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The Schrödinger equation (Eq. 1) is the cornerstone in quantum mechanics. In this equation, \hat{H} is the Hamiltonian operator, Ψ is the wavefunction, and E is the energy. This equation can also be expressed using the bra-ket notation. The Eq. 1 is time-independent, however, the Schrödinger equation can also be time-dependent. This dependence of time is useful when analyzing dynamics, but for our purposes dynamics is beyond the scope of the course. However, time-independent Schrödinger equation is relevant for analyzing the quantum behavior of many chemical systems. Indeed, nuclei and electrons can be appropriately described so a detailed chemistry at the atomic level could be achieved using time-independent Schrödinger equation. Therefore, appropriate both Hamiltonian and wavefunction should be taken to get a reasonable good energy for the molecular system.

$$\hat{H}\Psi = E\Psi \quad \equiv \quad \hat{H}|\Psi\rangle = E|\Psi\rangle \quad (\text{Eq. 1})$$

The wave function (Ψ) describes the way atoms, i.e. nuclei and electrons, are in a molecular system. For further reading, please refer to the article *Computational Chemistry Using Modern Electronic Structure Methods, Journal of Chemical Education, 84 (8), 2007*. The description of the wavefunction as a Gaussian basis set was discussed in other topics of the course and no additional discussion is provided in the current document. The Hamiltonian is an operator which has several components in terms of kinetic, \hat{T} , and potential operators, \hat{V} (for details, please refer to the initial document provided in UVirtual platform and your classnotes). The molecular Hamiltonian can be expressed as shown in Eq 2.

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN} \quad (\text{Eq. 2})$$

In Eq. 2, \hat{T}_e is the kinetic term of electrons, while \hat{T}_N is the kinetic of nuclei. The term \hat{V}_{ee} is the interaction between electrons, \hat{V}_{NN} is the interaction between nuclei, and \hat{V}_{eN} is the interaction between nuclei and electrons. The operators in Eq. 2 can be expressed more in detail as shown in Eq 3 in atomic units, indicating electrons with lowercase letter n (or i, j) and nuclei with capital letter N (or A, B).

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \frac{1}{2} \sum_{A=1}^N \frac{\nabla_A^2}{M_A} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} + \sum_{A=1}^N \sum_{B>A}^N \frac{Z_A Z_B}{R_{AB}} - \sum_{i=1}^n \sum_{A=1}^N \frac{Z_A}{r_{iA}} \quad (\text{Eq. 3})$$

For using Eq. 1 in Eq. 1 leads to complex terms which are impossible to solve with the current infrastructure. It can only be solved analytically for the hydrogen atom and using the rigid rotor and the harmonic approximation for the hydrogen molecule. However, going into systems with three electrons or above that makes it impossible to solve Eq. 1. Therefore Eq. 3 can be simplified by using several approximations. One of them is the Born-Oppenheimer approximation, which states that the motion of the nuclei is very small as compared to electrons, since the ratio nucleus/electron in the hydrogen atom is ≈ 1800 times. Therefore, the kinetic term for the nuclei (\hat{T}_N) can be neglected and only consider the kinetic term for electrons (\hat{T}_e). Now, we should focus on the potential operators, V . A strategy is to fix the nuclear coordinates, then the \hat{V}_{NN} term is a constant at the end which could be further added up, as an integration constant. In summary, of the terms in Eqs. 2 and 3, \hat{T}_N vanishes and \hat{V}_{NN} is a constant. Therefore, Eq. 3 can now expressed as Eq. 4. Since all the nuclei terms were fixed and the variables are now moved into electrons, the Hamiltonian resultant Hamiltonian is purely electronic (\hat{H}_{elect}).

$$\hat{H}_{elect} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} - \sum_{i=1}^n \sum_{A=1}^N \frac{Z_A}{r_{iA}} \quad (\text{Eq. 4})$$

Therefore, the electronic Hamiltonian (\hat{H}_{elect}) can now be used for obtaining the electronic energy (E_{elect}) of the system (see Eq. 5); the wavefunction now regards only for electrons, then it is called as electronic wavefunction (Ψ_{elect}).

$$\hat{H}_{elect} |\Psi_{elect}\rangle = E_{elect} |\Psi_{elect}\rangle \quad (\text{Eq. 5})$$

Using the electronic Hamiltonian could let us think that the light inside a tunnel can now been visible. However, there is a problem, the second term in Eq. 4 (electron-electron interactions), which is written in detail in Eq. 6 has non-separable variables between electrons i and j . Therefore, there are not exact solutions even for Eq. 5!

$$\frac{1}{r_{ij}} = \frac{1}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \quad (\text{Eq. 6})$$

Consequently, several approximation should be addressed to overcome the issue in Eq. 6, so Eq. 5 can be solved. There are four types of approximations: 1) ab-initio methods (first principles), 2) Semiempirical methods, 3) Density functional theory (DFT) methods.

Within the ab-initio approximations, there are mainly two types of approximations: a) Hartree-Fock (HF) methods and b) post-Hartree-Fock approximations. The post-HF methods are sub-

divided into i) Moller-Plesset perturbation theory (MPⁿ), ii) configuration interaction (CI), iii) Quadratic configuration interaction (QCI), iv) coupled clusters (CC).

The semiempirical methods are based on the most simple ab-initio method, i.e. HF method, improving its limitations by parametrizing several integrals based on experimental data, which leads to a fast process to get the energy of the system. These methods are useful for large systems involving several atoms, however, for several systems, there is a lack of accuracy; then post-HF and DFT methods should be used. Hence, there is not additional information regarding semiempirical methods in the current document. The DFT methods will be presented by the students of the course. Ab-initio methods are described below.

Variational method

When dealing with approximation methods, one always should refer to a reference system. Hence, one has a guide to choose an appropriate method. Here is when the variational method helps us to decide. The variational principle states that the true (ground state) energy of any system can never be achieved, but by using several approximations in the Hamiltonian operator (\hat{H}_{elect} in our case) and trial wavefunctions (Ψ_{elect} in our case) and solving Eq. 5, and energy (E) above the ground state can be achieved. Therefore, the expectation value (E) can be expressed as in Eq. 7, where the letter *t* represents *trial*.

$$\hat{H}_t |\Psi_t\rangle = E_t |\Psi_t\rangle \rightarrow E_t = \langle \Psi_t | \hat{H}_t | \Psi_t \rangle \quad (\text{Eq. 7})$$

As a consequence, the trial energy is always above the true (ground) energy, i.e. $E_t > E_0$, which is the smallest possible eigenvalue.

Therefore, a criterion when analyzing different approximation methods, is to get one which better apply for the variational method. In other words, the appropriate combination of Hamiltonian and wavefunction which leads to the lowest energy, i.e. close to the E_0 (ground energy), should be chosen to describe the desired molecular system.

The combination of Hamiltonian and basis set is usually described under the following scheme: Hamiltonian/basis set. This combination is called *level of theory*. For instance, in the Hartree-Fock method and the basis set 6-31g(d) are used, then the level of theory is HF/6-31g(d).

ab-initio methods

The term ab-initio comes from Latin, meaning “from the beginning”; hence, ab-initio methods are usually known as “first principles”. The most basic ab-initio method is the Hartree-Fock (H-F or HF) method, which was developed by the English scientist Hartree and the Russian Fock. In the current document, there is an emphasis in the HF method instead of other ab-initio methods. The post-HF methods are not considered here, but further reading is suggested to get deeper understanding about post-HF methods. This is part of the autonomy of a graduate student.

Hartree-Fock method

In this method, we take Eq. 4, neglecting the electron-electron interaction, as shown in Eq. 8.

$$\hat{H}_{elect} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} - \sum_{i=1}^n \sum_{A=1}^N \frac{Z_A}{r_{iA}} \rightarrow \hat{f}_i = \hat{h}_i + \hat{V}_i^{\widehat{HF}} \quad (\text{Eq. 8})$$

In Eq. 8, the Hamiltonian is renamed as \hat{f}_i , which is the operator for electron i of the system. The \hat{h}_i term is named as core Hamiltonian and $\hat{V}_i^{\widehat{HF}}$ is the HF potential for the i -th electron of the molecular system. Hence, the total Hamiltonian can be expressed as:

$$\widehat{H}^0 = \sum_{i=1}^n \hat{h}_i \quad (\text{Eq. 9})$$

The electrons are located in spatial orbitals a, b, c, ... Hence, the modified Hamiltonian in Eq. applied for an electron in the ψ_a spatial orbital is described as in Eq. 10, where ε_a^0 is the energy of the electron in the spatial orbital a . An orbital is defined as one-electron wavefunction.

$$\hat{h}_i \psi_{a(i)}^0 = \varepsilon_a^0 \psi_{a(i)}^0 \quad (\text{Eq. 10})$$

Therefore, the overall wave function is $\psi^0 = \psi_{a(1)}^0 \psi_{b(2)}^0 \psi_{c(3)}^0 \dots \psi_{z(n)}^0$, while the overall energy is $E^0 = \sum_{i=1}^n \varepsilon_i^0$. Therefore, the overall wavefunction can be expressed as a determinant.

$$\psi^0 = \frac{1}{\sqrt{2}} \det |\phi_{a(1)} \phi_{b(2)} \dots \phi_{z(n)}| \quad (\text{Eq. 11})$$

In Eq. 11, $1/\sqrt{2}$ is a normalization constant. The term $\phi_{a(1)}$ not only include spatial part but also spin. Now, the electrons are now better described. Hence, the spatial orbitals ψ_a are now improved by ϕ_a , named as spin-orbital, which includes both spatial and spin components. The spin can be expressed as α (+1/2) or β (-1/2)

For a two electron system, the spin functions can be expressed accounting for all possibilities:

$$\alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \beta(1)\alpha(2)$$

This possibilities can be included in determinant of Eq. 11, leading to Eq. 12

$$\frac{1}{\sqrt{2}} \det |\alpha(1)\beta(2) - \beta(1)\alpha(2)| = -\frac{1}{\sqrt{2}} \det |\alpha(2)\beta(1) - \beta(2)\alpha(1)| \quad (\text{Eq. 12})$$

The spin functions are named as antisymmetric functions, which is a key property for all the spin-orbitals considered hereon, with the concomitant results for the application of the eigenequation and the eigenvalue (energy) for the desired molecular system. With the inclusion of the spin, the wave function that directs toward the ground state for two electron systems is described as:

$$\psi = 1S(1)1S(2) \cdot \frac{1}{\sqrt{2}} \det[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (\text{Eq. 13})$$

The Eq. 13 can be expressed as:

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 1S1\beta(1) \\ 1S(2)\alpha(2) & 1S2\beta(2) \end{vmatrix} \quad (\text{Eq. 14})$$

The determinant in Eq. 14 is named as Slater determinant. A similar procedure applies for n-electron system. The terms $1S(1)1S(2)$ can be named (for sake of simplicity) ϕ as in Eq. 11. The spatial and spin inclusion to a one-electron orbital leads to the name of *atomic orbital*. Therefore, the heart of the Hartree-Fock method is given by Eq. 15, where \hat{F} is the Fock operator.

$$\hat{F}\phi_i = \varepsilon_i\phi_i \quad (\text{Eq. 15})$$

Applying an operator to an atomic orbital in Eq. 15 leads to eigenvalue related to the electronic energy of the system for every electron. However, the expected value for the total energy, i.e. considering all the electrons of the system can be established. Hence, the expectation value for the total electronic energy is expressed as in Eq. 16, where ψ^* is the conjugate complex of the function ψ .

$$\varepsilon = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (\text{Eq. 16})$$

In the Hartree-Fock method, the electron-repulsion is treated in an “average” way. Each electron is considered to be moving in the electrostatic field of the nuclei and the average field of the n-1 electrons. Using a trial conditions (see Eq. 7) and applying HF method, not necessarily a low energy is obtained according to the variational method. Therefore, if this is the case, the nuclear coordinates should be modified to achieve new values. In other words, the energy of Eq. 16 should be minimized to get the lowest possible value within the framework of the HF method.

Now, let's zoom into the Fock operator to understand the two key components of the potential operator (V^{HF}) in the HF approximation. The Eq. 15 for the electron 1 in the atomic orbital (spin-orbital) a is expressed as:

$$\hat{f}_1 \phi_{a(1)} = \varepsilon_a \phi_{a(1)} \quad (\text{Eq. 17})$$

The Fock operator (\hat{f}_1) in Eq. 17 has the form shown in Eq. 18.

$$\hat{f}_1 = \hat{h}_1 + \sum_u \{2J_{u(1)} - K_{u(1)}\} \quad (\text{Eq. 18})$$

In Eq. 18, \hat{h}_1 is the core Hamiltonian for electron 1, J_u is the Coulomb operator and K_u is the exchange operator. The letter u belongs to all spin-orbitals, i.e. $u = a, b, c, \dots, z$. The Coulomb operator represents the electrostatic interaction of the i -th electron relative to the rest of the system; in other words, it is the potential electron one feels taking an average value considering the rest of electrons and nuclei. The exchange potential does not have physical meaning since it leaves from the antisymmetric spin wavefunction. The Coulomb and exchange operators are shown in Eqs. 19 and 20, operating on the respective spin-orbital.

$$J_{u(1)} \phi_{a(1)} = j_0 \left\{ \int \phi_u^*(2) \frac{1}{r_{12}} \phi_u(2) dx_2 \right\} \phi_{a(1)} \quad (\text{Eq. 19})$$

$$K_{u(1)} \phi_{a(1)} = j_0 \left\{ \int \phi_u^*(2) \frac{1}{r_{12}} \phi_u(2) dx_2 \right\} \phi_{u(1)} \quad (\text{Eq. 20})$$

In Eqs. 19 and 20, $j_0 = e^2/4\pi\varepsilon_0$. The Coulomb operator takes into account the Coulombic repulsion between electrons. The exchange operator represents the modification of the energy (due to Coulombic repulsion) that can be ascribed to the effects of spin-correlation.

As shown in Eqs. 7 and 17, if we want to analyze and unknown systems, we need to start from a known value, i.e. we need trial Fock operator and spin-orbitals. Therefore, the first step is to have an initial set of spin-orbitals which are used to build the concomitant Fock operator. Then, Eqs. 17 to 20 are solved according to Eq. 15 to get a trial energy. According to the variational method, we need to test this procedure several times to achieve the lowest possible energy. Therefore, the solution to the initial HF equations are used to build a second set of spin-orbitals, a new Fock operator and then a new energy. This procedure continues until the energy converges to an acceptable value, close to the ground energy according to the variational method; in other words, there is a minimization procedure. This iterative procedure is known as the self-consistent field (SCF) method. The criteria for energy convergence is usually predefined, which depends on the desired accuracy and particular purposes.

Now, we focus on the SCF method to understand the practical use of computers into the minimization procedure of the energy, widely known as minimization energy.

The wave function for the i -th electron is expressed as shown in Eq. 21. We need to start from something known to get the unknown part. The known part are the basis functions θ_i . Please remember that we choose the type of wavefunction to start with. Now, the unknown part are the coefficients C_{ij} .

$$\psi_i = \sum_{j=1}^M C_{ij} \theta_j \quad (\text{Eq. 21})$$

The new problem now is to calculate the new coefficients. Therefore, we can put Eq. 21 in a similar equation to Eq. 15 (see Eq. 22)

$$f_1 \sum_{j=1}^M C_{ja} \theta_j(1) = \varepsilon_a \sum_{j=1}^M C_{ja} \theta_j(1) \quad (\text{Eq. 22})$$

Now, Eq. 22 is multiplied by the conjugate complex of the θ_j function (θ_i^*) and operator f_1 operates on the new set of functions, hence, the integral for the differential dr_1 can now be detailed (see Eq. 23).

$$\sum_{j=1}^M C_{ja} \int \theta_i^*(1) f_1 \theta_j(1) dr_1 = \varepsilon_a \sum_{j=1}^M C_{ja} \int \theta_i^*(1) \theta_j(1) dr_1 \quad (\text{Eq. 23})$$

In Eq. 23, the term $\int \theta_i^*(1) f_1 \theta_j(1) dr_1$ is known as Fock matrix (F_{ij}) and the term $\int \theta_i^*(1) \theta_j(1) dr_1$ is called as the overlap matrix (S_{ij}). Therefore, Eq. 23 can now be expressed as:

$$\sum_{j=1}^M F_{ij} C_{ja} = \varepsilon_a \sum_{j=1}^M S_{ij} C_{ja} \quad (\text{Eq. 24})$$

Using Eq. 24 into the SCF, all the problems until now are converted into a matrix problem, since Eq. 24 can be expressed as matrices:

$$\mathbf{FC} = \mathbf{SC}\varepsilon \quad (\text{Eq. 25})$$

The Eqs. 24 and 25 are known as the Roothaan equations. In Eq. 25, \mathbf{c} : MxM matrix composed of elements C_{ja} , while ε MxM matrix of the orbital energies ε_a . Hence, obtaining the energy of a molecular system is a minimization procedure which involves the diagonalization of a matrix MxM within the framework of the Roothaan equations.

The purpose of the HF methods is to improve the HF method to get even lower energy values, i.e. the energies are closer to the ground energy according to the variational method. Further reading is suggested to cover the post-HF methods. This is part of the autonomy of a graduate student.