Introduction to Model hamiltonians

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Abstract

A simple introduction to model hamiltonians for quantum chemists.

Contents

1 Introduction

Model hamiltonians are of premordial 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.

$$L = T - V \tag{1.}$$

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.

$$\begin{aligned} L(r, \dot{r}) &= T - V \\ L(r, \dot{r}) &= \sum_i \frac{1}{2} m \dot{r}_i^2 - V(r_1, ..., r_n) \end{aligned} \tag{2.}$$

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.

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

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

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

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

$$\frac{\partial}{\partial t}\frac{\partial L}{\partial \dot{r}_i} = m\frac{\partial \dot{r}_i}{\partial t} = ma_i \tag{5.}$$

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

$$F_i = ma_i \tag{6.}$$

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.

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

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.

$$\int_{t_a}^{t_b} \delta L dt = 0 \qquad \delta S = 0 \tag{8.}$$

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

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

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. [1]

Feynman's postulates of Quantum Mechanics: Postulate I

The first postulate says that the total action is the sum of the actions of individual paths, i.e. Equation 10.

$$S = \sum_i S[r_i(t)] \tag{10.}$$

Note that the sum is over all possible paths $r_i(t)$ which are possible to take from point r_0 to r_1 in time t_0 to t_1.

Feynman's postulates of Quantum Mechanics: Postulate II

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

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

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).

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

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).

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

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

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

now the Equation 13 becomes,

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

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

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

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

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

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).

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

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

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

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.

$$H\psi = \lambda\psi \tag{20.}$$

3 Discretization of the Hamiltonian

The position operator can be written as shown in Equation 21

$$\hat{q}\varphi(x) = x\varphi(x) \tag{21.}$$

Similarly, the momentum operator can be written as given in Equation 22.

$$\hat{p}\varphi(x) = -i\frac{\partial\varphi(x)}{\partial x} \quad (\hbar = 1 \text{ in a.u}) \tag{22.}$$

Both these operators can be discretized on a uniform grid of a fixed number of points separated by a distance d as shown in Equation 23.

$$\begin{aligned} \hat{q}\varphi(x_i) &= x_i\varphi(x) \\ \hat{p}\varphi(x_i) &= -i\frac{\varphi(x_{i+1}) - \varphi(x_{i-1})}{2d} \end{aligned} \tag{23.}$$

The hamiltonian is then given by the square of the momentum operator p Equation 24.

$$\widehat{H} = \frac{\hat{p}^2}{2m} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} \tag{24.}$$

Note that the hamiltonian is real and depends on the coordinate x in this one-dimensional example.

$$\widehat{H} = -\frac{\varphi(x_{i+1}) + \varphi(x_{i-1}) - 2\varphi(x_i)}{2d^2} \tag{25.}$$

This follows from the fact that the second derivative can be discretized using the approximation $\frac{f(x_{i+1})+f(x_{i-1})-2f(x_i)}{d^2}$.

4 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 for the wavefunction of the particle $\psi(x)$, i.e. Equation 26.

$$\begin{aligned} \psi(0) &= 0 \\ \psi(L) &= 0 \end{aligned} \tag{26.}$$

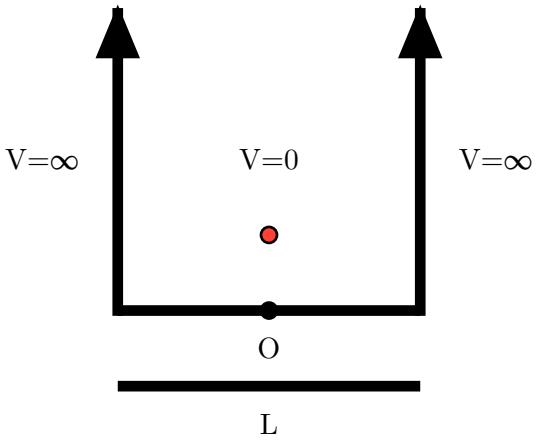

Figure 1: Particle in an infinite potential well.

4.1 Finite difference equations

The schrodinger equation is given as shown in Equation 27.

$$\widehat{H}\psi(x) = -\frac{1}{2}\boldsymbol{\nabla}^2\psi(x) = -\frac{1}{2}\frac{d^2\psi}{dx^2} = \lambda\psi(x) \tag{27.}$$

Here, λ represents the eigenvalues and ψ the eigenvectors of the hamiltonian. The Equation 27 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 27, one can obtain the finite difference formulae to evaluate the derivative at point x_i.

$$\begin{aligned}
\left.\frac{d\psi}{dx}\right|_{x_i} &= \lim_{\varepsilon\to 0}\frac{\psi\left(x_i+\frac{\varepsilon}{2}\right)-\psi\left(x_i-\frac{\varepsilon}{2}\right)}{\varepsilon} \\
\left.\frac{d\psi}{dx}\right|_{x_i+\frac{\varepsilon}{2}} &= \lim_{\varepsilon\to 0}\frac{\psi(x_i+\varepsilon)-\psi(x_i)}{\varepsilon} \\
\left.\frac{d\psi}{dx}\right|_{x_i-\frac{\varepsilon}{2}} &= \lim_{\varepsilon\to 0}\frac{\psi(x_i)-\psi(x_i-\varepsilon)}{\varepsilon} \\
\left.\frac{d^2\psi}{dx^2}\right|_{x_i} &= \lim_{\varepsilon\to 0}\frac{\psi'\left(x_i+\frac{\varepsilon}{2}\right)-\psi'\left(x_i-\frac{\varepsilon}{2}\right)}{\varepsilon} \\
\left.\frac{d^2\psi}{dx^2}\right|_{x_i} &= \lim_{\varepsilon\to 0}\frac{\psi(x_i+\varepsilon)-2\psi(x_i)+\psi(x_i-\varepsilon)}{\varepsilon^2}
\end{aligned} \tag{28.}$$

The above operator on the right hand side of Equation 28 (called T) can be used to write the finite difference form of the schrodinger equation Equation 27. This finite difference form shown in Equation 29 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.

$$T\psi(x) = \varepsilon^2\lambda\psi(x) \tag{29.}$$

The matrix form of T is shown in Equation 30 below where one can clearly see the tridiagonal form of the Laplace operator.

$$T = \frac{1}{2\varepsilon^2}\begin{bmatrix} -1 & 2 & -1 & . & ... & . & . & . \\ . & -1 & 2 & -1 & ... & . & . & . \\ ... & ... & ... & ... & ... & ... & ... & ... \\ . & . & . & . & ... & 2 & -1 & . \\ . & . & . & . & ... & -1 & 2 & -1 \end{bmatrix} \tag{30.}$$

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 31.

$$\begin{aligned} T\psi(x) &= \lambda\psi(x) \\ (T-\lambda)\psi(x) &= 0 \end{aligned} \tag{31.}$$

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.

4.2 Eigenvalues and eigenvectors

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

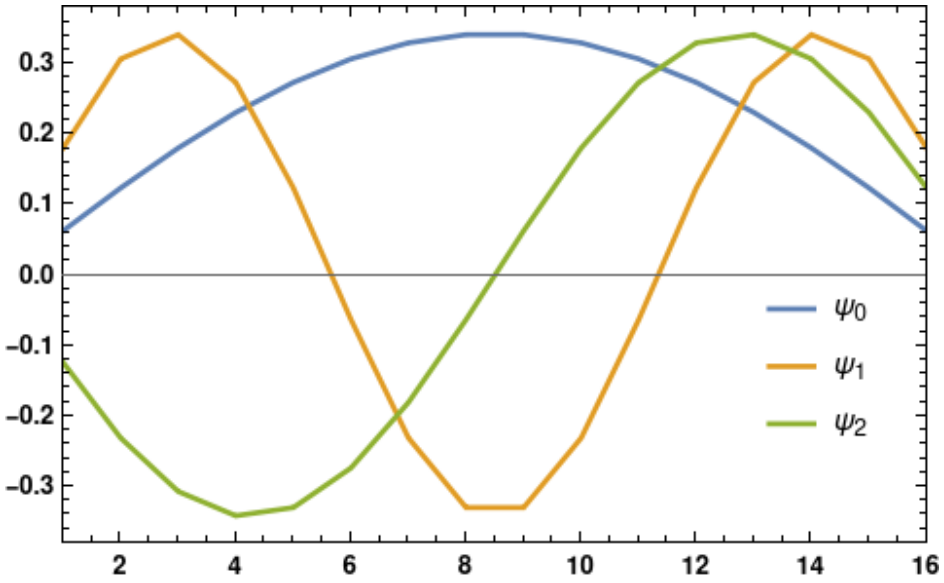

Figure 2: The solution of the Laplace equation with $n = 16$ points.

As one can see, the boundary values are not consistent with the boundary conditions defined for the problem in Equation 26. 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 bounday values defined above.

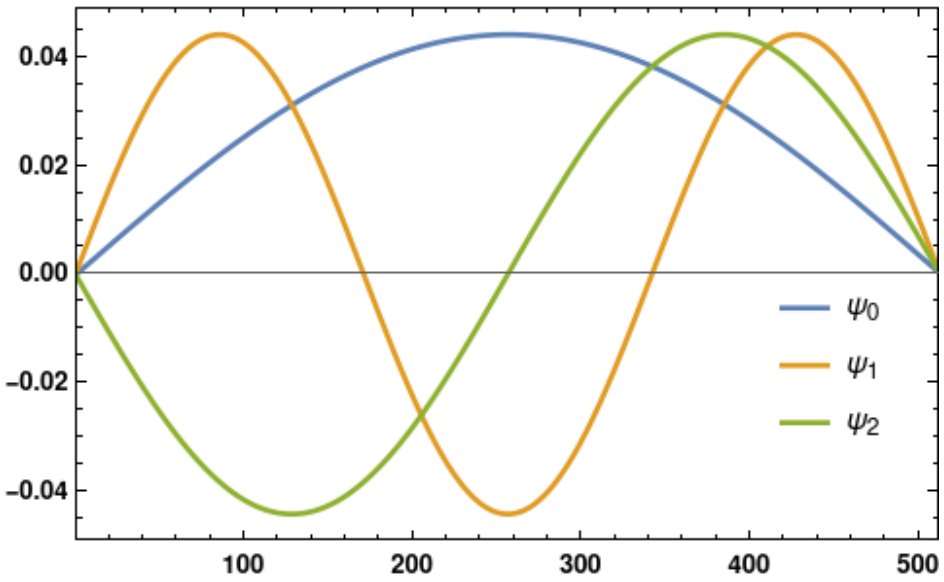

Figure 3: The solution of the Laplace equation with $n = 1024$ points.

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

$$\begin{aligned} \langle \psi_i | \psi_i \rangle &= 1, \forall i \\ \langle \psi_i | \psi_j \rangle &= 0, \forall i, j \end{aligned} \tag{32.}$$

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 33.

$$\langle \psi(x) | \psi(x) \rangle = \int_0^1 \psi(x)^\dagger \psi(x) dx \tag{33.}$$

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 34.

$$\int_0^1 \psi(x)^\dagger \psi(x) dx = \sum_k^N \psi_i^\dagger(k) \psi_i(k) = 1 \tag{34.}$$

where N is the total number of points. Similarly, the orthogonality constraint says that Equation 35 holds.

$$\int_0^1 \psi(x)^\dagger \psi(x) dx = \sum_k^N \psi_i^\dagger(k) \psi_j(k) = 0 \tag{35.}$$

As can be easily verified using basic linear algebra.

4.3 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 36.

$$\rho(x) = \psi(x)^\dagger \psi(x) \tag{36.}$$

Numerically, this can be written as the dot product between the wavefunction as shown in Equation 37.

$$\rho_i = \sum_k \psi_i(k)\psi_i(k) \tag{37.}$$

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.

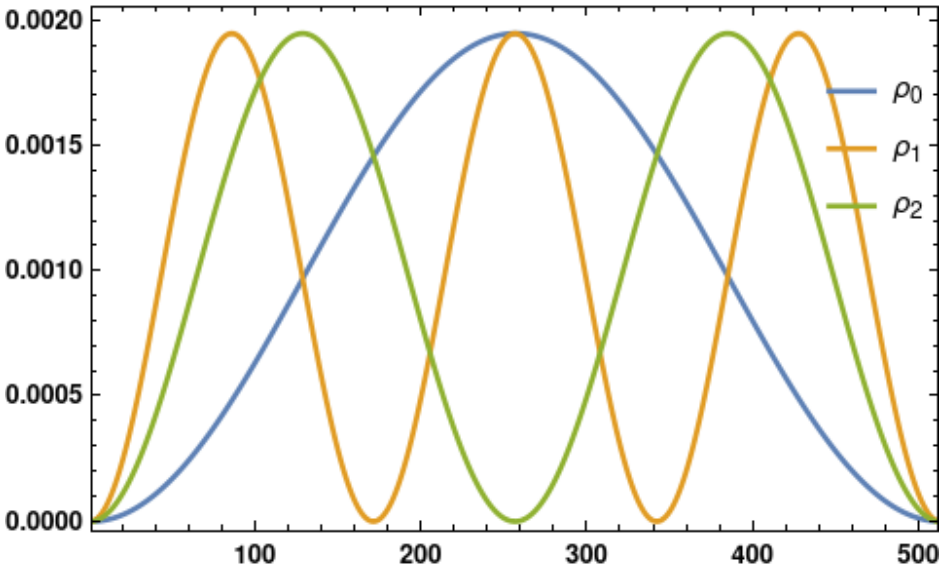

Figure 4: The solution of the Laplace equation with $n = 1024$ points.

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.

4.4 Analytic solution

Analytic solution to the problem of particle in a one-dimensional box is of the form shown in Equation 38.

$$\psi_k(x) = A_k \cos(kx) + B_k \sin(kx) \tag{38.}$$

where, k refers to the state in question. The unknowns, A_k and B_k can be found using the boundray conditions and the Equation 27. Using the boundray conditions, we get Equation 39.

$$\begin{aligned} \psi\left(-\frac{L}{2}\right) &= \psi\left(\frac{L}{2}\right) = 0 \\ \psi_k\left(-\frac{L}{2}\right) &= A_k \cos\left(k\frac{L}{2}\right) - B_k \sin\left(k\frac{L}{2}\right) = 0 \\ \psi_k\left(\frac{L}{2}\right) &= A_k \cos\left(k\frac{L}{2}\right) + B_k \sin\left(k\frac{L}{2}\right) = 0 \end{aligned} \tag{39.}$$

which gives the final analytical solution as shown in Equation 40.

$$\psi(x) := \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \text{ if } n \text{ is even} \\ \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi}{L}x\right) \text{ if } n \text{ is odd} \end{cases} \tag{40.}$$

5 Second quantization

6 Huckel hamiltonian

7 Hubbard hamiltonian

8 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.