

# Chapter 1: A reminder of the Schrödinger equation

## 1.1 Introduction

Quantum chemistry takes into account the electronic structure of a system and is based on Schrödinger's equation.

The use of theoretical methods to obtain models that can predict and understand molecular structures, properties and interactions is known as "Molecular Modeling". Molecular modeling can provide information that is not available through experiment, and thus plays a complementary role to that of experimental chemistry. Molecular modeling can, for example, provide a precise idea of the structure of the transition state for a given reaction, which is difficult - or impossible - to obtain with experimental chemistry.

Quantum chemistry involves the use of methods based on solving the time-independent Schrödinger equation. By solving the equation with eigenvalues and eigenvectors  $\hat{H}\Psi = E\Psi$ , where  $\hat{H}$  is a Hamiltonian operator,  $E$  the total energy and  $\Psi$  the wave function of the system. it will then be possible to determine all the information of the system under study.

However, it is not possible to solve such an equation rigorously, except for single-electron systems, and so approximations had to be introduced into the quantum theory proposed in the 1920s in order to solve this equation approximately.

## 1.2 Atomic units

For a system of units specific to the electron, we apply the following system of atomic units:

The unit of length is  $a_0 = 0.529 \text{ \AA}$ , Bohr radius

The unit of mass is  $m_e = 9.109 \times 10^{-31} \text{ kg}$ .

The unit of charge is  $e = 1.602 \times 10^{-19} \text{ C}$ .

The unit of energy is called Hartree and is  $E_h = 4.36 \times 10^{-18} \text{ J}$ .

The unit of angular momentum is  $\hbar = 1.054 \times 10^{-34} \text{ J}\cdot\text{s}$ .

## 1.3 Schrödinger equation

Quantum mechanics postulates the wave-particle duality of matter and defines a particle (electron) as a wave. I.e. distributed throughout space rather than having a well-defined trajectory.

Classical mechanics     ri Trajectory

Quantum mechanics     m Wave functions

In 1926, the Austrian physicist Schrödinger proposed an equation to find the wave function of a system.

The evolution over time  $t$  of the state of a system of atoms consisting of  $N$  nuclei and  $n$  electrons is described by a wave function satisfying the following Schrödinger equation:

$$\hat{H}\Psi(\{r\}, \{R\}, t) = E\Psi(\{r\}, \{R\}, t) \quad (\text{S.1})$$

where the vectors  $\{r\} = r_1, \dots, r_n$  and  $\{R\} = R_1, \dots, R_N$  represent the system's electronic and nuclear coordinates respectively.

The latter equation is called a time-dependent Schrödinger equation, with a Hamiltonian operator  $H$  of the system.

For an isolated system, Schrödinger's equation depends only on the coordinates of the particles and are time-independent

$$\hat{H}\Psi(\{r\}, \{R\}, \{t\}) = \hat{H}\Psi(\{r\}, \{R\}) \cdot e^{-i\frac{Et}{\hbar}} \quad (\text{S.2})$$

Where  $E$  is the energy associated with the wave function  $\Psi$ , obtained by solving the time-independent Schrödinger equation, we have:

$$\hat{H}\Psi(\{r\}, \{R\}) = E\Psi(\{r\}, \{R\}) \quad (\text{S.3})$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \quad (\text{S.4})$$

where  $\nabla^2$  is the Laplacian,  $E$  is the total energy of the system and  $V$  is the energy of the system potential.

Solving equation (S.3), which is nothing other than the eigenvalue and vector equation of the Hamiltonian.

## 1.4 Standard interpretation of the wave function

1/ wave function means nothing; mathematical function such that  $|\Psi|^2$  represents a particle probability density. You can't measure  $\Psi$ , but you can calculate it.

The  $\Psi$  functions, solutions to Schrödinger's equation, are called states of the system associated with energies  $E$ ,

The  $E=0$  state associated with the lowest energy  $E=0$  is called the ground state of the system. Here are a few conditions that define this eigenfunction:

1/ The probability of finding (observing) the particle in a volume  $dV$  is given by

$$dP(\{r\}, \{R\}) = |\Psi(\{r\}, \{R\})|^2 \cdot dV$$

$$dV(x, y, z) = dx \cdot dy \cdot dz, \text{ in Cartesian coordinates}$$

$$dV(r, \theta, \phi) = r \cdot \sin \theta \cdot d\theta \cdot d\phi \cdot dr, \text{ in spherical coordinates}$$

and  $|\Psi|^2$  is like a probability density.

2/ The  $\Psi$  function is said to have a summable square, i.e.:

$$\int_V \Psi \cdot \Psi^* dV = 1$$

3/  $\Psi$  must be regular at all points.

## 1.5 Hamiltonian operator of a molecule

The total  $H$  Hamiltonian of a molecule with  $N$  nuclei and  $n$  electrons is defined by the sum of five terms (electron kinetic term, nucleus kinetic term, electron-electron repulsion term, nucleus-nucleus repulsion term and electron-nucleus attraction term).

$$\hat{H}(\{r\}, \{R\}) = M(\{r\}, \{R\})$$

Where:

$$\hat{H} = T_e + T_N + V_{ee} + V_{NN} + V_{eN} \quad (\text{S.5})$$

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i^n \frac{\Delta_i}{m_i} - \frac{\hbar^2}{2} \sum_k^N \frac{\Delta_k}{M_k} + K.e^2 \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} - \sum_k^N \sum_{l>k}^N \frac{Z_k Z_l}{R_{kl}} - K.e^2 \sum_i^n \sum_k^N \frac{Z_k}{r_{ik}} \quad (\text{S.6})$$

We can simplify the last equation in u.a. as follows:

$$\hat{H} = -\frac{1}{2} \sum_i^n \Delta_i - \frac{1}{2} \sum_k^N \frac{\Delta_k}{M_k} - \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} + \sum_k^N \sum_{l>k}^N \frac{Z_k Z_l}{R_{kl}} - \sum_i^n \sum_k^N \frac{Z_k}{r_{ik}} \quad (\text{S.7})$$

Exact solution of equation (S.3) is only possible for the hydrogen atom and hydrogenoid systems. For poly-electronic systems, it is necessary to use approximation methods to solve Schrödinger's equation in an approximate way.

## Born-Oppenheimer approximation

One of the first approximations that can be used to solve the Schrodinger equation of a complex molecular system is the Born-Oppenheimer approximation. It is based on the fact that the mass of nuclei is much greater than that of electrons. The kinetic energy of the nuclei can then be neglected, which is equivalent to considering that electrons move in a field of spatially fixed nuclei.

The system's electronic Hamiltonian operator is defined by:

$$\hat{H} = -\frac{1}{2} \sum_i^n \Delta_i + \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} - \sum_i^n \sum_k^N \frac{Z_k}{r_{ik}} \quad (\text{S.8})$$

and the shape of the wave function as follows:

$$\Psi(\{r\}, \{R\}) = \Psi_R^{el}(r) \cdot \Psi_N(R) \quad (\text{S.9})$$

Where  $\Psi_R^{el}(r)$  is an electronic wave function and a nuclear wave function  $\Psi_N(R)$ . It is then a matter of solving the following equation:

$$H_{el} \Psi_R^{el}(r) = E_{el}(R) \Psi_R^{el}(r) \quad (\text{S.10})$$

Where  $H_{el} = T_e + V_{ee} + V_{eN}$  and  $H = H_{el} + \sum_k^N \sum_{l>k}^N \frac{Z_k Z_l}{R_{kl}}$ . Born-Oppenheimer energy  $E_{BO}(R)$  is the sum of the electronic energy and the repulsive interaction term between the nuclei.

$$E_{BO} = E_{el} + \sum_k^N \sum_{l>k}^N \frac{Z_k Z_l}{R_{kl}} = E_{el} + V_{NN} \quad (\text{S.11})$$

## Orbital approximation and Slater determinant :

The orbital approximation consists in expressing the wave function  $\Psi$ , solution of the Schrodinger equation limited to the electronic Hamiltonian  $H$  described above, by a product of functions each dependent on the coordinates of a single electron:

$$\Psi(1, 2, \dots, n) = \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n) \quad (\text{S.12})$$

Monoelectronic 'P' functions are called orbitals.

R consequences on  $\hat{H}$

$$\hat{H} = \frac{p^2}{2m} + V(r) \quad (S.13)$$

R each 'P' orbital is the solution of an eigenvalue equation :

$$\hat{H}\psi = E\psi \quad (S.14)$$

R consequences on  $E$

$$E = \epsilon_1 + \epsilon_2 + \dots + \epsilon_n = \sum \epsilon_i \quad (S.15)$$

with  $s$ , does not depend on spin.

Unfortunately, this 'P' wave function does not satisfy Pauli's principle, which states that the wave function describing a

multi-electron system must change sign when the coordinates of any two electrons are swapped. In

In the orbital approximation, the wave function that satisfies this principle takes the form of a Slater determinant:

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_n(2) \\ \dots & \dots & \dots & \dots \\ \chi_1(n) & \chi_2(n) & \dots & \chi_n(n) \end{vmatrix} \quad (S.16)$$

$$Z_i^{\circ} 1^{\circ} - 1^{\circ} <$$

The normalization factor for the function is  $\frac{1}{\sqrt{n!}}$  where  $n$  is the number of electrons with  $\chi_i(r) = \psi(r, \sigma_i)$  or  $\chi_i(r) = \psi(r, \sigma_i)$ .  $\chi_i$  are the spinorbitals

Typically, orbitals are developed as a finite linear combination of atomic orbitals. This approach is called LCAO: Linear Combination of Atomic Orbitals.

$$\Psi_i = \sum c_{ij} \phi_j \quad (S.17)$$