

Introduction to Model hamiltonians

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ABSTRACT

A simple introduction to model hamiltonians for quantum chemists.

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1 Introduction

Model hamiltonians are of primordial importance for understanding chemical and physical behavior of molecules and materials. Here, we shall briefly describe the various models and their formulation in as simple terms as possible.

2 Derivation of the Schrodinger equation

The schrodinger equation can be derived using the path integral formulation as shown by Feynman.[1]

2.1 Lagrangian

In order to demonstrate the derivation by Feynman, one needs to first define the notion of the lagrangian Equation 1.

$$L = T - V \quad 1.$$

Where, T is the kinetic energy and V is the potential energy. In order to better understand the lagrangian and its relation to Newton's equations of motion, in Equation 2, Equation 3 we derive the equations of motion in lagrange formulation and its connection to the usual newtons equations of motion.

$$L(r, \dot{r}) = T - V$$

$$L(r, \dot{r}) = \sum_i \frac{1}{2} m \dot{r}_i^2 - V(r_1, \dots, r_n) \quad 2.$$

where, r is the position and $\dot{r} = \frac{dr}{dt}$ is the velocity. Using this definition of the lagrangian, we can derive the so called Euler-Lagrange equation which is equivalent to Newton's equation Equation 3.

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_i} \right) - \frac{\partial L}{\partial r_i} = 0 \quad 3.$$

Where, the second term on the left of Equation 3 is the derivative of the potential i.e. the force (Equation 4).

$$\frac{\partial L}{\partial r_i} = \frac{\partial V(r_1, \dots, r_n)}{\partial r_i} = F_i \quad 4.$$

and the first term of Equation 3 is the acceleration (Equation 5).

$$\frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{r}_i} = m \frac{\partial \dot{r}_i}{\partial t} = m a_i \quad 5.$$

where, $a_i = \ddot{r}_i$. Therefore Equation 3 is equivalent to Newton's equation (Equation 6).

$$F_i = m a_i \quad 6.$$

2.2 Action

The action is defined as the integral of the Lagrangian along a specific path between two points, A at time t_a to point B in time t_b Equation 7.

$$S[r(t)] = \int_{t_a}^{t_b} L(r(t), \dot{r}(t)) dt \quad 7.$$

The action is an important quantity and describes the weight and phase of each path. Using the action, we can derive the Equation 3. This can be done using the principle of least action which says that the path that survives is the one that minimises the action Equation 8.

$$\int_{t_a}^{t_b} \delta L dt = 0$$

$$\delta S = 0$$
8.

The derivation of Equation 3 follows from the above Equation 8 once it is simplified using integration by parts (Equation 9).

$$\begin{aligned} \int_{t_a}^{t_b} \delta L dt &= \int_{t_a}^{t_b} \sum_i^n \left(\frac{\partial L}{\partial r_i} + \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_i} \right) - \frac{d}{dt} \frac{\partial L}{\partial \dot{r}_i} \right) dt \\ &= \sum_i^n \left[\frac{\partial L}{\partial \dot{q}} \delta q_j \right]_{t_a}^{t_b} + \int_{t_a}^{t_b} \sum_i^n \left(\frac{\partial L}{\partial r_i} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_i} \right) \right) dt \end{aligned}$$
9.

Therefore, if $\int_{t_a}^{t_b} \delta L dt = 0$, the left hand side of Equation 9 is 0. All terms of Equation 9 including the value of the integral. This implies Equation 3.

2.3 Postulates of Feynman

Feynman put forth two postulates to derive the schrodinger equation. The first postulate says that the total action is the sum of the actions of individual paths, i.e. Equation 10.

$$S = \sum_i S[r(t)_i]$$
10.

The second postulate says that the wavefunction φ can be expressed as an exponential function of the position $r(t)$ and its first derivative $\dot{r}(t)$, i.e. Equation 11.

$$\varphi(x_k, t) = \lim_{\varepsilon \rightarrow 0} \int_R \exp \left(\frac{i}{\hbar} \sum_i S[r(t)_i] \right) \dots \frac{dx_{i-1}}{A} \frac{dx_{i-2}}{A} \dots$$
11.

where the integral is over the region R which contains all the paths.

2.4 Derivation

The equation of motion describes the evolution of the wavefunction $\varphi(x_{k+1}, t)$ from time t to time $t + \varepsilon$ (Equation 12).

$$\varphi(x_{k+1}, t + \varepsilon) = \lim_{\varepsilon \rightarrow 0} \int_R \exp \left(\frac{i}{\hbar} \sum_i S[r(t)_i] \right) \dots \frac{dx_i}{A} \frac{dx_{i-1}}{A} \dots$$
12.

Using the definition of $\varphi(x_k, t)$ given in Equation 11, we can use it to obtain the wavefunction at time $t + \varepsilon$ (Equation 13).

$$\varphi(x_{k+1}, t + \varepsilon) = \left[\int_R S[x_{k+1}, x_k] \right] \varphi(x_k, t) \frac{dx_k}{A}$$
13.

The integral in Equation 13 can be interpreted as the hamiltonian once we substitute the action (Equation 14).

$$S(x_{k+1}, x_k) = \frac{m\varepsilon}{2} \left(\frac{x_{k+1} - x_k}{\varepsilon} \right)^2 - \varepsilon V(x_{k+1}) \quad 14.$$

now the Equation 13 becomes,

$$\varphi(x_{k+1}, t + \varepsilon) = \left[\int \frac{m\varepsilon}{2} \left(\frac{x_{k+1} - x_k}{\varepsilon} \right)^2 - \varepsilon V(x_{k+1}) \right] \varphi(x_k, t) \frac{dx_k}{A} \quad 15.$$

Expanding the wavefunction $\varphi(x_{k+1}, t)$ around x_k using the taylor series gives,

$$\begin{aligned} \varphi(x_{k+1}, t + \varepsilon) = \\ \exp\left(\frac{-i\varepsilon V}{\hbar}\right) \times \int \exp\left(\frac{i\varepsilon\xi^2}{2\hbar\varepsilon}\right) \left[\psi(x, t) - \xi \frac{\partial\psi(x, t)}{\partial x} + \frac{\xi^2}{2} \frac{\partial^2\psi(x, t)}{\partial x^2} - \dots \right] \frac{d\xi}{A} \end{aligned} \quad 16.$$

where, $x_{k+1} - x_k = \xi$. Expanding the left hand also around ξ gives.

$$\begin{aligned} \varphi(x_{k+1}, t) + \varepsilon \frac{\partial\varphi(x, t)}{\partial t} = \\ \exp\left(\frac{-i\varepsilon V}{\hbar}\right) \times \int \exp\left(\frac{i\varepsilon\xi^2}{2\hbar\varepsilon}\right) \left[\psi(x, t) - \xi \frac{\partial\psi(x, t)}{\partial x} + \frac{\xi^2}{2} \frac{\partial^2\psi(x, t)}{\partial x^2} - \dots \right] \frac{d\xi}{A} \end{aligned} \quad 17.$$

The factors in the integrand on the right of Equation 17 which contain ξ, ξ^3 etc are zero because they are odd integrals (Equation 18).

$$\begin{aligned} \varphi(x_{k+1}, t) + \varepsilon \frac{\partial\varphi(x, t)}{\partial t} = \\ \exp\left(\frac{-i\varepsilon V}{\hbar}\right) \times \frac{\sqrt{2\pi\hbar\frac{i}{m}}}{A} \left[\psi(x, t) + \frac{\hbar\varepsilon i}{2m} \frac{\partial^2\psi(x, t)}{\partial x^2} + \dots \right] \end{aligned} \quad 18.$$

Finally, equating the terms of same order in ε , we get Equation 19

$$\begin{aligned} -\frac{\hbar}{i} \frac{\partial\psi}{\partial t} &= \frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \psi + V(x)\psi \\ -\frac{\hbar}{i} \frac{\partial\psi}{\partial t} &= H\psi \end{aligned} \quad 19.$$

The above equation can be compared to the time dependent schrodinger equation. The time independent form describes stationary wavefunctions which is given as Equation 20.

$$H\psi = \lambda\psi \quad 20.$$

3 1D particle in a box

The problem of a particle in a box can be defined as shown in Figure 1. The position of the particle inside the box can be defined via the wavefunction $\psi(x)$. The particle is inside a box with infinitely large walls. Therefore, the probability of finding the particle on the wall is zero. These constitute the boundary conditions for the wavefunction of the particle $\psi(x)$, i.e. Equation 21.

$$\begin{aligned} \psi(0) &= 0 \\ \psi(L) &= 0 \end{aligned} \quad 21.$$

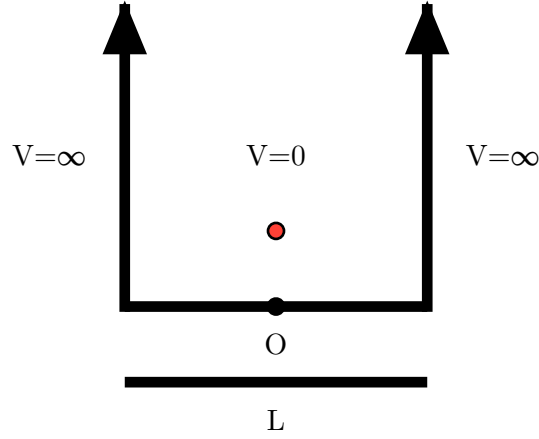


Figure 1: Particle in an infinite potential well.

3.1 Finite difference equations

The schrodinger equation is given as shown in Equation 22.

$$\nabla^2 \psi(x) = \frac{d^2 \psi}{dx^2} = \lambda \psi(x) \quad 22.$$

Here, λ represents the eigenvalues and ψ the eigenvectors of the hamiltonian. The Equation 22 is a second order differential equation also known as the one dimensional Laplace equation or the Poisson equation. This equation can be solved using numerical integration techniques. Using Taylor series expansion of Equation 22, one can obtain the finite difference formulae to evaluate the derivative at point x_i .

$$\begin{aligned} \left. \frac{d\psi}{dx} \right|_{x_i} &= \lim_{\varepsilon \rightarrow 0} \frac{\psi(x_i + \frac{\varepsilon}{2}) - \psi(x_i - \frac{\varepsilon}{2})}{\varepsilon} \\ \left. \frac{d\psi}{dx} \right|_{x_i + \frac{\varepsilon}{2}} &= \lim_{\varepsilon \rightarrow 0} \frac{\psi(x_i + \varepsilon) - \psi(x_i)}{\varepsilon} \\ \left. \frac{d\psi}{dx} \right|_{x_i - \frac{\varepsilon}{2}} &= \lim_{\varepsilon \rightarrow 0} \frac{\psi(x_i) - \psi(x_i - \varepsilon)}{\varepsilon} \\ \left. \frac{d^2 \psi}{dx^2} \right|_{x_i} &= \lim_{\varepsilon \rightarrow 0} \frac{\psi'(x_i + \frac{\varepsilon}{2}) - \psi'(x_i - \frac{\varepsilon}{2})}{\varepsilon} \\ \left. \frac{d^2 \psi}{dx^2} \right|_{x_i} &= \lim_{\varepsilon \rightarrow 0} \frac{\psi(x_i + \varepsilon) - 2\psi(x_i) + \psi(x_i - \varepsilon))}{\varepsilon^2} \end{aligned} \quad 23.$$

The above operator on the right hand side of Equation 23 (called T) can be used to write the finite difference form of the schrodinger equation Equation 22. This finite difference form shown in Equation 24 can be used to find the eigenvalues and eigenvectors of the schrodinger equation by dividing the segment into a finite numebr of uniformly distributed points.

$$T\psi(x) = \varepsilon^2 \lambda \psi(x) \quad 24.$$

The matrix form of T is shown in Equation 25 below where one can clearly see the tridiagonal form of the Laplace operator.

$$T = \begin{bmatrix} 1 & -2 & 1 & . & . & . & . \\ . & 1 & -2 & 1 & . & . & . \\ . & . & 1 & -2 & 1 & . & . \\ . & . & . & 1 & -2 & 1 & . \\ . & . & . & . & 1 & -2 & 1 \end{bmatrix} \quad 25.$$

The parts not shown in the matrix above are all zeros. The finite difference form of the schrodinger equation can then be written as Equation 26.

$$\begin{aligned} T\psi(x) &= \lambda\psi(x) \\ (T - \lambda)\psi(x) &= 0 \end{aligned} \quad 26.$$

The matrix above can be diagonalized using the Lanczos or other algorithms to obtain the eigenvalues and eigenvectors for the problem of particle in a box.

3.2 Eigenvalues and eigenvectors

The eigenvectors with $n = 16$ is shown in Figure 2.

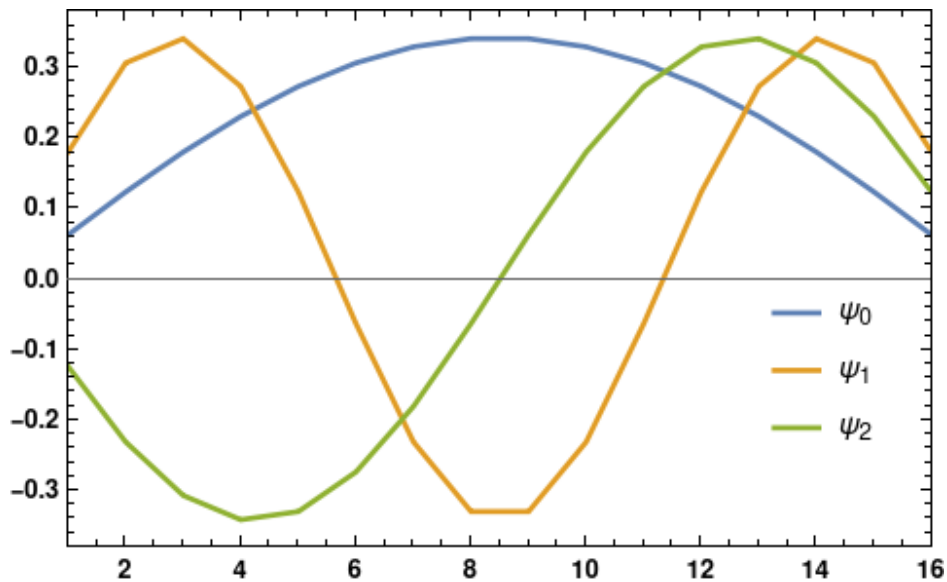


Figure 2: The solution of the Laplace equation with $n = 16$ points.

As one can see, the boundary values are not consistent with the boundary conditions defined for the problem in Equation 21. This is due to the finite step size (i.e. ε) and depends on the number of points chosen for the discretization. Increasing the number of points from $n = 16$ to $n = 1024$ gives a much better agreement to the boundary values defined above.

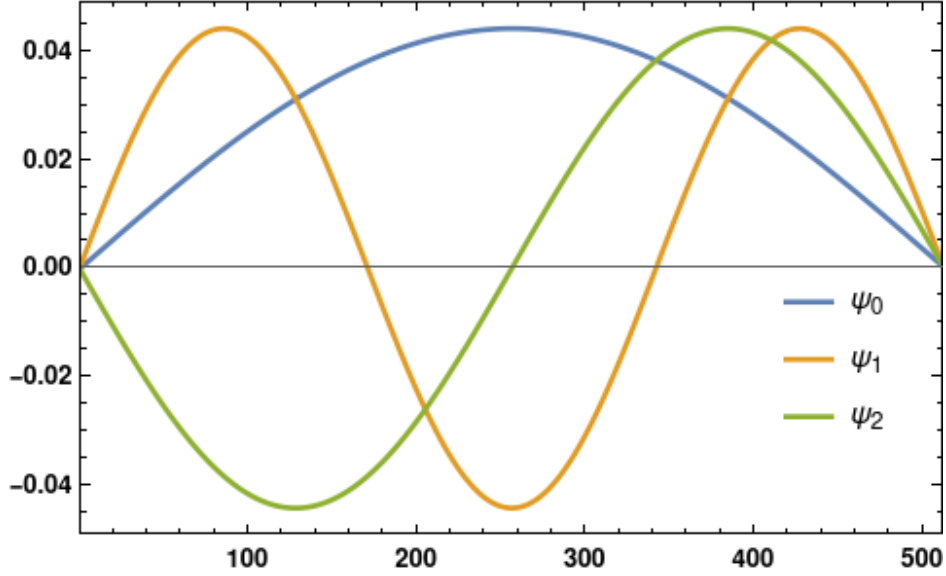


Figure 3: The solution of the Laplace equation with $n = 1024$ points.

Since the solutions ψ_i are eigenfunction of the laplacian operator, they are by definition orthonormalized.

$$\begin{aligned}\langle \psi_i | \psi_i \rangle &= 1, \forall i \\ \langle \psi_i | \psi_j \rangle &= 0, \forall i, j\end{aligned}\tag{27}$$

Since we are here in real space, i.e. real coordinates x , the overlap (also known as the measure) is defined as simply the integral Equation 28.

$$\langle \psi(x) | \psi(x) \rangle = \int_0^1 \psi(x)^\dagger \psi(x) dx \tag{28}$$

where $\psi(x)^\dagger$ is the complex conjugate of $\psi(x)$. Here, since the laplacian T is hermitian (i.e. $T^\dagger = T$), the eigenvalues are real.

In the present case, where we have used a numerical method to perform the integration, we can also perform the integral numerically as shown in Equation 29.

$$\int_0^1 \psi(x)^\dagger \psi(x) dx = \sum_k^N \psi_i^\dagger(k) \psi_i(k) = 1 \tag{29}$$

where N is the total number of points. Similarly, the orthogonality constraint says that Equation 30 holds.

$$\int_0^1 \psi(x)^\dagger \psi(x) dx = \sum_k^N \psi_i^\dagger(k) \psi_j(k) = 0 \tag{30}$$

As can be easily verified using basic linear algebra.

3.3 Probability density

The eigenvectors obtained in the previous section $\psi(x)$, can be used to plot the probability density for the various states as given by Equation 31.

$$\rho(x) = \psi(x)^\dagger \psi(x) \tag{31}$$

Numerically, this can be written as the dot product between the wavefunction as shown in Equation 32.

$$\rho_i = \sum_k \psi_i(k) \psi_i(k) \quad 32.$$

where we have assumed that the wavefunction $\psi(x)$ is real. The probability density can be shown to be positive everywhere and defines the nodes of the state, i.e. the regions where the probability of finding the particle is zero as shown in Figure 4.

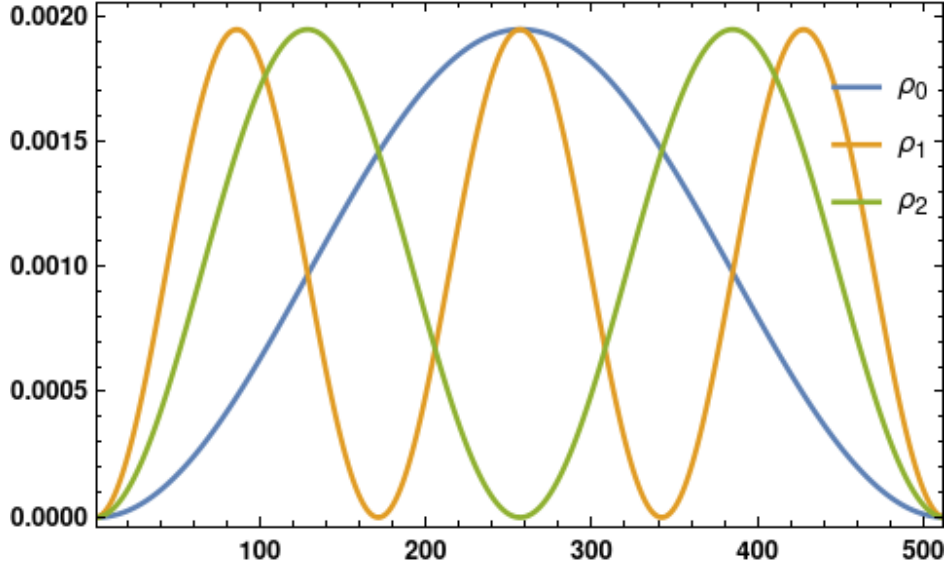


Figure 4: The solution of the Laplace equation with $n = 1024$ points.

The ground state has zero nodes, the first excited state has exactly one node, the second excited state has two nodes etc. In general, the nodes of the function increase with increasing energy compared to the ground state.

3.4 Dipole moment and transition dipole moment

The dipole moment operator for a given state is given as shown below Equation 33.

$$\langle x_i \rangle = \int_0^1 \rho(x) x dx \quad 33.$$

The transition dipole moment between two states i and j is defined as shown in Equation 34.

$$\langle x_{ij} \rangle = \int_0^1 \psi_{i(x)} x \psi_{j(x)} dx \quad 34.$$

The table Table 1 shows the dipole moment for the first state and the transition dipole between the ground and first excited state.

(i, j)	$\langle x \rangle_{\Psi^2}$
(1,1)	0.000489237
(1,2)	-0.180655
(1,3)	0.0
(2,2)	0.000489237
(2,3)	0.195108

Table 1: The dipole moment and transition dipole moment between the pairs of states shown in the first column.

4 Second quantization

5 Huckel hamiltonian

6 Hubbard hamiltonian

7 Double exchange hamiltonian

Bibliography

- [1] R. P. Feynman, “Space-Time Approach to Non-Relativistic Quantum Mechanics”, *Rev. Mod. Phys.*, no. 2, pp. 367–387, Apr. 1948, doi: 10.1103/RevModPhys.20.367.