b := u(x) = sqrt(diff(rhs(eq15a), x));**

$$eq15b := u(x) = \sqrt{-a e^{-ax}} \quad (48.35)$$

yields this result.

**> eq15c := expand(simplify(subs(eq15a, eq15b, eq13), exp));**

$$eq15c := \frac{d^2}{dx^2} F(x) - \frac{F(x) a^2}{4} + \frac{2 F(x) a^2 B}{e^{ax}} - F(x) a^2 A + \frac{2 F(x) a^2 Ec}{(e^{ax})^2} = 0 \quad (48.36)$$

We make some appropriate substitutions for  $B, Ec$  and  $A$ ,

**> eq15d := simplify(subs(B=-2\*Ec\*exp(-a\*x0), eq15c), exp);**

$$eq15d := -4 F(x) a^2 Ec e^{-a(x+x0)} + 2 F(x) a^2 e^{-2ax} Ec + \frac{d^2}{dx^2} F(x) + \frac{(-4A-1) a^2 F(x)}{4} \quad (48.37)$$

$$= 0$$

**> eq15e := simplify(subs(Ec=-De\*exp(2\*a\*x0)/(2\*a^2), eq15d), exp);**

$$eq15e := 2 F(x) De e^{-a(-x0+x)} - F(x) De e^{-2a(-x0+x)} + \frac{d^2}{dx^2} F(x) + \frac{(-4A-1) a^2 F(x)}{4} \quad (48.38)$$

$$= 0$$

**> eq15f := simplify(expand(subs(A=-EM/a^2-1/4, eq15e), exp));**

$$eq15f := 2 F(x) De e^{-a(-x0+x)} - F(x) De e^{-2a(-x0+x)} + \frac{d^2}{dx^2} F(x) + EM F(x) = 0 \quad (48.39)$$

to produce a result in a standard form.

**> eq15 := collect(eq15f, [diff(F(x), x\$2), F(x)]);**

$$eq15 := \frac{d^2}{dx^2} F(x) + (-De e^{-2a(-x0+x)} + 2 De e^{-a(-x0+x)} + EM) F(x) = 0 \quad (48.40)$$

This result has the form  $\frac{d^2}{dx^2} F(x) + Q(x) F(x) = 0$  with  $Q(x)$  as

**> eq16 := 'Q^M' = op(1, op(2, [op(lhs(eq15))]));**

$$eq16 := Q^M = -De e^{-2a(-x0+x)} + 2 De e^{-a(-x0+x)} + EM \quad (48.41)$$

Hence  $Q(x)$  for this case has a form  $Q(x)^M = E_M - V_M(x)$  with potential energy of Morse's form, treated in section 1.49.

$$V_M(x) = D_e \left( e^{-2a(x-x_0)} - e^{-a(x-x_0)} \right).$$

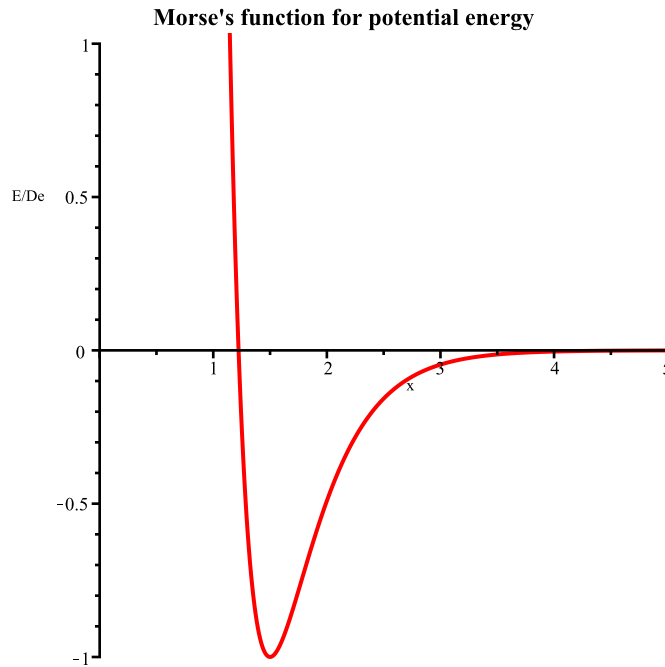
**> eq17 := V[M](x) = eval(-rhs(eq16), EM=0);**

$$(48.42)$$

$$eq17 := V_M(x) = De e^{-2a(-x0 + x)} - 2 De e^{-a(-x0 + x)} \quad (48.42)$$

Adopting characteristic values  $x0 = 1.5$  and  $a = 2.5$  in convenient units, we plot the reduced function  $\frac{V_M(x)}{De}$ .

```
> plot(eval(rhs(eq17)/De, [a=2.5, x0=1.5]), x=0..5, -1..1, colour=
red,
      numpoints=500, title="Morse's function for potential energy",
      titlefont=[TIMES,BOLD,14], labels=["      x", "E/De"]
);
```



The minimum of this function  $V_M(x)$  is at

```
> x = solve(diff(rhs(eq17), x), x);
      x = x0 \quad (48.43)
```

As discussed in section 1.49, this function  $V_M(x)$  supports states of discrete energy of finite number for

$\frac{E}{D_e} < 0$  and a continuum for  $\frac{E}{D_e} > 0$ .

### 1.49 coupling of angular momenta

```
> restart;
```

Clebsch–Gordan (CG) coefficients are numbers that arise in the coupling of angular momenta, in quantum mechanics; they appear as the expansion coefficients of eigenstates of total angular momentum in an uncoupled tensor product basis. The name derives from German mathematicians Alfred Clebsch and Paul Gordan, who encountered an equivalent problem in invariant theory. This section is adapted from a worksheet developed by Professor M. Horbatsch and appears here with permission.

This calculation of coefficients for vector coupling is based on representing  $J_{total}^2$  in a basis of the eigenstates of angular momentum for a single particle and the diagonalization of the matrix of these coefficients. We apply matrix elements of operators for raising and lowering to assemble the matrix.

$$\langle j, m+1 | J_+ | j, m \rangle = \langle j, m | J_- | j, m+1 \rangle = -\hbar \sqrt{(j-m)(j+m+1)}$$

We apply this decomposition:  $J_{total}^2 = J_1^2 + J_2^2 + 2 J_{1z} J_{2z} + J_{1-} J_{2+} + J_{1+} J_{2-}$ . When assembling the matrix representation we bear in mind that the five terms on the right side of the above equation separate into two groups: the former three terms contribute only on the principal diagonal; the latter two terms are on adjacent diagonals. To couple  $J_1=3/2$  and  $J_2=1$ , we work in units in which  $\frac{\hbar}{2\pi}$  is denoted  $\hbar_- = 1$ .

```
> interface(warnlevel=0):
  with(linalg):
> j1 := 3/2;
  j2 := 1;
```

$$j1 := \frac{3}{2}$$

$$j2 := 1 \quad (49.1)$$

Our general interest is to choose an allowed value of total angular momentum to which  $j1$  and  $j2$  couple, i.e., within range  $|j1 - j2| \dots (j1 + j2)$ , but in this approach in which  $J^2$  is diagonalized in basis  $|j1 j2 m1 m2\rangle$ , we use not a specification of  $J$  but rather find the Clebsch-Gordan coefficients for all possible values of  $J$ . To leave the  $z$ -projection of total  $J$  maximally unrestricted, we determine the maximum allowed length:

```
> J := j1 + j2;
```

$$J := \frac{5}{2} \quad (49.2)$$

Our task is to represent  $J^2$  in basis  $|j1 j2 m1 m2\rangle$  with  $j1$  and  $j2$  specified through their quantum numbers.

The matrix representation of  $J^2$  hence becomes labeled with  $m1$  and  $m2$ , which do not vary independently but are restricted according to condition  $m1 + m2 = M$ ; we thus choose a projection from the range  $M = -J \dots J$ . To obtain coupling, we choose any but the largest or smallest; the reason to avoid the largest projection is that only one combination of  $z$ -projections of  $J_1$  and  $J_2$  works in that case.

```
> M := -J + j2 + 1;
```

$$M := -\frac{1}{2} \quad (49.3)$$

The solution of the eigenvalues and eigenvectors of  $J^2$  provide

- through the eigenvalues the allowed quantum numbers of  $J^2$ , i.e.,  $\hbar_-^2 J(J+1)$ , with the possible choices of  $J$  that are compatible with the chosen  $M$ ,
- in anticipation of half-integer spins we choose  $M$  such that it is compatible with  $J$ , i.e., for integer  $J$  we choose integer  $M$ , whereas for half-integer  $J$  we choose half-integer  $M$ , and
- the eigenvector for a given eigenvalue of  $J^2$  produces the set of coupling coefficients that indicates how the uncoupled states combine to form an eigenvector of  $J^2$ .

The question arises how to find the correct range of values ( $m1, m2$ ) through the use of restrictions, such as  $M = m1 + m2$ . This range determines the size of the matrix. With a counting method we determine the matrix size in variable  $ic$ ; the configurations are stored in  $cf$ :

```
> ic := 0:
  for m1 from -j1 to j1 do
    for m2 from -j2 to j2 do
      if m1+m2=M then
        ic := ic + 1:
        cf[ic] := [m1,m2]:
        print(`Combination `,ic,` involves [m1,m2]= `,cf[ic],` with
m1+m2=M: `,M);
      end if;
    end do:
  end do:
ic;
```

$$\text{Combination , 1, involves [m1,m2]} = , \left[ -\frac{3}{2}, 1 \right], \text{ with } m1 + m2 = M: , -\frac{1}{2}$$

$$\text{Combination , 2, involves [m1,m2]} = , \left[ -\frac{1}{2}, 0 \right], \text{ with } m1 + m2 = M: , -\frac{1}{2}$$

$$\text{Combination , 3, involves [m1,m2]} = , \left[ \frac{1}{2}, -1 \right], \text{ with } m1 + m2 = M: , -\frac{1}{2}$$

3

(49.4)

Herein  $j2$ , which is the smaller of the two, steps through all allowed values:

```
> Jsqr := matrix(ic,ic,0);
```

$$Jsqr := \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(49.5)

In this square matrix the row and column indices pass through all allowed values of  $m1, m2$ , i.e., each index from 1 to  $ic$ ; We call them  $m1, m2$  and  $m1p, m2p$  for row and column indices respectively. We require also indices to refer to the matrix entries, in a range from 1 to  $ic$ , called  $im2$  and  $im2p$ . To understand the diagonal matrix entries is straightforward: they are simply the sum of the diagonal

elements of the operators  $J1^2 + J2^2 + 2*J1z*J2z$ , i.e., of the eigenvalues of these operators. The off-diagonal elements require one to understand the following structure:

when  $m2 = m2p + 1$ , from  $m1 = M - m2 = M - m2p - 1$  and  $m1p = M - m2p = m1 + 1$ ,  $m1 = m1p - 1$ , and vice versa, when  $m2 = m2p - 1$ ,  $m1 = m2p + 1$ , so that  $J1 + J2-$  and  $J1 - J2+$  have entries on diagonals just above and below the principal diagonal.

```
> for irow from 1 to ic do
  m1 := cf[irow][1]:
  m2 := cf[irow][2]:
  for icol from 1 to ic do
```



```

m1p := cf[icol][1]:
m2p := cf[icol][2]:
if m2=m2p then
  Jsq[irow,icol] := j1*(j1+1)+j2*(j2+1)+2*m1*m2:
elif m1=m1p-1 and m2=m2p+1 then
  Jsq[irow,icol] := sqrt((j2-m2+1)*(j2+m2)*(j1+m1+1)*(j1-m1)):

  print(m1,m1p,m2,m2p,Jsq[irow,icol]);
elif m1=m1p+1 and m2=m2p-1 then
  Jsq[irow,icol]:=sqrt((j1-m1+1)*(j1+m1)*(j2+m2+1)*(j2-m2)):
  print(m1,m1p,m2,m2p,Jsq[irow,icol]);
end if:
end do:
end do:

```

$$\begin{aligned}
& -\frac{3}{2}, -\frac{1}{2}, 1, 0, \sqrt{6} \\
& -\frac{1}{2}, -\frac{3}{2}, 0, 1, \sqrt{6} \\
& -\frac{1}{2}, \frac{1}{2}, 0, -1, 2\sqrt{2} \\
& \frac{1}{2}, -\frac{1}{2}, -1, 0, 2\sqrt{2}
\end{aligned} \tag{49.6}$$

The result for  $\mathbf{J}^2$  is

```
> 'Jsq' = eval(Jsq);
```

$$Jsq = \begin{bmatrix} \frac{11}{4} & \sqrt{6} & 0 \\ \sqrt{6} & \frac{23}{4} & 2\sqrt{2} \\ 0 & 2\sqrt{2} & \frac{19}{4} \end{bmatrix} \tag{49.7}$$

To find the allowed total angular momentum for which the chosen  $M$  sublevel becomes realized, we

$2$

calculate the eigenvalues and bear in mind that they follow  $h_- J(J+1)$ .

```
> eigenvalues(Jsq);
```

$$\frac{15}{4}, \frac{35}{4}, \frac{3}{4} \tag{49.8}$$

Among the three possible eigenvalues of  $\mathbf{J}^2$  we find both the previously selected maximum configuration  $J=j1+j2$  and the minimum  $J=j1-j2$ , and one between these extrema.

```
> J*(J + 1);
```

$$\frac{35}{4} \quad (49.9)$$

```
> abs(j1 - j2)*(abs(j1 - j2)+1);
```

$$\frac{3}{4} \quad (49.10)$$

The mixing coefficients indicate that the uncoupled basis states labeled with  $[j1\ m1]$  and  $[j2\ m2]$  can be coupled to  $[JM]$  values specified with fixed  $M$  and with calculated  $J$  from the diagonalization of  $J^2$ . The meaning of the eigenvector entries is that the coefficients indicate how much of the product of states  $[j1\ m1]$  and  $[j2\ m2]$  is required with  $m1, m2$  specified in table cf. The first eigenvector component is thus the admixing coefficient for values  $(m1, m2)$  given in cf[1]; the second eigenvector entry is that for the product of  $[j1\ m1]$  with  $[j2\ m2]$  with  $m1$  and  $m2$  given in cf[2], etc.

```
> vec := eigevecs(Jsq);
```

$$vec := \left[ \frac{3}{4}, 1, \{r\} \right], \left[ \frac{15}{4}, 1, \{r\} \right], \left[ \frac{35}{4}, 1, \{r\} \right] \quad (49.11)$$

The eigenvector corresponding to the chosen value of  $J$  when normalised gives the coupling coefficients.

```
> nops([vec]);
```

$$3 \quad (49.12)$$

```
> myvec := Vector(3):
```

```
  for i from 1 to nops([vec]) do
```

```
    if vec[i][1] = J*(J+1) then
```

```
      myvec := op(vec[i][3]);
```

```
      print(`unnormalised eigenvector: `, myvec);
```

```
    end if:
```

```
  end do:
```

$$unnormalised\ eigenvector: , \left[ \frac{\sqrt{3}\sqrt{2}}{6} \quad 1 \quad \frac{\sqrt{2}}{2} \right] \quad (49.13)$$

```
> CG := map(combine, normalize(myvec));
```

$$CG := \left[ \frac{\sqrt{10}}{10} \quad \frac{\sqrt{15}}{5} \quad \frac{\sqrt{30}}{10} \right] \quad (49.14)$$

The normalisation is important to maintain unitarity, and thereby a probabilistic interpretation. If we prepare the system in eigenstate  $[J, M, j1, j2]$ , and then measure  $j1\_z$  and  $j2\_z$ , the square of the Clebsch-Gordan coefficient provides the probabilities to measure a particular set of allowed values  $(m1, m2)$ . First we verify this interpretation.

```
> add(CG[i]^2, i=1..vectdim(CG));
```

$$1 \quad (49.15)$$

```
> print(cf);
```

$$(49.16)$$

$$\text{table}\left(\left[1=\left[-\frac{3}{2}, 1\right], 2=\left[-\frac{1}{2}, 0\right], 3=\left[\frac{1}{2}, -1\right]\right]\right) \quad (49.16)$$

```
> seq(CG[j]^2, j=1..3);
```

$$\frac{1}{10}, \frac{3}{5}, \frac{3}{10} \quad (49.17)$$

The statement is that, for eigenstate  $|J=5/2, M=-1/2, j_1=3/2, j_2=1\rangle$ , the probabilities are

10 % to be in combination  $(m_1, m_2) = (-3/2, 1)$ ,

60 % to be in combination  $(m_1, m_2) = (-1/2, 0)$ ,

30 % to be in combination  $(m_1, m_2) = (1/2, -1)$ .

In a procedure to calculate the Clebsch-Gordan coefficients, to generate a general formula given, e.g., in W. J. Thompson: *Angular Momentum*, Wiley 1994, eq. 7.51, one introduces first the related  $(3j)$  coefficient for coupling three angular momenta to zero, which involves a sum over  $k$ , implemented as a sum over  $2*k$ , to allow a half-integer projection of angular momentum.

```
> ThreeJ := proc(j1,m1,j2,m2,j3,m3)
  local k,tk,tkmin,tkmax,res,phas,n1,n2,d1,d2,d3,term;
  if m1+m2+m3 <> 0 then
    RETURN(0)
  end if;
  tkmin := 2*max(0, j2 - j1 - m3);
  tkmax := 2*min(j3 - m3, j3 - j1 + j2);
  res := 0;
  phas := (-1)^(tkmin/2 + j2 + m2);
  for tk from tkmin to tkmax by 2 do
    k := tk/2;
    n1 := (j2 + j3 + m1 - k)!;
    #print("n1= ",n1);
    n2 := (j1 - m1 + k)!;
    #print("n2= ",n2);
    d1 := k!*(j3 - j1 + j2 - k)!;
    #print("d1= ",d1);
    d2:=(j3 - m3 - k)!;
    #print("d2= ",d2,k,j1,j2,m3);
    d3 := (k + j1 - j2 + m3)!;
    #print("d3= ",d3);
    term := phas*n1*n2/(d1*d2*d3);
    phas := -phas;
    res := res + term;
  end do;
  simplify(res)*(-1)^(j1-j2-m3)*sqrt((j3+j1-j2)!*(j3-j1+j2)!*(j1+
j2-j3)!*(j3-m3)!*(j3+m3)!
/((j1+j2+j3+1)!*(j1-m1)!*(j1+m1)!*(j2-m2)!*(j2+m2)
!));
```

end proc;

```
> CGC := (j1,m1,j2,m2,J) -> combine(ThreeJ(j1,m1,j2,m2,J,-m1-m2)*
sqrt(2*J+1)*(-1)^(j1-j2+m1+m2));
```

$$CGC := (j1, m1, j2, m2, J) \mapsto combine(ThreeJ(j1, m1, j2, m2, J, -m1 - m2) \cdot \sqrt{2 \cdot J + 1} \cdot (-1)^{j1 - j2 + m1 + m2}) \quad (49.18)$$

For our example we have  $j1$   $j2$  and the range of  $m2$  and  $m1$ :

```
> j1,j2,[-1,0,1],[M-(-1),M,M-1]; # The matrix is formed on
stepping with m2 [-1,0,1].
```

$$\frac{3}{2}, 1, [-1, 0, 1], \left[ \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \right] \quad (49.19)$$

We calculate and test the Clebsch-Gordan coefficients.

```
> CG[1];
```

$$\frac{\sqrt{10}}{10} \quad (49.20)$$

```
> CGC(j1,M+1,j2,-1,J);
```

$$\frac{\sqrt{30}}{10} \quad (49.21)$$

```
> % - %%;
```

$$\frac{\sqrt{30}}{10} - \frac{\sqrt{10}}{10} \quad (49.22)$$

```
> CG[2];
```

$$\frac{\sqrt{15}}{5} \quad (49.23)$$

```
> CGC(j1,M,j2,0,J);
```

$$\frac{\sqrt{60}}{10} \quad (49.24)$$

```
> simplify(% - %%);
```

$$0 \quad (49.25)$$

```
> CGC(j1,M-1,j2,1,J);
```

$$\frac{\sqrt{90}}{30} \quad (49.26)$$

```
> CG[3];
```

$$\frac{\sqrt{30}}{10} \quad (49.27)$$

```
> % - %%;
```

$$\frac{\sqrt{30}}{10} - \frac{\sqrt{90}}{30} \quad (49.28)$$

The effect of the calculation is that  $|JMj_1j_2\rangle = |5/2, -1/2, 3/2, 1\rangle = \text{add}(\text{CG}[M-m_2, m_2] * |j_1, M-m_2\rangle |j_2 m_2\rangle, m_2 = -1..1)$

> J,M,j1,j2;

$$\frac{5}{2}, -\frac{1}{2}, \frac{3}{2}, 1 \quad (49.29)$$

There are sum rules for Clebsch-Gordan coefficients given in Thompson's book (or other books on group theory or angular momentum algebra), which can be verified with explicit calculations.

An application of Clebsch-Gordan coefficients or (3j) symbols is the evaluation of angular integrals over three spherical harmonics. Thompson listed it as eq. 7.102 and shows how it follows as a special case of an integral over three Wigner rotation matrices. We begin with a definition of the spherical harmonics.

```
> with(orthopoly):
> Plm := proc(theta, l::nonnegint, m::integer)
    local x,y,f;
    x := cos(theta);
    if m>0 then
        f := subs(y=x, diff(P(l,y), y$m));
    else
        f := subs(y=x,P(l,y));
    end if;
    (-1)^m*sin(theta)^m*f;
end proc:
> Plm(theta,3,2);
```

$$15 \sin(\theta)^2 \cos(\theta) \quad (49.30)$$

For spherical harmonics Plm with negative argument are unnecessary.

```
> Y := proc(theta, phi, l::nonnegint, m::integer)
    local m1;
    m1 := abs(m);
    if m1>l then
        RETURN("|m} must be <= l for Y_lm");
    end if;
    exp(I*m*phi)*Plm(theta,l,m1)*(-1)^m*sqrt((2*l+1)*(l-m1)!/(4*Pi*
(1+m1)!));
end proc:
> Y(theta,phi,3,0);
```

$$\frac{\left(\frac{5 \cos(\theta)^3}{2} - \frac{3 \cos(\theta)}{2}\right) \sqrt{7}}{2 \sqrt{\pi}} \quad (49.31)$$

> Y(theta,phi,3,1);

$$\frac{e^{i\phi} \sin(\theta) \left( \frac{15 \cos(\theta)^2}{2} - \frac{3}{2} \right) \sqrt{21}}{12 \sqrt{\pi}} \quad (49.32)$$

> No := (l,m) -> int(int(evalc(Y(theta,phi,l,m)\*conjugate(Y(theta,phi,l,m))),phi=0..2\*Pi)\*sin(theta),theta=0..Pi);

$$No := (l, m) \mapsto \int_0^\pi \left( \int_0^{2\pi} evalc(Y(\theta, \phi, l, m) \cdot \overline{Y(\theta, \phi, l, m)}) d\phi \right) \cdot \sin(\theta) d\theta \quad (49.33)$$

> No(1,0);

$$1 \quad (49.34)$$

We test the following double integral.

> AI := (J,M,j1,m1,j2,m2) -> int(int(evalc(Y(theta,phi,j1,m1)\*Y(theta,phi,j2,m2)\*conjugate(Y(theta,phi,J,M))),phi=0..2\*Pi)\*sin(theta),theta=0..Pi);

$$AI := (J, M, j1, m1, j2, m2) \mapsto \int_0^\pi \left( \int_0^{2\pi} evalc(Y(\theta, \phi, j1, m1) \cdot Y(\theta, \phi, j2, m2) \cdot \overline{Y(\theta, \phi, J, M)}) d\phi \right) \cdot \sin(\theta) d\theta \quad (49.35)$$

The restrictions on the angular-momentum parameters are a triangle rule on  $(j1, j2, J)$ , that  $j1 + j2 + J$  must be an even integer, and that  $m1 + m2 = M$ . For example,

> AI(2,1,1,0,1,1);

$$\frac{\sqrt{3} \sqrt{5}}{10 \sqrt{\pi}} \quad (49.36)$$

In terms of (3j) symbols the integral can be calculated as

> AI3j := (J,M,j1,m1,j2,m2) -> simplify((-1)^M\*sqrt((2\*j1+1)\*(2\*j2+1)\*(2\*J+1)/(4\*Pi))\*ThreeJ(j1,m1,j2,m2,J,-M)\*ThreeJ(j1,0,j2,0,J,0));

$$AI3j := (J, M, j1, m1, j2, m2) \mapsto simplify \left( (-1)^M \cdot \sqrt{\frac{(2 \cdot j1 + 1) \cdot (2 \cdot j2 + 1) \cdot (2 \cdot J + 1)}{4 \cdot \pi}} \cdot ThreeJ(j1, m1, j2, m2, J, -M) \cdot ThreeJ(j1, 0, j2, 0, J, 0) \right) \quad (49.37)$$

> AI3j(2,1,1,0,1,1);

$$\frac{\sqrt{15}}{10 \sqrt{\pi}} \quad (49.38)$$

Integrals of this type arise in atomic physics in the computation of multipole expansions of the potential energy of a charge distribution, and in the computation of matrix elements of dipolar moment, e.g., in radiative decay, in which cartesian components of the position vector are represented as  $r^*Y(l,m)$ , e.g.,  $x + iy = r Y(1,1)$ .

### *e1.50 exercise*

- i) Undertake the calculation for the other allowed  $M$  values and the same  $J$  value, i.e.,  $J = j_1 + j_2$ ; calculate the probabilities to find the system in a particular  $(m_1, m_2)$  configuration, and display graphically using arrows for the  $(j_1, m_1)$  and  $(j_2, m_2)$  angular momentum vectors how state  $(JM)$  arises.
- ii) Inspect other  $J$  values for which the set of  $(j_1, m_1)$  and  $(j_2, M - m_1)$  configurations couples to  $(JM)$  and construct the probabilities as well as the graphical representations discussed in i).
- iii) Choose another combination of  $j_1$  and  $j_2$ , and repeat the calculations for parts i) and ii).
- iv) Verify the short formula by comparing it against the symbolic computation of the integral; apply large values of the angular momentum parameters and verify its computational advantage.

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