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).

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

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

$$F_i = m a_i \tag{6.}$$

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.

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

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

$$S = \sum_i S\big[r(t)_i\big] \tag{10.}$$

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.

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

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).

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

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,

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

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

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

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).

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

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

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

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 1D particle in a box

The problem of a particle in a box can be defined as shown in Equation 21

$$\frac{d^2\psi}{dx^2} = \lambda\psi \tag{21.}$$

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.