CHAPTER 2

QUANTUM THEORY

In classical mechanics, the dynamics of a system can be calculated using Newton's laws of motion. In quantum mechanics, there are several ways to obtain the solution. However, the most commonly used is 'wave mechanics,' where the fundamental equation of motion is the Schrödinger equation.

2.1 Schrödinger Equation

According to wave mechanics, the state of a system is described by a wave function, which satisfies the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left(-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)\Psi(\vec{r},t). \tag{2.1}$$

If the potential $V(\vec{r})$ is not explicitly time-dependent, and for appropriate boundary conditions, we can find a separable solution, so that the wave function can be written as

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{-iEt/\hbar}, \tag{2.2}$$

where E is interpreted as the energy, which leads to the time-independent Schrödinger equation

$$E\,\psi(\vec{r})=\left(-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)\psi(\vec{r})=\mathbf{H}\psi(\vec{r}), \tag{2.3}$$

where **H** is called the Hamiltonian operator.

It has been postulated that the wave function ψ completely defines the dynamical state. The probability density, $P(\vec{r})$, of the system is defined as $\psi^*(\vec{r})\psi(\vec{r})$. The energy of the system can be obtained from the expectation value of the Hamiltonian of the system under consideration,

$$E = \langle \psi | \mathbf{H} | \psi \rangle . \qquad (2.4)$$

However, in the case of the many electron problem, the solution of the problem must also satisfy the Pauli exclusion principle, i.e., the wavefunction must be antisymmetric with respect to the interchange of the coordinates of any pair of electrons.

2.2 Quantum Mechanical Calculations

To obtain a numerical approximate solution of the Schrödinger equation, all electrons in the system will be treated using one-electron wavefunctions called spin orbitals. These spin orbitals will be combined to form the many-electron wavefunction. This technique is called molecular orbital theory (MO). There are two categories: semiempirical and empirical methods.

2.2.1 Semiempirical methods

In the semiempirical methods, some simple Hamiltonians are used instead of the exact Hamiltonian, and some free parameters are included. The value of parameters can usually be derived from experimental data or, in many cases, from *ab initio* calculations (empirical method). The advantage of this method is that it can be applied to systems with a large number of atoms, such as in systems of organic molecules.

2.2.2 Empirical methods

On the other hand, empirical methods, known as *ab initio* calculations, use the full, accurate Hamiltonian, and no added parameters are needed for compensation. This method is commonly limited to work for about 50 or fewer atoms. However, the advantage of this method is that it can be applied to all kinds of molecules, and it requires no external data except the fundamental physical constants. In general, there are three steps to performing the *ab initio* calculations.

- Define the Hamiltonian of the system.
- Choose one trial wave function.
- Vary the combination of wave functions in order to minimize the total energy.

2.2.3 Approximations in quantum mechanics

For a system of one electron, it is sometimes possible to solve to obtain an exact solution of the Schrödinger equation, but for many-electron systems, only approximate solutions can be achieved. Many approximation techniques and procedures are needed and implemented.

2.2.3.1 Born-Oppenheimer approximation

The idea behind this approximation is that since the mass of the electrons is much smaller than the masses of the nuclei while the forces to which they are subjected are of compatible magnitude, the nuclear motion is much slower than that of the electrons. Therefore, one can separate the nuclear and electron translation parts of the Schrödinger equation. It is a reasonable approximation that the force and potential acting on the electrons depend on the fixed positions of nuclei. On the other hand, the nuclei approximately interact with electrons by the average value over several electron revolutions. This approximation is called the Born-Oppenheimer or adiabatic approximation [Born and Oppenheimer 1927]. In mathematical language, one can begin by considering the Hamiltonian equation,

$$\mathbf{H}\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R}), \tag{2.5}$$

with the Hamiltonian operator written as

$$\mathbf{H} = \mathbf{T}_n + \mathbf{V}_n + \mathbf{H}_e , \tag{2.6}$$

where

$$\mathbf{T}_n = -\sum_{\text{all nuclei}} \frac{1}{2M_n}\nabla_n^2$$
$$\mathbf{V}_n = \sum_{A<B} \frac{Z_A \cdot Z_B}{R_{AB}}$$
$$\mathbf{H}_e = -\sum_i \tfrac{1}{2}\nabla_i^2 \quad - \quad \sum_{iA}\frac{Z_A}{r_{iA}} \quad + \quad \sum_{i<j}\frac{1}{r_{ij}}.$$

Assume that the solution of the Schrödinger equation can be separated and written in the form

$$\psi(\vec{r},\vec{R}) = \Phi(\vec{r},\vec{R})\,\mathrm{X}(\vec{R}). \tag{2.7}$$

The Schrödinger equation will be separated to two equations:

$$\left[\mathbf{H}_e + \mathbf{V}_n(\vec{R})\right]\Phi(\vec{r},\vec{R}) = \mathrm{U}(\vec{R})\Phi(\vec{r},\vec{R}) \tag{2.8}$$

for the electronic wavefunction, and

$$\left[\mathbf{T}_n + \mathrm{U}(\vec{R})\right]\mathrm{X}(\vec{R}) = E\mathrm{X}(\vec{R}) \tag{2.9}$$

for the nuclear motion.

It can be seen that the potential term $\mathbf{U}(\vec{R})$ depends on only the position of the nuclei. This is used for an important construct known as the potential energy surface [ibid.].

2.2.3.2 Linear Combinations of Atomic Orbitals approximation

To approximately solve the electronic Schrödinger equation more conveniently, the idea of Linear Combinations of Atomic Orbitals (LCAO) is involved in the calculation. The essential concept of this approximation is to suppose that each individual molecular wavefunction can be obtained from some linear combination of a finite set of one-electron wavefunctions called the *basis set*, ϕ, and can be written as

$$\chi_i(x) = \sum_{\mu=1}^{N} c_{\mu i}\phi_{\mu}(x), \tag{2.10}$$

where $c_{\mu i}$ are the molecular orbital expansion coefficients. Then the one-electron functions are brought together to approximate the full wave function $\psi(x_1, x_2, \ldots, x_N)$ in a well-known form, the Slater determinant:

$$\psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \chi_1(x_3) & \cdots & \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) & \cdots & \cdots & \cdots \\ \vdots & \vdots & & & \vdots \\ \chi_n(x_1) & \cdots & \cdots & \cdots & \chi_N(x_N) \end{vmatrix}, \tag{2.11}$$

where $x_i = (\vec{r}_i, \omega_i)$ and $\vec{r}_i$ is the space coordinate and ω_i is the spin coordinate (a spinor). The electronic energy can be calculated from

$$E = \langle\psi|\mathbf{H}_e|\psi\rangle. \tag{2.12}$$

2.2.3.3 Basis functions

For convenient one-electron wave function or spin orbitals $\chi_i(x_i)$, some analytical forms will be selected to represent the primitive functions $\phi_{\mu}(x)$. There are normally two types of basis functions used in calculation, Slater Type Orbitals (STO), and Gaussian Type Orbitals (GTO).

2.2.3.3.1 Slater-type atomic orbitals, STO

This set of functions is derived from exact solutions in the case of the hydrogen atom. Its general form can be written as [Slater 1930]

$$\phi_{\mathrm{STO}}(n,l,m,\zeta) = |\vec{r}|^{n-1} \exp(-\zeta|\vec{r}|)\, \mathrm{Y}_{lm}(\theta,\phi). \qquad (2.13)$$

It is usually used for small systems. Functions of this type yield a very good approximation for orbital wave functions and produce good results of calculations. However, the exponential term in the function causes some difficulty to evaluate numerical integrals.

2.2.3.3.2 Gaussian-type atomic orbital, GTO

Functions of this type were introduced into molecular orbital computations by Boys [1950]. Their general form can be written as

$$\phi_{\mathrm{GTO}}(\lambda,\mu,\nu,\alpha) = x^{\lambda}y^{\mu}z^{\nu}\exp(-\alpha|\vec{r}|^{2}). \qquad (2.14)$$

They are less satisfactory than STO in representing atomic orbitals, because they do not have a cusp at the origin. However, they have the advantage that all integrals in the computations can be evaluated without numerical integration.

In the case that GTO functions are located off center, and omitting their angular part, we will obtain a Gaussian Lobe Orbital (GLO) [Whitten 1966] which provides an easy and accurate integral calculation for a large system [Sagarik, Ahlrichs, and Brode 1986].

2.2.3.4 Hartree equation

The fundamental concept of Hartree-Fock theory is the variational method which is one of the standard techniques used in quantum mechanics. Hartree-

Fock theory seeks the optimized energy for the system under consideration. We can write the Hamiltonian for the system of many electrons as

$$\mathbf{H}=\sum_{k}\frac{-\hbar^2}{2m}\nabla_k^2+\tfrac{1}{2}\sum_{k,l}\frac{e^2}{\left|\bar{r}_k-\bar{r}_l\right|}, \tag{2.15}$$

which can be separated into two components,

$$\mathbf{H}=\mathbf{H}_1+\mathbf{H}_2, \tag{2.16}$$

where

$$\mathbf{H}_1=\sum_{k}\frac{-\hbar^2}{2m}\nabla_k^2=\sum_{k}\mathbf{h}^{(k)} \tag{2.17}$$

and

$$\mathbf{H}_2=\tfrac{1}{2}\sum_{k\neq l}\frac{e^2}{\left|\bar{r}_k-\bar{r}_l\right|}=\tfrac{1}{2}\sum_{k\neq l}\mathbf{w}^{(kl)}. \tag{2.18}$$

The total energy of the system can be written as

$$\begin{aligned}E&=E[\tilde{\psi}]\\&=\langle\tilde{\psi}|\mathbf{H}|\tilde{\psi}\rangle\\&=\langle\tilde{\psi}|\mathbf{H}_1|\tilde{\psi}\rangle+\langle\tilde{\psi}|\mathbf{H}_2|\tilde{\psi}\rangle\end{aligned} \tag{2.19}$$

where $|\tilde{\psi}\rangle$ is a eigenfunction constituted from tensor products of Z arbitrary kets $|\alpha^{(1)}\rangle$, $|\beta^{(2)}\rangle$, ...

$$\begin{aligned}|\tilde{\psi}\rangle&=|\alpha^{(1)}\rangle|\beta^{(2)}\rangle\ldots|\lambda^{(k)}\rangle\ldots|\zeta^{(Z)}\rangle\\&=|\alpha^{(1)}\beta^{(2)}\ldots\lambda^{(k)}\ldots\zeta^{(Z)}\rangle,\end{aligned} \tag{2.20}$$

where α, β, χ, …, λ, …, ζ represent the states of one-electron states, and (1), (2), …, (k), …, (Z) represent coordinate of an individual electron with an orthonormalized constraint

$$\langle\lambda|\mu\rangle=\delta_{\lambda\mu} \qquad \text{where} \quad \lambda,\ \mu\ =\ \alpha,\ \beta,\ \ldots\ldots,\ \zeta\,. \tag{2.21}$$

The expectation value of $\mathbf{H}_1$ becomes successively

$$\begin{aligned}\langle\mathbf{H}_1\rangle&=\langle\widetilde{\psi}|\mathbf{H}_1|\widetilde{\psi}\rangle=\left\langle\widetilde{\psi}\middle|\sum_k\mathbf{h}^{(k)}\middle|\widetilde{\psi}\right\rangle\\&=\sum_k\left\langle\widetilde{\psi}\middle|\mathbf{h}^{(k)}\middle|\widetilde{\psi}\right\rangle\\&=\sum_\lambda\left\langle\lambda\middle|\mathbf{h}^{(1)}\middle|\lambda\right\rangle\end{aligned} \tag{2.22}$$

and

$$\begin{aligned}\langle\mathbf{H}_2\rangle&=\langle\widetilde{\psi}|\mathbf{H}_2|\widetilde{\psi}\rangle=\left\langle\widetilde{\psi}\middle|\tfrac{1}{2}\sum_{k\neq l}\mathbf{w}^{(kl)}\middle|\widetilde{\psi}\right\rangle\\&=\tfrac{1}{2}\sum_{k\neq l}\left\langle\widetilde{\psi}\middle|\mathbf{w}^{(kl)}\middle|\widetilde{\psi}\right\rangle\\&=\tfrac{1}{2}\sum_{\lambda\neq\mu}\left\langle\lambda^{(1)}\mu^{(2)}\middle|\mathbf{w}^{(12)}\middle|\lambda^{(1)}\mu^{(2)}\right\rangle.\end{aligned} \tag{2.23}$$

According to the variational technique, we seek to minimize with respect to variations in the single-electron wave functions, $|\lambda\rangle$. At the same time, the wave functions are constrained to be orthonormal, $\langle\lambda|\mu\rangle=\delta_{\lambda\mu}$. Therefore we use the method of Lagrange multipliers:

$$\delta\left\{E[\widetilde{\psi}]+\sum_{\lambda\mu}\varepsilon_{\lambda\mu}\langle\lambda|\mu\rangle\right\}=0\,, \tag{2.24}$$

where δ is a variation with respect to any of the single-electron wave functions, Using linear combinations of $|\alpha\rangle$, $|\beta\rangle$, …, $|\zeta\rangle$ that diagonalize $\varepsilon_{\lambda\mu}$, we get

$$\delta E[\tilde{\psi}] + \sum_{\lambda} \varepsilon_{\lambda}\, \delta\langle\lambda|\lambda\rangle = 0 . \tag{2.25}$$

This can be developed to

$$\begin{aligned} &\sum_{\lambda} \langle\delta\lambda| \left\{ \mathbf{h}^{(1)}|\lambda^{(1)}\rangle + \sum_{\mu} \langle\mu^{(2)}|\mathbf{w}^{(12)}|\mu^{(2)}\rangle|\lambda^{(1)}\rangle - \varepsilon_{\lambda}|\lambda\rangle \right\} \\ &+ \sum_{\lambda} \left\{ \langle\lambda^{(1)}|\mathbf{h}^{(1)} + \sum_{\mu} \langle\lambda^{(1)}|\langle\mu^{(2)}|\mathbf{w}^{(12)}|\mu^{(2)}\rangle - \varepsilon_{\lambda}\langle\lambda| \right\}|\delta\lambda\rangle = 0 \end{aligned} \tag{2.26}$$

it is clearly seen that whole left side of equation can be zero if

$$\mathbf{h}^{(1)}|\lambda^{(1)}\rangle + \sum_{\mu} \langle\mu^{(2)}|\mathbf{w}^{(12)}|\mu^{(2)}\rangle|\lambda^{(1)}\rangle - \varepsilon_{\lambda}|\lambda\rangle = 0 . \tag{2.27}$$

This equation is called the Hartree equation.

2.2.3.5 Hartree-Fock equation

The Hartree equation was derived based on the assumption that $|\tilde{\psi}\rangle$ is a tensor product of Z arbitrary kets, $|\alpha^{(1)}\rangle$, $|\beta^{(2)}\rangle$, ..., which can give a good approximation for some systems. However, the Hartree equation itself does not include the effect of Pauli exclusion principle, which requires the electron wave function to be antisymmetric under particle interchanges. The wave function now becomes

$$\begin{aligned} |\psi\rangle &= (Z!)^{-1/2} \sum_{P} (-1)^{P} \mathbf{P} |\tilde{\psi}\rangle \\ &= (Z!)^{-1/2} \mathbf{A} |\tilde{\psi}\rangle \end{aligned} \tag{2.28}$$

where **P** is permutation operators, and **A** is the antisymmetric operator defined by

$$\mathbf{A} = \frac{1}{Z!} \sum_{P} (-1)^{P} \mathbf{P} .$$

Then we apply the variational method with $|\psi\rangle$ in the same way as did with $|\tilde{\psi}\rangle$ yields

$$\langle \mathbf{H}_1 \rangle = \sum_{\lambda} \langle \lambda | \mathbf{h}^{(1)} | \lambda \rangle \tag{2.29}$$

and

$$\langle \mathbf{H}_2 \rangle = \tfrac{1}{2} \sum_{\lambda\mu} \langle \lambda^{(1)} \mu^{(2)} | \mathbf{w}^{(12)} | \lambda^{(1)} \mu^{(2)} \rangle - \langle \lambda^{(1)} \mu^{(2)} | \mathbf{w}^{(12)} | \mu^{(1)} \lambda^{(2)} \rangle, \tag{2.30}$$

where the first term of $\langle \mathbf{H}_2 \rangle$ is the coulomb interaction term, and the second term is the exchange interaction term. Then we can obtain

$$\mathbf{h}^{(1)} | \lambda^{(1)} \rangle + \sum_{\mu} \langle \mu^{(2)} | \mathbf{w}^{(12)} | \mu^{(2)} \rangle | \lambda^{(1)} \rangle - \sum_{\mu} \langle \mu^{(2)} | \mathbf{w}^{(12)} | \lambda^{(2)} \rangle | \mu^{(1)} \rangle - \varepsilon_{\lambda} | \lambda \rangle = 0$$

or

$$\mathbf{F} | \lambda \rangle - \varepsilon_{\lambda} | \lambda \rangle = 0 \tag{2.31}$$

which is called the Hartree-Fock equation,

where the Fock operator $\mathbf{F}$ is defined as

$$\mathbf{F} | \lambda \rangle = \mathbf{h} | \lambda \rangle + \sum_{\mu} \langle \mu^{(2)} | \mathbf{w}^{(12)} | \mu^{(2)} \rangle | \lambda^{(1)} \rangle + \sum_{\mu} \langle \mu^{(2)} | \mathbf{w}^{(12)} | \lambda^{(2)} \rangle | \mu^{(1)} \rangle \tag{2.32}$$

2.2.3.6 Roothaan Hartree-Fock Self Consistent Field method

Some more approximations must be introduced in order to solve the Hartree-Fock equation. The wave function, $|\lambda\rangle$, can be written as a linear combination of basis function.

$$| \lambda \rangle = \sum_{j} c_{\lambda j} | j \rangle \tag{2.33}$$

substituting this into Hartree-Fock equation and multiply by $\langle i |$ we obtain the result

$$\sum_{j} c_{\lambda_j} \langle i | \mathbf{F} | j \rangle = \varepsilon_{\lambda} \sum_{j} c_{\lambda_j} \langle i | j \rangle \tag{2.34}$$

It can be rewritten in form of matrix equation

$$\sum_j c_{\lambda j}\left(F_{ij} - \varepsilon_\lambda S_{ij}\right) = 0 \tag{2.35}$$

where $F_{ij} = \langle \phi_i | \mathbf{F} | \phi_j \rangle$ are elements of the Fock matrix $\mathbf{F}$, and $S_{ij} = \langle \phi_i | \phi_j \rangle$ are elements of the overlap matrix $\mathbf{S}$. The equation can be rewritten in the more compact matrix form

$$\mathbf{Fc} = \mathbf{Sc\varepsilon}. \tag{2.37}$$

This equation is called the Roothaan-Hall equation, which provides the ability to solve the Hartree-Fock equation with numerical procedures using digital computers [Roothaan 1951; Hall 1951]. This technique is commonly used in problem solving and is called the Roothaan Hartree-Fock Self Consistent Field method (SCF). The procedure is shown in the Figure 2.1. The whole procedure will be repeated until the linear combination coefficients $c_{\lambda j}$ are converge.

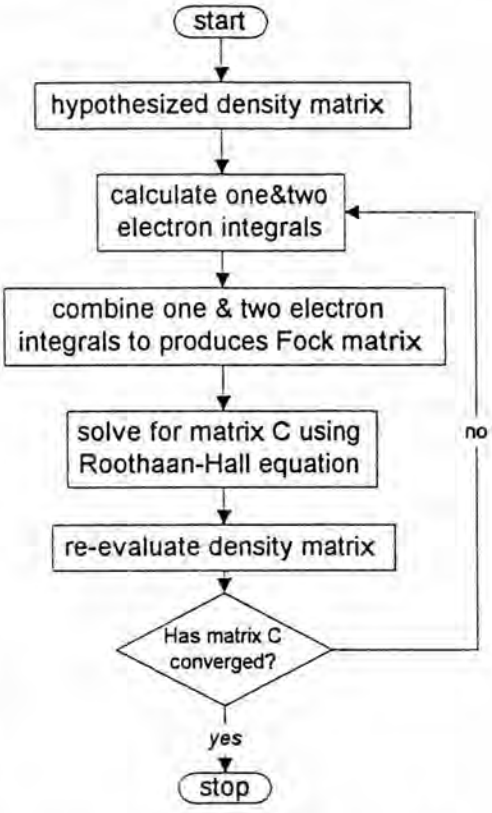

Figure 2.1 The steps in SCF calculation.

2.2.3.7 Basis set superposition error

In the calculation of stabilization energies, using the SCF method, of two species, **A** and **B**, an erroneous result is obtained when finite bases are employed. The reason is the finite separation of two species sites of **A** and **B**. The basis set located on B sites can overlap and improve the basis set of **A**, and vice versa. To estimate the effect, the energy of the **A** species is calculated with both basis sets of **A** and **B**, but without the **B** species itself. Next, calculate for the **B** species with both basis sets of **A** and **B**, without the **A** species. The results can be used to improve the value of the total energy. The counterpoise method was first introduced by Boys and Bernardi [1970] to correct the inaccuracy. This method determines the subsystem energies using the same basis set functions as used in the full system. Suppose that {A} and {B} are the basis sets of subsystems A and B, respectively. The interaction energy of whole system can be written as

$$\Delta E = E_{AB}(\{A\},\{B\}) - \left(E_A(\{A\}) + E_B(\{B\})\right) \tag{2.36}$$

and the counterpoise correction as

$$\Delta e = \left(E_A(\{A\}) - E_A(\{A\},\{B\})\right) + \left(E_B(\{B\}) - E_B(\{A\},\{B\})\right) \tag{2.37}$$

The counterpoise corrected interaction energy can be written

$$\Delta E_{c.p.} = \Delta E + \Delta e\,. \tag{2.38}$$