

Path Integrals and Interferometry

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Review of the Fundamentals of Quantum Mechanics

A discussion of the path integral formulation of quantum mechanics requires a reasonable understanding of the fundamentals of quantum mechanics written in the language of linear algebra and functional analysis. The Dirac notation will be adopted for this review, and a general familiarity with many of the concepts will be assumed. Nonetheless, a brief but explicit discussion of the necessary elements ought to be instructive.¹

Physical theories may, in general, be considered complete if there is a rigorous definition of the state in which the system currently exists, and the laws of motion dictating how that state will evolve with time.

The state of a quantum mechanical system may be described by an object in a complex, abstract vector space known as Hilbert space. This space may be described in terms of a particular basis, often represented as column vectors. However, the objects, the states, exist separately from any representation. Complex, here, merely indicates that the coefficients of a linear combination of vectors may be members of the complex numbers.

$$|\Psi\rangle$$

There exists a dual space of vectors conjugate to the state vectors. That is, there is a space of vectors such that each vector has one and only one conjugate vector. The relationship is analogous to that of complex conjugates. In fact, if the state is represented as a column vector, these would be the complex transpose of that vector.

$$\langle\Psi|$$

There is defined, an inner product between every state vector and every conjugate vector.

$$\langle\Psi|\Phi\rangle$$

This inner product roughly corresponds to the overlap between the states, S ; that is, how much of one state can be represented in the other.

$$\langle\Psi_i|\Psi_j\rangle = S_{ij}$$

If a the inner product of a state with its own conjugate is equal to unity, it is considered normalized.

$$\langle\Psi|\Psi\rangle = 1$$

If the inner product between two states is zero, those states are considered orthogonal and may be distinguished with complete certainty.

$$\langle\Psi|\Phi\rangle = 0$$

Observables of a quantum system are described by Hermitian operators. Such operators are equal to their own Hermitian adjoint. If they are represented in some basis as a matrix, the adjoint is just the conjugate transpose of the matrix.

$$\hat{A}^\dagger = \hat{A}$$

These operators have an associated set of eigenvectors, with corresponding eigenvalues.

$$\hat{A} |a\rangle = a |a\rangle$$

The eigenvectors of such an operator form a complete basis, meaning any state can be represented as a linear combination of these eigenvectors.

$$|\Psi\rangle = \sum_i \langle a_i | \Psi \rangle |a_i\rangle$$

It may be convenient to express the state in terms of an orthonormal basis, for simplification of computation. In that case, each vector in the basis will exhibit the following property.

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$$

Eigenvectors with different eigenvalues are orthogonal. Eigenvectors with the same eigenvalue may be used to construct an orthogonal set if they are not already orthogonal by the Gram-Schmidt process.

$$\begin{aligned} \hat{A} |a_i\rangle &= a |a_i\rangle \\ \hat{A} |a_j\rangle &= a |a_j\rangle \\ |a_k\rangle &= |a_i\rangle - \langle a_i | a_j \rangle |a_i\rangle \\ \langle a_k | a_j \rangle &= 0 \end{aligned}$$

Upon measuring an observable of a quantum system, the state will "collapse" into one of the eigenvectors of the corresponding operator. The probability that this will occur is equal to the absolute square of the coefficient in the linear combination. The only values which may be measured are the eigenvalues. No other values will be observed.

$$P(a_i) = \langle \Psi | a_i \rangle \langle a_i | \Psi \rangle$$

An example of such an observable is the position of a particle along some axis, x . The eigenvectors of the position must be some function along the continuous space of position which has definite, unambiguous probability of existing at a particular location.

$$|x_o\rangle = \delta(x - x_o)$$

The operator for position in its own basis must return the corresponding location of each eigenvector.

$$\hat{x} |x_o\rangle = x_o |x_o\rangle$$

$$\begin{aligned}\hat{x} |x_o\rangle &= \hat{x} \delta(x - x_o) \\ &= x \delta(x - x_o) \\ \hat{x} &\equiv x\end{aligned}$$

For a more complete description in the position basis, the momentum operator must be defined. The eigenvectors of momentum must have a well-defined wavelength by the deBroglie relation.

$$\begin{aligned}e^{ikr} \\ p &= \hbar k \\ e^{i\frac{p}{\hbar}r} \\ \left| p_o \right\rangle &= e^{i\frac{p_o}{\hbar}r}\end{aligned}$$

The momentum operator must return the value of the momentum; upon inspection, it must be the following.

$$\hat{p} \equiv -i\hbar\nabla$$

Many physically interesting quantities may be described in terms of some generalized position and some conjugate momentum which will have the same form as the preceding. Linear momentum will correspond to linear position. Angular momentum will correspond to angular position. By association, the momentum conjugate to time is the energy. The function corresponding to this quantity is the Hamiltonian. The equation describing this operation on a general vector is known as the Schrodinger equation. By convention, the version without an initial negative is often used.

$$\begin{aligned}\hat{H} &\equiv i\hbar\partial_t \\ i\hbar\partial_t |\Psi\rangle &= \hat{H}|\Psi\rangle\end{aligned}$$

With the state of a quantum system described, what remains is a description of the time-evolution. The time evolution operator can be derived from the time-dependent Schrodinger equation. If the time interval over which the evolution takes place is small enough, the Hamiltonian can be regarded as constant.

$$\begin{aligned}\left| \Psi(dt) \right\rangle &= \left| \Psi(0) \right\rangle + \frac{d}{dt} \left| \Psi(0) \right\rangle dt + \frac{1}{2} \frac{d^2}{dt^2} \left| \Psi(0) \right\rangle (dt)^2 + \dots \\ &= \left(1 - \frac{i}{\hbar} \hat{H} dt - \frac{1}{2} \frac{1}{(\hbar)^2} \hat{H} \hat{H} (dt)^2 + \dots \right) \left| \Psi(0) \right\rangle \\ &= U(dt) \left| \Psi(0) \right\rangle \\ U(dt) &= e^{-\frac{i}{\hbar} \hat{H} dt}\end{aligned}$$

The general time evolution operator can be constructed in terms of the infinitesimal operators.

$$\left| \Psi(t) \right\rangle = U(t) \left| \Psi(0) \right\rangle = \prod_i U(dt_i) \left| \Psi(0) \right\rangle$$

$$= e^{-\frac{i}{\hbar} \int \hat{H} dt} |\Psi(0)\rangle$$

A more complete discussion of the fundamentals of quantum mechanics would include aspects of uncertainty and whether certain operators commute with one another. These discussions are unnecessary for this particular topic and have been left out.

The Path Integral Formula

Some understanding of Lagrangian mechanics may be necessary to fully appreciate the following discussion, but a brief, conceptual review should be adequate to follow the proceeding derivations.² The Lagrangian in classical mechanics is a function of generalized coordinates and their first derivatives which describes the state of a system. It is found by obeying the principle of least action and is wholly equivalent to Newtonian mechanics. The action, is the path integral of the Lagrangian between two points and the principle of least action is stated as follows. (The action may also be written as S).

$$\delta \mathcal{A} = 0 = \delta \int \mathcal{L}(q, \dot{q}) dt$$

Once the Lagrangian is found, the time-evolution of the system may be described by a set of Euler-Lagrange equations corresponding to each generalized coordinate.

$$\frac{d}{dt} \left(\frac{\partial}{\partial \dot{q}} \mathcal{L} \right) - \frac{\partial}{\partial q} \mathcal{L} = 0$$

The definition of the Hamiltonian is, in fact, in terms of a Lagrangian. So the Lagrangian may be written as follows.

$$\mathcal{L} = \sum_i p \dot{q}_i - H$$

In classical mechanics, Lagrangian and Hamiltonian mechanics exist as equivalent, but separate ways of calculating the trajectory of a particle. Hamiltonian mechanics takes the initial positions and momenta of particles and computes the next set of positions and momenta. Lagrangian mechanics takes the endpoints of a trajectory and computes the path that minimizes the action, replicating the results.

There exists a similar approach to quantum mechanics which will now be derived. The analogous quantity for a particle trajectory is the probability that a particle will be found at a given location at a particular time. The first consideration is that any state can be represented in the position basis, and so defining this "trajectory" operator for position is sufficient to describe the trajectory of any state. This is known as the path integral kernel, or the propagator.

The propagator can be derived as the combined propagator for small intervals.³ For a simple Hamiltonian with separable kinetic and potential components, the following is valid.

$$\begin{aligned} & \langle x, dt | x_o, 0 \rangle \\ &= \langle x | U(dt) | x_o \rangle \\ &= \sum_p \langle p | \langle x | p \rangle U(dt) | x_o \rangle \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{\hbar}} \int dp e^{\frac{i}{\hbar} (px + Hdt + O(d^2))} |x_o\rangle \\
&= \frac{1}{\sqrt{\hbar}} \int dp e^{\frac{-i}{\hbar} \left(px + \frac{p^2}{2m} + V(x_o) dt + O(d^2) \right)} \\
&= \sqrt{\frac{m}{i\hbar dt}} e^{\frac{i}{\hbar} \left(\frac{m}{2} \frac{(x-x_o)^2}{dt} - V(x_o) dt + O(d^2) \right)}
\end{aligned}$$

The expression in the exponent is just the Lagrangian times a small interval of time, or the action over a small interval of time.

$$\begin{aligned}
&\langle x, dt | x_o, 0 \rangle \\
&= N e^{\frac{i}{\hbar} \mathcal{L} dt} = N e^{\frac{i}{\hbar} \mathcal{A}}
\end{aligned}$$

To find the form of the path integral kernel for a larger interval of time, one must combine many smaller intervals. However, one must be careful to account for all of the contributions. The position basis is complete, but each component of position may overlap with every other component at a future time. Therefore, the expression for the general path integral kernel is as follows. Let the number of small time intervals be M, and each basis be written in terms of a subscript which indicates the time relative to the endpoint.

$$\begin{aligned}
&\langle x, dt | x_o, 0 \rangle \\
&= \int dx \langle x | x_{-dt} \rangle dx_{-dt} \langle x_{-dt} | x_{-2dt} \rangle \cdots dx_{-Mdt} \langle x_{-Mdt} | x_o \rangle
\end{aligned}$$

This integral describes each position and how it overlaps with the next along a trajectory. In effect, this is a sum over all the possible paths between the endpoints weighted by the exponential of the action. Of course this quantity may be normalized.

$$\begin{aligned}
&\langle x, dt | x_o, 0 \rangle \\
&= \sum_{paths} \prod_{dt} e^{\frac{i}{\hbar} \mathcal{L} dt} \\
&= \sum_{paths} e^{\frac{i}{\hbar} \int_{path} \mathcal{L} dt}
\end{aligned}$$

The behavior of a particle can be described as a set of probabilities and associated trajectories. Therefore, the probability that a particle will travel along a given trajectory can be computed from the sum all possible paths between the endpoints weighted by the exponential of the action along the given path.

A More General Derivation

The derivation of the path integral can be achieved using a more general notion of the Lagrangian. As the Hamiltonian is defined in terms of the Lagrangian, again the Lagrangian may be written as follows.

$$\mathcal{L} = \sum_i p_i \dot{q}_i - H$$

The probability amplitude for a given endpoint in generalized coordinates is given below for an infinitesimal step forward in time. Here q is used to indicate a set of coordinates. p is likewise used for a set of conjugate momenta (excluding time).

$$\begin{aligned} & \langle q, dt | q_o, 0 \rangle \\ &= \langle q | U | q_o \rangle \\ &= \int dp e^{\frac{i}{\hbar} p \cdot q} e^{-\frac{i}{\hbar} H(q_o) dt} \end{aligned}$$

The general position and its conjugate momentum (by which one may construct the Hamiltonian) do not commute with each other. They do, however, commute with their commutator, $i\hbar$. The Baker-Campbell-Hausdorff formula for such a case (which will not be derived here) is as follows for exponential operators.

$$e^A e^B = e^{A+B + \frac{1}{2}[A, B]}$$

The commutator is second order in dt , and can be ignored for a sufficiently small interval of time. Therefore the propagator may be written as follows.

$$\begin{aligned} & \int dp e^{\frac{i}{\hbar} \left(p \cdot q - \frac{p^2}{2m} dt - V dt \right)} \\ &= N e^{\frac{i}{\hbar} (p \cdot \dot{q} dt - H dt)} \\ &= N e^{\frac{i}{\hbar} \mathcal{L} dt} \end{aligned}$$

The remaining derivation is the same as that shown above.

Free Particle Lagrangian

The Lagrangian for a free particle, regardless of mass, is the following.

$$\mathcal{L} = p\dot{q}$$

The state of a general particle can be written in the momentum basis, and so the action for a given eigenvector can be written as follows.

$$\begin{aligned} \mathcal{A} &= \int_{path} \mathcal{L} dt \\ &= \int p\dot{q} dt \\ &= p\Delta q \end{aligned}$$

Mach-Zehnder Interferometer

A simple example of employing the path integral formalism is in the single-photon experiments of a Mach-Zehnder interferometer. A sketch of the apparatus is shown below (*Figure 1*). Despite the suggestive drawing, the apparatus does not need to be a parallelogram, and so the path lengths in the higher and lower paths may differ.

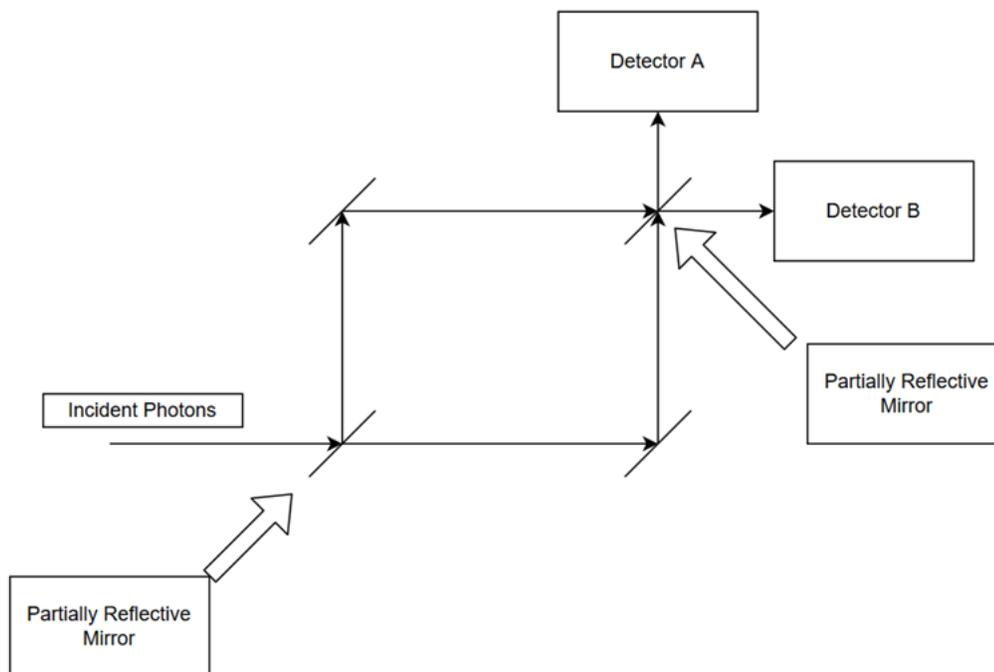


Figure 1. A single photon Mach-Zehnder interferometer. (John Peterson, 2020)

The single photon experiment is essentially the same as the conventional experiment. However, the light source is dimmed until there exists, with reasonable certainty, one particle in the apparatus at a time.

Assuming the principle of least time holds, there exist only two outcomes of measurement using this apparatus and four possible paths over which the photon can travel. The photon may reflect off the first partially reflective mirror, take the upper path, and then reflect again arriving at A. The photon may also reflect off the first partially reflective mirror, take the upper path, and then transmit through the second partially reflective mirror arriving at B. If the photon transmits through the first mirror, it can either reflect off the second, or transmit, leading to a total of four paths. Eventually, the particle will be detected, so the two end states are to arrive at either A or B.

If one performs this measurement using detectors which can only measure one frequency, the experimental outcome can be determined using the previously derived action. (Note that this means the particle momentum is known before it hits the detector, and the position is known after). This discussion can also be thought of as an explanation of what happens to each momentum eigenfunction, the general state being a linear combination thereof.

There are two other considerations before computation may begin. If a mirror has empirically been measured to reflect half of the incoming photons, the probability amplitude corresponding to transmission (or reflection) upon hitting the mirror is the square root of one half. In addition, reflection against a hard boundary is known to shift the phase of an incoming wave by one half. Reflection against

a soft boundary has no such effect. Here, soft means that the material after the reflection surface has a index index of refraction than the one before the boundary. (See figure 2)

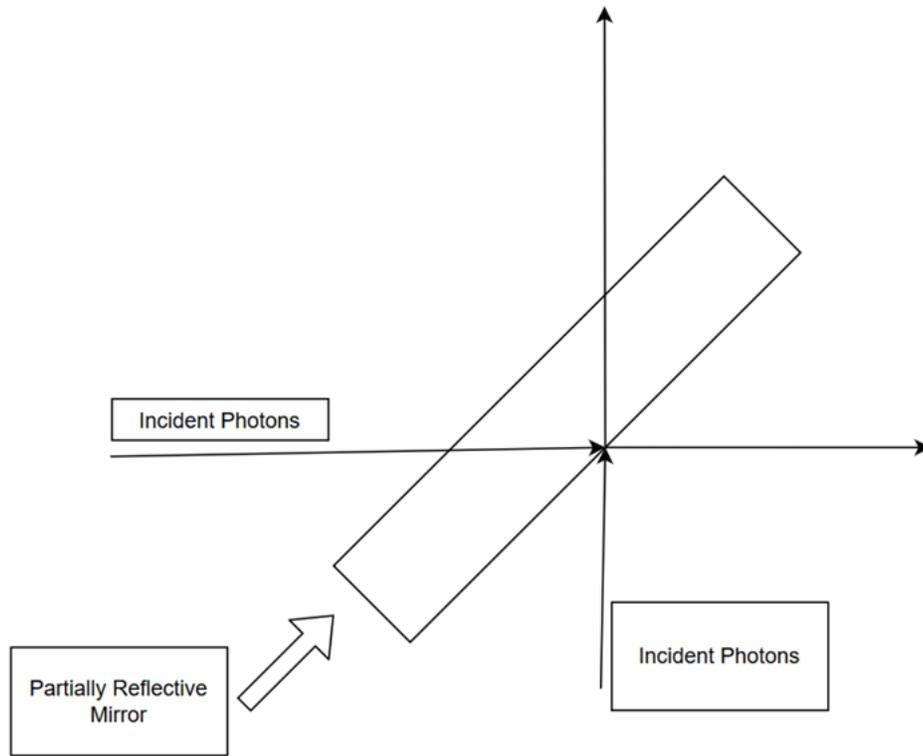


Figure 2. Second partially reflective mirror encountered by the photons. (John Peterson, 2020)

The reflection of the upper path at the second partially reflective mirror occurs at the inner surface, which is a soft boundary. If the reader does not believe this fact, then the apparatus can be made such that the mirror is coated to only transmit at the first surface.

With all this considered, the probability amplitudes corresponding to the photon reaching detectors A and B are given below.

$$\begin{aligned} \Psi_A &= \frac{-1}{\sqrt{2}} (-1) \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar} p x_1} + \frac{1}{\sqrt{2}} (-1) \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar} p x_2} \\ &= \frac{1}{2} e^{\frac{i}{\hbar} p x_1} - \frac{1}{2} e^{\frac{i}{\hbar} p x_2} \\ \Psi_B &= \frac{-1}{\sqrt{2}} (-1) \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar} p x_1} + \frac{1}{\sqrt{2}} (-1) \frac{-1}{\sqrt{2}} e^{\frac{i}{\hbar} p x_2} \\ &= \frac{1}{2} e^{\frac{i}{\hbar} p x_1} + \frac{1}{2} e^{\frac{i}{\hbar} p x_2} \end{aligned}$$

With these probability amplitudes, one may obtain the probabilities, that the particle will be detected at a particular detector over the interval defined by the experiment.

$$\begin{aligned}
P_A = \langle \Psi_A | \Psi_A \rangle &= \left(\frac{1}{2} e^{\frac{-i}{\hbar} p x_1} - \frac{1}{2} e^{\frac{-i}{\hbar} p x_2} \right) \left(\frac{1}{2} e^{\frac{i}{\hbar} p x_1} - \frac{1}{2} e^{\frac{i}{\hbar} p x_2} \right) \\
&= \frac{1}{2} - \frac{1}{4} \left(e^{\frac{i}{\hbar} p (x_1 - x_2)} + e^{\frac{-i}{\hbar} p (x_1 - x_2)} \right) \\
&= \frac{1}{2} \left(1 - \cos \left(\frac{1}{\hbar} p (x_1 - x_2) \right) \right) \\
&= \sin^2 \left(\frac{1}{2\hbar} p (x_1 - x_2) \right) \\
P_B = \langle \Psi_B | \Psi_B \rangle &= \left(\frac{1}{2} e^{\frac{-i}{\hbar} p x_1} + \frac{1}{2} e^{\frac{-i}{\hbar} p x_2} \right) \left(\frac{1}{2} e^{\frac{i}{\hbar} p x_1} + \frac{1}{2} e^{\frac{i}{\hbar} p x_2} \right) \\
&= \frac{1}{2} + \frac{1}{4} \left(e^{\frac{i}{\hbar} p (x_1 - x_2)} + e^{\frac{-i}{\hbar} p (x_1 - x_2)} \right) \\
&= \frac{1}{2} \left(1 + \cos \left(\frac{1}{\hbar} p (x_1 - x_2) \right) \right) \\
&= \cos^2 \left(\frac{1}{2\hbar} p (x_1 - x_2) \right)
\end{aligned}$$

Note that these probabilities are already normalized. Indeed, there also a peculiar behavior. There exists a difference in the length of the paths such that there will be zero probability of the particle arriving at one of the detectors. If the difference in action between the upper path and the lower path is an integral multiple of \hbar , the particle will not arrive at detector A.

In the case of the classical interferometer, light of a given wavelength will interfere with itself if the path lengths are integral multiples of the wavelength apart offset by half a wavelength, due to destructive interference. However, this result suggests that each photon will interfere with itself in the same way. This result is not an artifact of the derivation, it is supported by experiment.

This is how it really works.⁴

Elitzur-Vaidman Bomb Tester⁵

The Elitzur-Vaidman bomb tester is a thought experiment which has since been realized in experimental form. The real experiment does not involve explosives, but the logic plays out the same way. The same interferometer is assembled, and then an object is placed in the lower path. This object is a bomb which has a detector on it. This detector will always absorb a photon, should it interact with it, if the bomb is "live". If the bomb is "dead" the detector will never absorb the photon. (See *figure 3*) Despite what the drawing might suggest, this apparatus does not have to be a parallelogram, and the path lengths may differ.

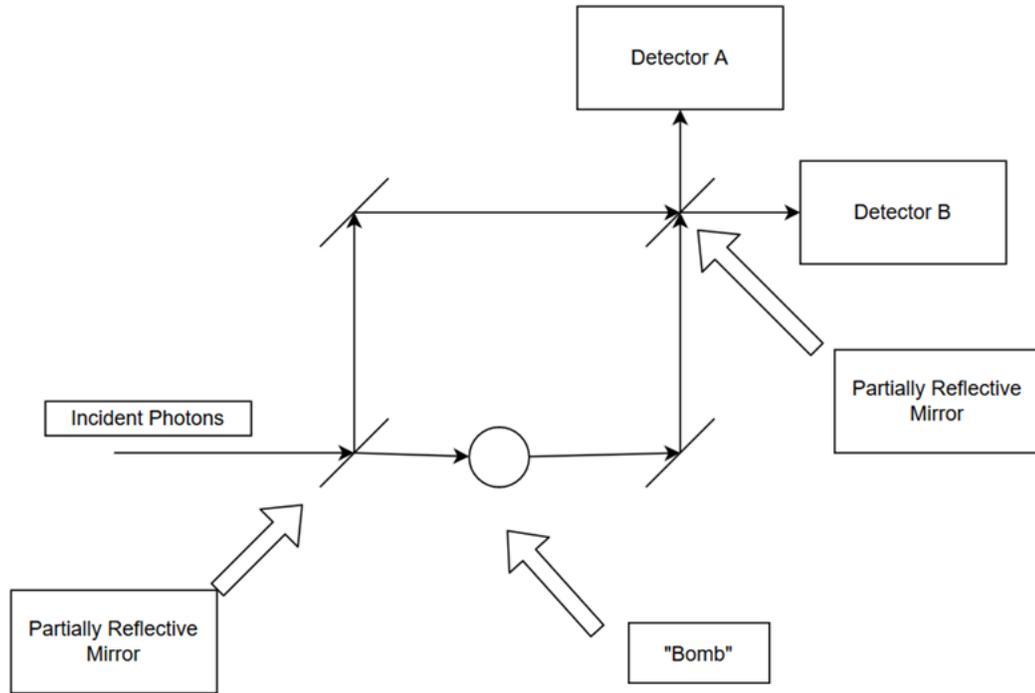


Figure 3. Block diagram of the Elitzur Vaidman bomb tester. (John Peterson, 2020)

In the case of the dead bomb, the probabilities are exactly the same as previously derived. In the case of the live bomb however, these probabilities change. One more case appears, that of triggering the bomb.

$$\Psi_X = \frac{1}{\sqrt{2}}$$

$$\Psi_A = \frac{-1}{\sqrt{2}} (-1) \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar} px_1}$$

$$= \frac{1}{2} e^{\frac{i}{\hbar} px_1}$$

$$\Psi_B = \frac{-1}{\sqrt{2}} (-1) \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar} px_1}$$

$$= \frac{1}{2} e^{\frac{i}{\hbar} px_1}$$

$$P_A = \langle \Psi_A | \Psi_A \rangle = \left(\frac{1}{2} e^{\frac{-i}{\hbar} px_1} \right) \left(\frac{1}{2} e^{\frac{i}{\hbar} px_1} \right)$$

$$= \frac{1}{4}$$

$$P_B = \langle \Psi_B | \Psi_B \rangle = \left(\frac{1}{2} e^{\frac{-i}{\hbar} px_1} \right) \left(\frac{1}{2} e^{\frac{i}{\hbar} px_1} \right)$$

$$= \frac{1}{4}$$

$$x = \langle \Psi_X | \Psi_X \rangle$$

$$= \frac{1}{2}$$

The probabilities are fixed, but what this offers is a unique opportunity. Suppose the apparatus was assembled in such a way that there was zero probability of initially detecting the particle at detector A. Then, each photon may act as an experiment to determine whether each bomb is "live" or "dead".

If the bomb is dead, one will still never detect the particle at detector A. If the bomb is live, there is a 50% chance that the experiment will set it off. There is also a 25% chance that it will give the same outcome as the dead bomb. Finally, there is a 25% chance that it will hit detector A.

This last outcome has determined the state of the bomb, and yet the particle was found at detector A, not at the bomb. The experiment has determined that the bomb is active without interacting with it.

Path Integrals and Chemical Dynamics

The most straight forward, if sometimes impractical, way to simulate chemical dynamics with quantum effects is to numerically solve for the wavefunction, solve the Schrodinger equation, for some complete basis determining the wavefunction at an instant later, and repeat the process until the desired endpoint is reached. This may be done; in fact, if the Hamiltonian for the system is non-trivial in time, the state of the system may be solved for through perturbative expansion. This is the topic of time-dependent perturbation theory.

However, another approach is to simulate the quantum fluctuations that occur around the classical path. The path integral (of all the paths that are approximately near the classical trajectory) for the nuclear motion defines an effective Hamiltonian. This is then used to simulate the trajectory of the nuclei in a quasi-classical manner, and the electronic wavefunction is calculated separately by the Born-Oppenheimer approximation. Such a computation is seen in the algorithm for Ring-Polymer Molecular Dynamics. Other such methods also exist which employ the same basic principle. In order to accomplish this, one still needs to compute the electronic structure for every point. In essence, the electronic structure defines a "potential energy surface" which the heavier nuclei will use as an effective potential, giving an effective Lagrangian. Such a calculation is shown below. First, a set of geometries is defined. Then, the electronic energy is calculated for each geometry. Finally, plotting the energy over the range of coordinates gives the potential energy surface. Here, that surface is computed for molecular nitrogen.

> **Digits := 15;**

Digits := 15 (2.5.1)

> *with(QuantumChemistry);*

[AOLabels, ActiveSpaceCI, ActiveSpaceSCF, AtomicData, BondAngles, BondDistances, (2.5.2)

Charges, ChargesPlot, CorrelationEnergy, CoupledCluster, DensityFunctional, DensityPlot3D, Dipole, DipolePlot, Energy, FullCI, GeometryOptimization, HartreeFock, Interactive, Isotopes, MOCoefficients, MODiagram, MOEnergies, MOIntegrals, MOOccupations, MOOccupationsPlot, MOSymmetries, MP2, MolecularData, MolecularGeometry, NuclearEnergy, NuclearGradient, Parametric2RDM, PlotMolecule, Populations, RDM1, RDM2, ReadXYZ, SaveXYZ, SearchBasisSets, SearchFunctionals, SkeletalStructure, Thermodynamics, Variational2RDM, VibrationalModeAnimation, VibrationalModes, Video]

> *R := [0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9];*

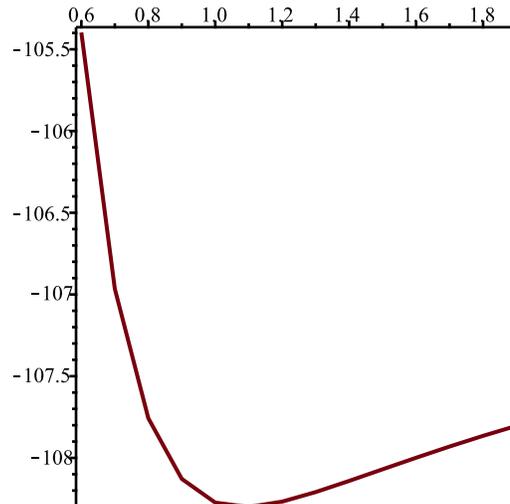
R := [0.60000000, 0.70000000, 0.80000000, 0.90000000, 1.00000000, 1.10000000, (2.5.3)

1.20000000, 1.30000000, 1.40000000, 1.50000000, 1.60000000, 1.70000000, 1.80000000,
1.90000000]

```
> mols := [seq(["N", 0, 0, 0], ["N", 0, 0, R]), R in R];
mols := [[["N", 0, 0, 0], ["N", 0, 0, 0.60000000]], [["N", 0, 0, 0], ["N", 0, 0, 0.70000000]], (2.5.4)
[["N", 0, 0, 0], ["N", 0, 0, 0.80000000]], [["N", 0, 0, 0], ["N", 0, 0, 0.90000000]], [["N",
0, 0, 0], ["N", 0, 0, 1.00000000]], [["N", 0, 0, 0], ["N", 0, 0, 1.10000000]], [["N", 0, 0, 0],
["N", 0, 0, 1.20000000]], [["N", 0, 0, 0], ["N", 0, 0, 1.30000000]], [["N", 0, 0, 0], ["N", 0,
0, 1.40000000]], [["N", 0, 0, 0], ["N", 0, 0, 1.50000000]], [["N", 0, 0, 0], ["N", 0, 0,
1.60000000]], [["N", 0, 0, 0], ["N", 0, 0, 1.70000000]], [["N", 0, 0, 0], ["N", 0, 0,
1.80000000]], [["N", 0, 0, 0], ["N", 0, 0, 1.90000000]]]
```

```
> Es := [seq(Energy(m, Method = HartreeFock, basis = "3-21g"), m in mols)];
Es := [-105.39716384, -106.96547997, -107.75742018, -108.12842061, -108.27366872, (2.5.5)
-108.30004153, -108.26750168, -108.20899832, -108.14073970, -108.06972821,
-107.99904386, -107.93042458, -107.86505989, -107.80372856]
```

```
> plot(R, Es);
```



>

A method of sampling over that effective Lagrangian must be chosen, but then the propagator will provide an algorithm for determining the importance of any given particular path in the behavior of the molecule. This behavior could be as simple as the evolution of a wavefunction in a time-independent Hamiltonian, or it could be as complex as the dissociation of a bond. In this way, the path integral formalism may be applied to predict the behavior of bound systems and not just the trajectories of particles in a beam.

References

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