

The Hartree-Fock Method

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The Hartree-Fock Method plays an important role in atomic physics and quantum chemistry. The present work aims to briefly discuss the basic concepts of the Hartree-Fock theory and its basic principles for *ab initio* calculations of electronic orbitals of atoms and molecules within the Born-Oppenheimer approximation.

Introduction

If all relativistic effects are neglected and the Born-Oppenheimer approximation is used, the electronic Hamiltonian of a hydrogen atom can be written in atomic units as follows ($Z = 1$):

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{\hat{R}}. \quad (1)$$

The solutions for the correspondent eigenvalues equation can be obtained analytically [1] by means of the separation of variables *ansatz* ($\psi(\vec{r}) = R(r)A(\theta, \phi)$), where the angular dependence happens to be the spherical harmonics $Y_{l,m_l}(\theta, \phi)$ and the radial dependence is given by the solution of the equation:

$$\begin{aligned} \frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} R(r) \right] + 2 \left(E_n - \frac{1}{r^2} \right) R(r) = \\ = l(l+1) \frac{R(r)}{r^2}. \end{aligned}$$

However, for molecules and atoms with more than one electron, the Hamiltonian needs to take into account the Coulomb interaction between electrons. For a molecule with N electrons and M nuclei at positions \vec{R}_K and atomic numbers Z_K ($K = 1, 2, \dots, M$), the Hamiltonian assumes the form:

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$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2}\nabla_i^2 - \sum_{K=1}^M \frac{Z_K}{r_{iK}} \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}}, \quad (2)$$

where $r_{iK} = |\vec{r}_i - \vec{R}_K|$ and $r_{ij} = |\vec{r}_i - \vec{r}_j|$.

Note that the Schrödinger equation for this Hamiltonian is not separable due to the repulsion term $1/r_{ij}$. Additionally, the spherical symmetry is lost if there is more than one atom. There are no known solutions for these cases and the best approach possible to solve this problem is to calculate numerically approximate wave functions.

One of the most well-established methods for calculating approximate solutions for the Schrödinger equation for atoms and molecules is the Hartree-Fock Self-Consistent Field (SCF) Method. The next session presents the theory that preceded it: the Hartree Method.

The Hartree SCF Method

The Hartree product

In order to find a way to write the total wave function for multiple electrons, it is considered a system of N noninteracting electrons in the presence of a given potential $V(\vec{r})$ with the Hamiltonian of the form:

$$\hat{H} = \sum_{i=1}^N \hat{h}(i), \quad (3)$$

where

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 + V(\vec{r}_i).$$

The operators $\hat{h}(i)$ have a set of eigenfunctions that are spatial orbitals $\varphi_j(\vec{r}_i)$, *i.e.*, $\hat{h}(i)\varphi_j(\vec{r}_i) = \epsilon_j\varphi_j(\vec{r}_i)$. Since the Hamiltonian is a sum of one-electron Hamiltonians, it is possible to show that an acceptable

answer for the total wave function of the system is a simple product of the spatial orbitals describing each electron:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2)\dots\varphi_k(\vec{r}_N), \quad (4)$$

This *ansatz* is called the *Hartree product* and:

$$\langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = E_0 = \epsilon_a + \epsilon_b + \dots + \epsilon_k \quad (5)$$

assuming orthonormalized spatial orbitals and hence a normalized total wave function $\Psi(\vec{r}_1, \dots, \vec{r}_N)$.

First-order perturbation

Recalling the perturbation treatment of the helium atom [2], it is possible to obtain a zeroth-order approximation solution for many-electron atoms and molecules by solving the problem with the assumption of noninteracting electrons and then calculating a correction for the ground state total energy using the perturbation theory. *I.e.*, neglecting the interaction between electrons, the Hamiltonian can be written as shown in Eq. 3, where each $\hat{h}(i)$ ($i = 1, 2$) has the form of Eq. 1 with $Z = 2$. The spatial orbitals can be calculated analytically (a maximum of two electrons can occupy a same orbital because of the Pauli exclusion principle) as commented in the previous session and the zeroth-order approximation energy is the sum of the energies of each electron (Eq. 5). Then, a correction ΔE in the energy can be calculated using the first-order correction in the perturbation theory, where the perturbation is the Coulomb potential between the electrons: $\Delta E = \langle \Psi | 1/r_{12} | \Psi \rangle$. Using the Hartree Product *ansatz*:

$$\begin{aligned} \Delta E &= \int d^3r_1 \int d^3r_2 \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) \frac{1}{r_{12}} \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) \\ &= \int d^3r_1 \int d^3r_2 \left[\varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2) \frac{1}{r_{12}} \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) \right] \end{aligned}$$

Generalizing for the N electrons case:

$$\begin{aligned} \Delta E &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \Psi | 1/r_{ij} | \Psi \rangle \\ &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N \int d^3r_i \int d^3r_j \varphi_i^*(\vec{r}_i)\varphi_j^*(\vec{r}_j) \times \\ &\quad \frac{1}{r_{ij}} \varphi_i(\vec{r}_i)\varphi_j(\vec{r}_j). \end{aligned} \quad (6)$$

Variational theorem

The variational theorem states that: given a time independent Hamiltonian $\hat{\mathcal{H}}$ with a discrete spectrum of eigenvalues whose lowest eigenvalue is the energy ϵ_0 and given any normalized state $|\phi\rangle$:

$$\langle \phi | \hat{\mathcal{H}} | \phi \rangle \geq \epsilon_0. \quad (7)$$

This relation can be easily proved by expanding the state $|\phi\rangle$ in terms of the complete and orthonormal set $\{|\psi_i\rangle\}$ of eigenfunctions of $\hat{\mathcal{H}}$ and calculating the expected value of energy.

$$|\phi\rangle = \sum_i c_i |\psi_i\rangle \implies \langle \phi | \hat{\mathcal{H}} | \phi \rangle = \sum_i c_i^* c_i \epsilon_i \geq \epsilon_0,$$

where the equality is true only if $|c_0| = 1$ and $c_j = 0$ ($j = 1, 2, \dots$), *i.e.*, $|\phi\rangle = |\psi_0\rangle$.

This means that no trial function will have an expected energy value lower than the ground state energy of the system. The variational theorem is very important because it gives rise to the *variational method*, where a trial function $\phi(\vec{r}) = \langle \vec{r} | \phi \rangle$ is chosen with one or more free parameters that will be calculated to minimize the value of $E_t = \langle \phi | \hat{\mathcal{H}} | \phi \rangle$. The function that minimizes E_t will be the best approximation for the ground state wave function and the quality of the approximation is given by the quality of the chosen trial function $\phi(\vec{r})$ or basis of functions $\{\phi_n(\vec{r})\}$.

The Hartree method

The Hartree method goes a few steps beyond the perturbation theory and is essentially variational. It looks for a convergent solution calculating iteratively the coulomb potential produced by the distribution of charges given by the probability density obtained from the spatial orbitals (Self-Consistent Field).

Hartree developed the SCF method by intuitive physical arguments: each electron is governed by a single-particle Schrödinger equation experiencing the Coulomb potential from the nuclei and from the $N - 1$ other electrons [3].

The procedure to calculate the wave functions starts with one zeroth-order approximation step: choosing trial variational spatial orbitals $\varphi_i(\vec{r}_i)$ for each electron, calculating the value for the variational parameters that minimize $\langle \varphi_i | \hat{h}^{(0)}(i) | \varphi_i \rangle$ to obtain $\varphi_i^{(0)} = \varphi_i$ where $\hat{h}(i)$ is the one-electron Hamiltonian for the electron i :

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{K=1}^M \frac{Z_K}{r_{iK}}. \quad (8)$$

The next iteration will calculate, for one electron at a time, the variational parameters that minimize $\langle \varphi_i | \hat{g}_{\text{SCF}}^{(1)}(i) | \varphi_i \rangle$ to find $\varphi_i^{(1)} = \varphi_i$, where[†]:

$$\hat{g}_{\text{SCF}}^{(1)}(i) = \hat{h}(i) + \sum_{j \neq i} v_{ij}^{(1)}(\vec{r}_i) \quad (9)$$

and v_{ij} is the potential experienced by the electron i and produced by the electron j .

$$v_{ij}^{(1)}(\vec{r}_i) = \int d^3 r_j \frac{|\varphi^{(0)}(\vec{r}_j)|^2}{r_{ij}}.$$

For the n -th iteration:

$$v_{ij}^{(n)}(\vec{r}_i) = \int d^3 r_j \frac{|\varphi^{(n-1)}(\vec{r}_j)|^2}{r_{ij}} \quad (10)$$

The calculation continues until there are no significant changes in the results from one iteration to the next. After convergence, the final set of orbitals $\{\varphi_i^{(f)}\}$ gives the approximate wave function.

In the SCF approximation, the energy of the atom is not equals to:

$$\sum_{i=1}^N \langle \varphi_i^{(f)} | \hat{g}_{\text{SCF}}^{(f)}(i) | \varphi_i^{(f)} \rangle$$

because in this case the electronic repulsion potential is summed twice. The total energy E is calculated by $\langle \Psi | \hat{\mathcal{H}} | \Psi \rangle$ with $\hat{\mathcal{H}}$ given by Eq. 2.

$$E = \sum_{i=1}^N \langle \Psi | \hat{h}(i) | \Psi \rangle + \sum_{i=1}^{N-1} \sum_{j=i}^N \langle \Psi | \frac{1}{r_{ij}} | \Psi \rangle$$

$$E = \sum_{i=1}^N \langle \varphi_i^{(f)} | \hat{h}(i) | \varphi_i^{(f)} \rangle +$$

$$+ \sum_{i=1}^{N-1} \sum_{j=i+1}^N \int d^3 r_i \int d^3 r_j \varphi_i^{(f)*}(\vec{r}_j) \varphi_j^{(f)*}(\vec{r}_j) \times \quad (11)$$

$$\frac{1}{r_{ij}} \varphi_i^{(f)}(\vec{r}_j) \varphi_j^{(f)}(\vec{r}_j).$$

This result is very similar to the result obtained using the first-order correction in the perturbation theory (Eq. 6). The great improvement obtained in using the Hartree method is that the orbitals are iteratively calculated.

[†]The index (n) stands for the n -th iteration.

However, there are intrinsic problems with the Hartree method. Even if no more than two electrons are put in each each spatial orbital, there is no way to write an antisymmetric total wave function with the Hartree product *ansatz* to satisfy the strong statement of the Pauli exclusion principle. This problem was pointed and corrected by Vladimir Fock and John Slater, giving rise to the Hartree-Fock method.

The Hartree-Fock SCF Method

Spatial orbitals and spin orbitals

An *orbital* is defined by the wave function of a single electron. The spatial distribution of electrons in a molecule can be described by spatial orbitals $\varphi(\vec{r})$, where the probability density to find the electron at a given position \vec{r} is $|\varphi(\vec{r})|^2$.

However a spatial orbital is not sufficient to completely describe an electron since it is necessary to specify its spin. A complete set to describe this quantity is composed by two orthonormal functions $\alpha(\omega)$ and $\beta(\omega)$ representing the spins up and down respectively. It is possible to define a function which describes simultaneously the spin and the spatial distribution of the particles. Such a function is called a *spin orbital* and will be represented as $\chi(\vec{x}) = \chi(\vec{r}, \omega)$.

For each spatial orbital $\varphi(\vec{r})$ there are two possible spin orbitals:

$$\chi(\vec{x}) = \begin{cases} \varphi(\vec{r})\alpha(\omega) \\ \varphi(\vec{r})\beta(\omega) \end{cases} \quad (12)$$

For a more detailed discussion refer to [4].

Slater determinants

The Pauli exclusion principle states that a system of indistinguishable fermions should be described by an antisymmetric total wave function. For a two-electrons case, the antisymmetric wave function can be written as follows:

$$\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\vec{x}_1)\chi_2(\vec{x}_2) - \chi_1(\vec{x}_2)\chi_2(\vec{x}_1)]. \quad (13)$$

For the N electrons case, the antisymmetric wave function can be written as a Slater determinant of spin-orbitals:

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix}. \quad (14)$$

The Fock operator

Considering a system with two electrons and a given state $|\phi\rangle$ written as the Eq. 13, the expected energy value $E = \langle \phi | \hat{H} | \phi \rangle$ is:

$$E = \frac{1}{2} \int d\vec{x}_1 \int d\vec{x}_2 [\chi_1^*(\vec{x}_1) \chi_2^*(\vec{x}_2) - \chi_1^*(\vec{x}_2) \chi_2^*(\vec{x}_1)] \hat{H} [\chi_1(\vec{x}_1) \chi_2(\vec{x}_2) - \chi_1(\vec{x}_2) \chi_2(\vec{x}_1)],$$

where \hat{H} is the molecular Hamiltonian given by Eq. 2. Thus,

$$E = \langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle + \int d\vec{x}_1 \int d\vec{x}_2 [\chi_1^*(1) \chi_2^*(2) \frac{1}{r_{12}} \chi_1(1) \chi_2(2) - \chi_1^*(1) \chi_2^*(2) \frac{1}{r_{12}} \chi_1(2) \chi_2(1)],$$

where $\langle i | \hat{h} | i \rangle = \int dx_i \chi_i^*(\vec{x}_i) \hat{h}(i) \chi_i(\vec{x}_i)$.

Back to the N electron case, it is possible to see that minimizing E is the equivalent [4] to solving the eigenvalues equation:

$$\hat{f}(i) \chi_i(\vec{x}_i) = \varepsilon_i \chi_i(\vec{x}_i), \quad (15)$$

where

$$\hat{f}(i) = \hat{h}(i) + \sum_{j \neq i} [\mathcal{J}_j(i) - \mathcal{K}_j(i)], \quad (16)$$

$$\mathcal{J}_j(i) \chi_i(\vec{x}_i) = \left[\int d\vec{x}_j \chi_j^*(\vec{x}_j) \frac{1}{r_{ij}} \chi_j(\vec{x}_j) \right] \chi_i(\vec{x}_i), \quad (17)$$

and

$$\mathcal{K}_j(i) \chi_i(\vec{x}_i) = \left[\int d\vec{x}_j \chi_j^*(\vec{x}_j) \frac{1}{r_{ij}} \chi_i(\vec{x}_j) \right] \chi_j(\vec{x}_i) \quad (18)$$

The operators \mathcal{J} and \mathcal{K} are the *Coulomb* and *exchange operators*. The operator $\hat{f}(i)$ is called the *Fock operator*.

The Hartree-Fock Method

The Fock operator is an approximation for the one-electron Hamiltonian added by the effective potential generated by the other electrons. Somehow, $\hat{h}(i)$ is an improved version of the operator $\hat{g}_{\text{SCF}}^{(n)}(i)$ (Eq. 9) in the Hartree method because the Fock operator takes into account the fermionic nature of the electrons. The algorithm of the calculations using the Hartree-Fock Method follows basically the same steps of the Hartree method.

Roothan Equations

One possible set of trial functions to perform the Hartree-Fock calculations is a set of the atomic orbitals. This means that each electronic orbital will be a *Linear Combination of Atomic Orbitals*:

$$\chi_i = \sum_{k=1}^B C_k^i \chi_k^{OA}. \quad (19)$$

By writing this into the Hartree-Fock equations it is possible to obtain the Roothan [5] equations:

$$FC = SC\epsilon, \quad (20)$$

where F is the matrix with elements $\langle \chi_i | \hat{f} | \chi_j \rangle$ called *Fock matrix*, S is the overlap matrix of the basis functions ($\langle \chi_i^{AO} | \chi_j^{AO} \rangle$), ϵ is the matrix of orbital energies and C is the matrix of coefficients to be varied to minimize the functional $\langle \phi | \hat{H} | \phi \rangle$.

References

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