

Introduction to Model hamiltonians

Vijay Gopal CHILKURI
vijay-gopal.chilkuri@uni-amu.fr
University of Aix-Marseille
Avenue Escadrille Niemen - 130013
+33413945595

ABSTRACT

A simple introduction to model hamiltonians for quantum chemists.

Contents

1	Introduction	1
2	Derivation of the Schrodinger equation	1
2.1	Lagrangian	1
2.2	Action	1
2.3	Postulates of Feynman	2
2.4	Derivation	2
3	1D particle in a box	3
3.1	Finite difference equations	4
3.2	Eigenvalues and eigenvectors	5
4	Second quantization	5
5	Huckel hamiltonian	5
6	Hubbard hamiltonian	5
7	Double exchange hamiltonian	5
	Bibliography	6

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.

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

$$\delta S = 0 \quad 8.$$

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

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

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.

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

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.

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

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).

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

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).

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

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.

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

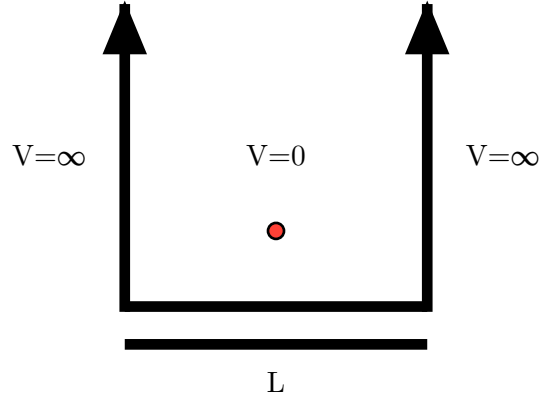


Figure 1: Particle in an infinite potential well.

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.

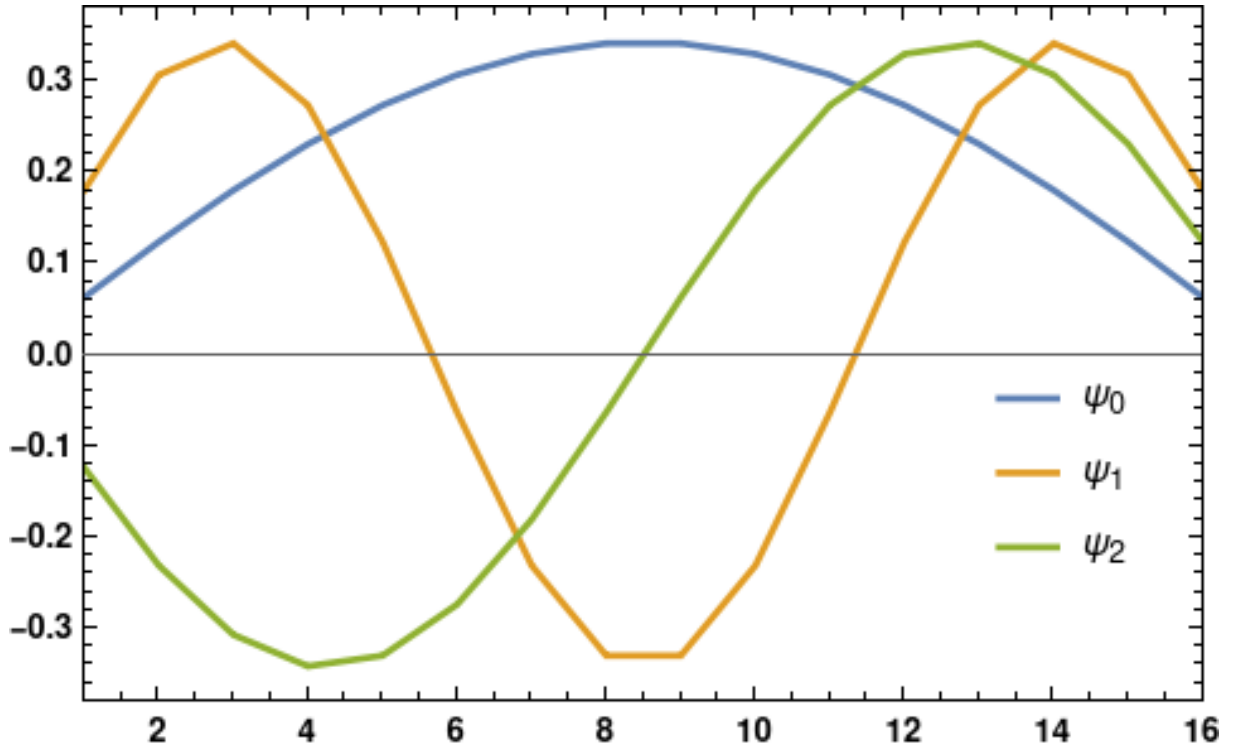


Figure 2: here comes text

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.