

# Adiabatic Process in Quantum Mechanics

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## 1. Introduction

Solving the time-dependent Schrodinger equation is essential for understanding the actual response of system to external stimuli. Especially, in the experimental point of view, everything we did during the experiment changes the Hamiltonian, so it is hard to explain the result without understanding the time-dependent Schrodinger equation. Unfortunately, however, there are few time-dependent Schrodinger equations which can be solved exactly. This is why we use some approximations to solve time-dependent problems. One of the approximations is time-dependent perturbation theory which can be applied when perturbation is much smaller than original Hamiltonian. This is very useful especially for perturbation in a very short time, such as laser pulse, but it also has serious drawbacks because we cannot use it when Hamiltonian changes a lot. In this case, we need to find other methods to solve the problem. In this worksheet, we will explore another approximation called adiabatic approximation which can be used in large, but slow change of Hamiltonian by using the mathematical approach and demonstration with well-known systems.

## 2. Theory

### a. Adiabatic Process

Even if adiabatic approximation in quantum mechanics is unfamiliar, it is not so different from the classical approach. Imagine the pendulum with string length  $L$  in the macroscopic world. The natural frequency of this pendulum is determined only by  $L$ . Now let's make a sudden change of  $L$ . In this case, the pendulum does not have enough time to follow the change of  $L$ , so the frequency right after the change is equal to the frequency with initial length  $L(t = 0)$  and then started to change. However, when we make a slow change instead of a sudden change, the pendulum has enough time to follow the small change of length. Therefore, a natural frequency for the pendulum will change

slowly. In addition to the classical example of a pendulum, we can also find similar phenomena in reversible and irreversible processes in thermodynamics. In the reversible process, since the change is slow, the system makes new equilibrium at every moment and its variables (volume, pressure, and temperature) change slowly. However, in the irreversible process which means sudden change, the system does not have enough time to make equilibrium for every moment and its variables do not change for a while.

This also can be happened in the microscopic world. The only difference is that we use Hamiltonian and wavefunction to describe the system. Assume that we make a sudden change in Hamiltonian. Then the system doesn't have enough time to follow the change and stays at the same wavefunction for a while. (Figure 1b) However, if we make a slow change in Hamiltonian, the system has enough time to follow the change and gradually change its wavefunction. (Figure 1c) This is what we called the adiabatic process in quantum mechanics, but there is not a full story for adiabatic process in quantum mechanics. The essential point of the quantum adiabatic process is the relationship between final wavefunction and initial wavefunction. 'Adiabatic approximation' states that the quantum number of wavefunction does not change during the adiabatic process. For example, let's assume that our wavefunction at the initial time is the ground state of particle-in-a-box. If the length of the box increases slowly, the wavefunction will also start to change slowly. The new wavefunction, however, still satisfies the boundary condition for every moment, so we can imagine the wavefunction will stretch during the process and still remain at the ground state. This is how we can understand adiabatic approximation qualitatively. In the next section, we will explain adiabatic approximation with a mathematical approach and show how it works.<sup>1</sup>

**Figure 1.** Graphical explanation of adiabatic process (particle-in-a-box)



(a) Initial wavefunction of particle-in-a-box. (b) The wavefunction right after we suddenly change the width of box. (c) The wavefunction when we slowly change the width of box.

## b. Mathematical approach of Adiabatic Approximation

Now, we will think about the mathematical approach to the adiabatic approximation.<sup>1</sup> If the Hamiltonian is a function of time, eigenket and its energy is also a function of time.

$$H(t) |n(t)\rangle = E_n(t) |n(t)\rangle$$

The notation for this equation can be confused since we used  $|n(t)\rangle$  for time-evolution with constant Hamiltonian. However, in this equation,  $|n(t)\rangle$  is the eigenket of a system at time  $t$  with  $H(t)$  and we can understand this equation as a snapshot of the system during the adiabatic process. Therefore,  $|n(t)\rangle$  is still an orthonormal basis set for the system at time  $t$  and we can write arbitrary wavefunction by the linear combination of  $|n(t)\rangle$ .

$$\Psi(t) = \sum_n c_n(t) \exp(i\theta_n(t)) \left( \left| n(t) \right\rangle \right)$$

$$\theta_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt'$$

In this equation, you can notice that there is a phase factor related to the energy which is similar to the time-evolution factor. However, similar to  $|n(t)\rangle$ ,  $|\Psi(t)\rangle$  is the wavefunction at time  $t$  with  $H(t)$  start from the  $|\Psi(t=0)\rangle$  which is different from time-evolution. Actually, this phase factor is just a general phase factor derived from the time-dependent Schrodinger equation with non-constant energy  $E(t)$ .

Now, by plugging  $\Psi(t)$  into the time-dependent Schrodinger equation  $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle$  and doing the inner product with  $|m(t)\rangle$ , we can get the differential equation for coefficient  $c_m(t)$ ;

$$i\hbar \sum_n \left[ \left( \frac{\partial}{\partial t} c_n(t) \right) |n(t)\rangle + c_n(t) \frac{\partial}{\partial t} |n(t)\rangle + ic_n(t) \left( \frac{\partial}{\partial t} \theta_n(t) \right) |n(t)\rangle \right] \exp(i\theta_n(t))$$

$$= \sum_n c_n(t) \exp(i\theta_n(t)) H(t) |n(t)\rangle$$

However, since  $H(t) |n(t)\rangle = E_n(t) |n(t)\rangle$  and  $\left(\frac{\partial}{\partial t} \theta_n(t)\right) |n(t)\rangle = -\frac{1}{\hbar} E_n(t)$ , last two term will disappear and we can get

$$\sum_n \left(\frac{\partial}{\partial t} c_n(t)\right) \exp(i\theta_n(t)) |n(t)\rangle = -\sum_n c_n(t) \exp(i\theta_n(t)) \frac{\partial}{\partial t} |n(t)\rangle$$

Finally, doing the inner product with  $\langle m |$  ( $m \neq n$ ), we can get differential equation for  $c_m(t)$

$$\begin{aligned} \left(\frac{\partial}{\partial t} c_m(t)\right) \exp(i\theta_m(t)) &= -\sum_n c_n(t) \exp(i\theta_n(t)) \langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle \\ \frac{\partial}{\partial t} c_m(t) &= -\sum_n c_n(t) \exp(i(\theta_n(t) - \theta_m(t))) \langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle \end{aligned}$$

On the other hand, by differentiating  $H(t) |n(t)\rangle = E_n(t) |n(t)\rangle$  and inner product with  $\langle m(t) |$ , we can write  $\langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle$  term with energy and Hamiltonian.

$$\begin{aligned} \left(\frac{\partial}{\partial t} H(t)\right) |n(t)\rangle + H(t) \left(\frac{\partial}{\partial t} |n(t)\rangle\right) &= \left(\frac{\partial}{\partial t} E_n(t)\right) |n(t)\rangle + E_n(t) \left(\frac{\partial}{\partial t} |n(t)\rangle\right) \\ \langle m(t) | \frac{\partial}{\partial t} H(t) |n(t)\rangle + \langle m(t) | H(t) \left(\frac{\partial}{\partial t} |n(t)\rangle\right) &= \left(\frac{\partial}{\partial t} E_n(t)\right) \langle m(t) | n(t)\rangle \\ + E_n(t) \langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle & \end{aligned}$$

$$\begin{aligned} \langle m(t) | \frac{\partial}{\partial t} H(t) |n(t)\rangle + E_m(t) \langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle &= E_n(t) \langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle \\ \langle m(t) | \frac{\partial}{\partial t} |n(t)\rangle &= \frac{1}{E_n(t) - E_m(t)} \langle m(t) | \frac{\partial}{\partial t} H(t) |n(t)\rangle \end{aligned}$$

Now, combining two equations, we can get the exact differentiate equation for  $c_m(t)$ .

$$\frac{\partial}{\partial t} c_m(t) = -c_m(t) \langle m(t) | \frac{\partial}{\partial t} |m(t)\rangle + \sum_{n \neq m} c_n(t) \frac{1}{E_n(t) - E_m(t)} \exp(i(\theta_n(t) - \theta_m(t))) \langle m(t) | \frac{\partial}{\partial t} H(t) |n(t)\rangle$$

$$- \theta_m(t) \rangle \langle m(t) \left| \frac{\partial}{\partial t} H(t) \right| n(t) \rangle$$

However, since this is a very slow process (adiabatic process),  $\frac{\partial}{\partial t} H(t)$  is very small so we can neglect the second term. Then, we can write the  $c_m(t)$  with  $c_m(0)$  and phase factor gamma.

$$\frac{\partial}{\partial t} c_m(t) \approx -c_m(t) \langle m(t) \left| \frac{\partial}{\partial t} \right| m(t) \rangle$$

$$c_m(t) = c_m(0) \exp(i\gamma_m(t))$$

$$\gamma_m(t) = i \int_0^t \langle m(t') \left| \frac{\partial}{\partial t'} \right| m(t') \rangle dt'$$

Using the relationship  $\frac{\partial}{\partial t} = \left( \frac{\partial}{\partial t} R \right) \cdot \nabla_R$ , we can also write

$$\gamma_n(t) = i \int_0^t \langle n(t') \left| \frac{\partial}{\partial t'} \right| n(t') \rangle dt' = i \int_0^t \langle n(t') \left| \nabla_R \right| n(t') \rangle \cdot \left( \frac{\partial}{\partial t} R \right) dt' = i \int_{R_i}^{R_f} \langle n(t') \left| \nabla_R \right| n(t') \rangle \cdot dR$$

Therefore, the total wavefunction will be

$$\Psi(t) = \sum_n c_n(0) \exp(i\theta_n(t)) \exp(i\gamma_n(t)) \left| n(t) \right\rangle$$

$$\theta_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt', \gamma_n(t) = i \int_{R_i}^{R_f} \langle n(t') \left| \nabla_R \right| n(t') \rangle \cdot dR$$

From this expression of the wavefunction, we can notice that there are two types of phase factors.  $\theta_n(t)$  is called the dynamic phase factor because it is related to how fast Hamiltonian changes. On the other hand,  $\gamma_n(t)$  is called the geometric phase factor because it only depends on the path and independent from the dynamics of Hamiltonian.

For proving the adiabatic approximation, let's assume that wavefunction was at  $|n(0)\rangle$  at the  $t = 0$  which means

$c_m(0) = \delta_{nm}$ . From this, we can notice  $\Psi(t)$

$= \exp(i\theta_n(t)) \exp(i\gamma_n(t)) |n(t)\rangle$  at time  $t$ , which means the wavefunction does not change its quantum number during the adiabatic process.

### 3. Application

#### a. 1-dimension Particle-in-a-box

Now, let's do the quick demonstration by comparing the result of adiabatic approximation and exact solution for 1-dimensional particle-in-a-box system. By solving the Schrodinger equation  $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = E\Psi$ , we already know that eigenfunction

$\varphi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$  and its energy  $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$  when  $L$  is the length of the box. Now

assume that the length of the box slowly increases with constant speed  $v$ . Then the length at time  $t$  is  $L(t) = L_0 + vt$ . Using this and the equations in the previous section, we can calculate the dynamic phase and geometric phase of this system and write the arbitrary wavefunction at time  $t$ .

$$\theta_n = -\frac{1}{\hbar} \int_0^t \frac{n^2 \pi^2 \hbar^2}{2mL^2} dt = -\frac{1}{\hbar} \int_{L_0}^L \frac{n^2 \pi^2 \hbar^2}{2mvL^2} dL = -\frac{n^2 \pi^2 \hbar}{2mv} \left[ -\frac{1}{L} \right]_{L_0}^L = \frac{n^2 \pi^2 \hbar}{2mv} \left( \frac{1}{L} - \frac{1}{L_0} \right)$$

$$\gamma_n(t) = i \int_{L_i}^{L_f} \left( \int_0^L \left( \varphi_n \frac{d}{dL} \varphi_n \right) dx \right) dL = i \int_{L_i}^{L_f} \left( \int_0^L \left( \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \frac{d}{dL} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \right) dx \right) dL$$

$$\begin{aligned}
&= i \int_{L_i}^{L_f} \left( \int_0^L \left( \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \left(-\frac{1}{L^2}\right) \left( \sqrt{\frac{L}{2}} \sin\left(\frac{n\pi}{L}x\right) \right. \right. \right. \\
&+ n\pi x \left. \left. \left. \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi}{L}x\right) \right) dx \right) dL = i \int_{L_i}^{L_f} (0) dL = 0
\end{aligned}$$

$$\varphi_n(x, L) = \exp(i\theta_n) \varphi_n(L_0) = \exp\left(i \frac{n^2 \pi^2 \hbar (L_0 - L)}{2 m v L L_0}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

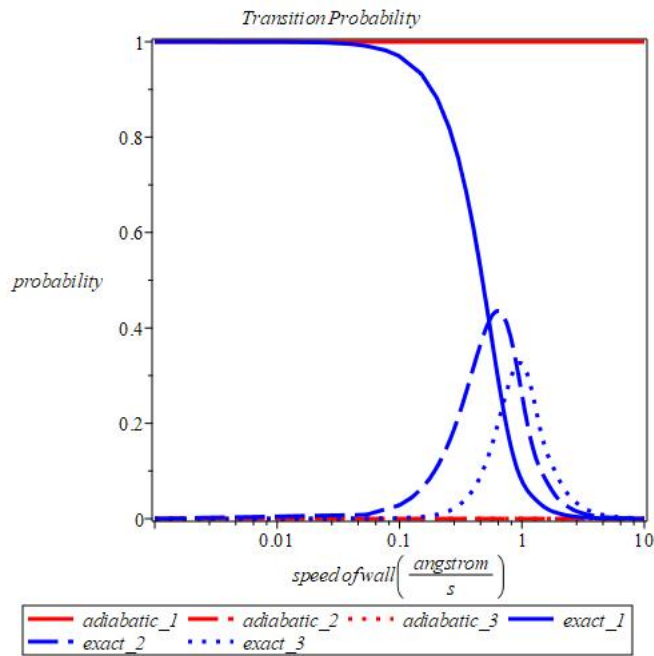
$$\Psi(x, L) = \sum_n c_n(0) \exp\left(i \frac{n^2 \pi^2 \hbar (L_0 - L)}{2 m v L L_0}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

However, particle-in-a-box with constantly increasing length, we already know the exact answer<sup>2</sup> is

$$\begin{aligned}
\varphi_n(x, L) &= \exp\left(i \left( \frac{m v x^2}{2 \hbar L} - \frac{n^2 \pi^2 \hbar (L - L_0)}{2 m v L L_0} \right)\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \\
\Psi(x, L) &= \sum_n c_n \exp\left(i \left( \frac{m v x^2}{2 \hbar L} - \frac{n^2 \pi^2 \hbar (L - L_0)}{2 m v L L_0} \right)\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)
\end{aligned}$$

Now, we will compare the transition probability to several states in adiabatic approximation and exact solutions with different speeds. (Figure 2) When we assume that the initial system is at the ground state, it will remain at the ground state even if the Hamiltonian is changed. (red lines) When we solve the problem exactly, however, system will react differently depends on speed (blue lines). With slow speed, it is almost at the ground state as we predict with adiabatic approximation. (blue solid line) With high speed, however, it starts to transition to other states (blue dashed, dotted lines). This shows that adiabatic approximation can describe the system very well when Hamiltonian changes slowly but cannot be used with fast change of Hamiltonian as we proved in the previous section.

**Figure 2.** Transition probability from ground state



Transition probability from ground state to  $n = 1$  (solid),  $n = 2$  (dashed),  $n = 3$  (dotted) for adiabatic approximation (red) and exact solution (blue) with different speed.

code

```

> restart;
digits := 15;
h := 6.626 · 10-34 · 1020;
m := 10-13;
l := 1;
L := 2;

basis(n) := √(2/L) · sin(n · π / L · x);
app_phase(n) := (n2 · h · (l - L) / (4 · m · v · l · L)) · π;
exac_phase(n) := (m · v · x2 / (h · L) - n2 · h · (L - l) / (4 · m · v · L · l)) · π;
app_pro(n, k) := (abs(∫0L exp(I · app_phase(n)) · basis(n) · basis(k) dx))2;
exac_pro(n, k) := (abs(∫0L exp(I · exac_phase(n)) · basis(n) · basis(k) dx))2;
plots:-display([plot(app_pro(1, 1), v = 0.001 .. 10, axis[1] = [mode = log], color = red,
thickness = 3, linestyle = solid),
plot(app_pro(1, 2), v = 0.001 .. 10, axis[1] = [mode = log], color = red, thickness = 3, linestyle

```



```

    = dash),
    plot(app_pro(1, 3), v = 0.001 .. 10, axis[1] = [mode = log], color = red, thickness = 3, linestyle
    = dot),
    plot(exac_pro(1, 1), v = 0.001 .. 10, axis[1] = [mode = log], color = blue, thickness = 3, linestyle
    = solid),
    plot(exac_pro(1, 2), v = 0.001 .. 10, axis[1] = [mode = log], color = blue, thickness = 3, linestyle
    = dash),
    plot(exac_pro(1, 3), v = 0.001 .. 10, axis[1] = [mode = log], color = blue, thickness = 3, linestyle
    = dot) ],
    axes = boxed, labels = [ speed of wall (  $\frac{\text{angstrom}}{s}$  ), probability ], title = 'Transition Probability',
    legend = [ adiabatic_1, adiabatic_2, adiabatic_3, exact_1, exact_2, exact_3 ] );

```

## b. Born-Oppenheimer Approximation

Now, let's move on to the adiabatic approximation example in Chemistry. When we talk about the molecule, the full Schrodinger equation contains electronic motion and nucleus motion. However, we all know that by the famous Born-Oppenheimer approximation, we can separate the electronic part and the nucleus part and get wavefunction for each motion. This is possible because nucleus motion (vibrational and rotational motion) is much slower than the electronic motion which we can apply adiabatic approximation.

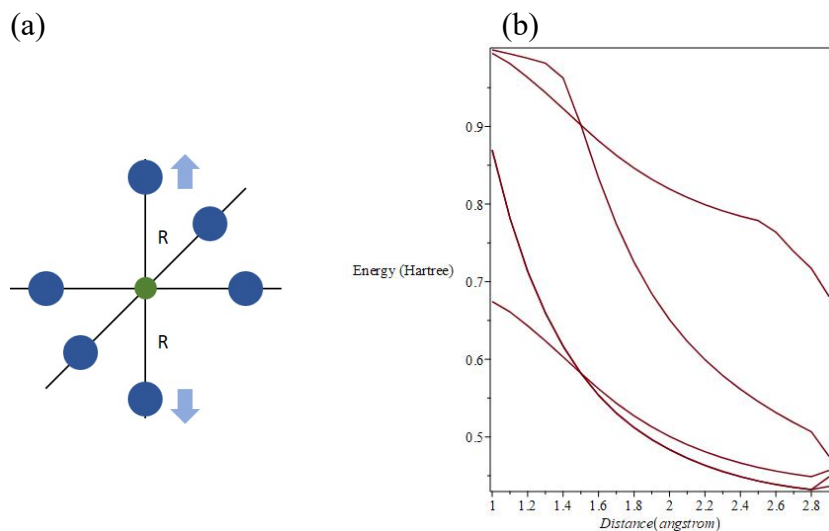
To explain Born-Oppenheimer approximation, we can rewrite the electronic Hamiltonian with nucleus distance  $R(t)$  which is a function of time. Then, the electronic Hamiltonian is also a function of time. However, since the motion of nucleus is very slow, we can also think that Hamiltonian changes very slowly which is the condition for adiabatic approximation. This means that electronic configuration or orbital occupation does not change regardless of nucleus motion since quantum number does not change during the adiabatic process. Therefore we can focus on electronic Hamiltonian with equilibrium nucleus distance  $R_{eq}$  to know electronic configuration for an actual molecule as stated in Born-Oppenheimer approximation.<sup>3</sup>

## 4. Discussion

Through this worksheet, we explore the adiabatic process and approximation in quantum mechanics. With the very slow change of Hamiltonian, the wavefunction will also slowly change and especially, the quantum number of the system does not change during this process. Also, by comparing the result of adiabatic approximation and the exact solution of particle-in-a-box, we demonstrate our physical intuition for the adiabatic process and sudden change. Finally, we discussed Born-Oppenheimer approximation, the well-known application of adiabatic approximation in the molecular system.

Even if the adiabatic approximation is useful in the molecular system, it also has a limitation: the energy for each eigenstate should not be crossed. When the energy order changes by slowly changed Hamiltonian, the system will be moved to lowest energy eigenket to minimize its energy and adiabatic approximation – the system will remain in the same eigenket – will be destroyed. (Landau-Zener transition<sup>4</sup>) For example, in gas ion molecule dissociation, we can find that energy for two neutral atoms case and two ions case change its order depend on nucleus distance  $R$ . From this energy diagram, we can say that there is a movement of electron (transition) during the dissociation to reach the minimum energy. Also, other examples of crossing energy state can be found in metal-ligand coordinate system which is called Jahn-Teller effect<sup>5</sup>. Here,  $t_{2g}$  and  $e_g$  molecular orbital energy will be crossed when we slowly remove 2 ligands from octahedral complex to make a planar square complex (Figure 4) and the occupation of each molecular orbital will be changed. In these cases, we need further consideration for the transition to explain the system. Also, obviously, we cannot use the adiabatic approximation if the Hamiltonian change is too fast which is not a condition for adiabatic process.

**Figure 3.** Molecular orbital energy for metal-ligand complex



(a) Graphical description of system used in DFT calculation.  $Ni^{2+}$  is at the center (green) and six  $F^-$  is on each axis (blue).  $F^-$  at x-axis and y-axis has fixed distance (1.5 angstrom) and  $F^-$  at z-axis has varying distance R. (b) Energy of molecular orbital  $t_{2g}$  and  $e_g$ .

codes

```

> restart :
  Digits := 15 :
  with(QuantumChemistry) :

  Rmin := 1 :
  v := 0.1 :
  imax := 20 :
  energy := Matrix(imax, 6) :

  for i from 1 by 1 to imax do
    R := Rmin + v · (i - 1) :
    mol := [ ["Ni", 0, 0, 0], ["F", 1.5, 0, 0], ["F", -1.5, 0, 0], ["F", 0, 1.5, 0], ["F", 0, -1.5, 0],
      ["F", 0, 0, R], ["F", 0, 0, -R] ] :
    data := DensityFunctional(mol, basis = "sto-6g", charge = -2) :
    energy[i, 1] := R :
    energy[i, 2] := data[mo_energy][40] :
    energy[i, 3] := data[mo_energy][41] :
    energy[i, 4] := data[mo_energy][42] :
    energy[i, 5] := data[mo_energy][43] :
    energy[i, 6] := data[mo_energy][44] :
  end do;

  p1 := plot(energy[ ..., 1 ], energy[ ..., 2 ]) :
  p2 := plot(energy[ ..., 1 ], energy[ ..., 3 ]) :
  p3 := plot(energy[ ..., 1 ], energy[ ..., 4 ]) :
  p4 := plot(energy[ ..., 1 ], energy[ ..., 5 ]) :
  p5 := plot(energy[ ..., 1 ], energy[ ..., 6 ]) :

  plots:-display([ p1, p2, p3, p4, p5 ], axes = boxed, labels = [ Distance(angstrom),
    "Energy (Hartree)"]);

```

## 5. Reference

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