Hartree-Fock Theory

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June 2015

1   Introduction

One of the most important applications of quantum theory is in the modeling of molecular systems. As we shall see shortly, any molecule with more than one electron is outside the reach of any analytical methods. In any reasonably interesting molecule, we are faced with the task of computationally determining an approximate solution to the many-body Schrödinger equation. There is a combination of theoretical properties and approximation techniques that allow us to find these solutions to high accuracy.

2   The Born-Oppenheimer Approximation

A full quantum model of a molecule would involve a wavefunction describing the behavior of nuclei and electrons together. However, there is a better approach that allows us to treat the electrons alone. Since a proton has a mass almost 2000 times that of an electron, nuclei move much slower than electrons. The Born-Oppenheimer approximation assumes that nuclei move slowly enough that they can be treated as static when analyzing the electrons. Therefore, our problem is simplified to finding a wavefunction for the electron coordinates, $\psi(\boldsymbol{e}_1, \boldsymbol{e}_2, \ldots, \boldsymbol{e}_n)$, with the nuclear coordinates fixed.

3   The Variational Method

The Schrödinger equation is an eigenvalue equation,

$$\hat{H}\psi_E = E\psi_E.$$

The Hamiltonian $\hat{H}$ is an operator and E is an energy eigenvalue; ψ_E is an eigenfunction. Additionally, $\hat{H}$ is a Hermitian operator, which means that its eigenfunctions form a complete orthonormal set: any wavefunction ψ can be expanded in a series of mutually orthogonal eigenfunctions of a given operator. That is, we can write

$$\psi = \sum_{i=0}^{\infty} a_i \psi_i,$$

where ψ_i is an eigenfunction of $\hat{H}$ with eigenvalue E_i.

Now, recall that the expected value of an operator $\hat{\mathcal{O}}$ is given by

$$\langle \hat{\mathcal{O}} \rangle = \int \psi^* \hat{\mathcal{O}} \psi \, d\tau,$$

where $d\tau$ indicates integration over the entire configuration space. It follows clearly from this definition that the expected value of $\hat{H}$ in an energy eigenstate ψ_i is simply the energy E_i. For an arbitrary wavefunction,

we can determine the expected value of the Hamiltonian by first expanding in series:

$$\langle \hat{H} \rangle = \int \left(\sum_{i=0}^{\infty} a_i^* \psi_i^* \right) \hat{H} \left(\sum_{i=0}^{\infty} a_i \psi_i \right) d\tau$$

$$= \int \left(\sum_{i=0}^{\infty} a_i^* \psi_i^* \right) \left(\sum_{i=0}^{\infty} a_i E_i \psi_i \right)$$

$$= \sum_{i=0}^{\infty} |a_i|^2 E_i,$$

where the last step follows from the orthogonality and normalization of the functions ψ_i. Since the quantities $|a_i|^2$ are positive semidefinite, we can assert that

$$\langle \hat{H} \rangle \geq E_0,$$

where E_0 denotes the minimum energy eigenvalue.

This property forms the basis for the so-called variational method. We are guaranteed that no wavefunction can have an energy expectation below that of the ground state wavefunction. Therefore, if we construct a parameterized family of wavefunctions and find the member with minimal $\langle \hat{H} \rangle$, we can be assured that it is a reasonable approximation to the ground state.

4   The Slater Determinant

The variational method permits us to find the best approximation to the ground state within a set of wavefunctions. We still must find a specification for this set. In the original Hartree theory, the wavefunctions were simple products of single-particle wavefunctions,

$$\psi(\boldsymbol{e}_1, \boldsymbol{e}_2, \ldots, \boldsymbol{e}_n) = \psi_1(\boldsymbol{e}_1)\psi_2(\boldsymbol{e}_2) \cdots \psi_n(\boldsymbol{e}_n).$$

The individual ψ_i would all be determined by a finite set of parameters, which we will discuss later. Regardless of the choice of the ψ_i, this Hartree product lacks one of the important properties of fermionic many-particle wavefunctions. The Pauli exclusion principle requires that no two electrons occupy the same state. We can show that this implies an antisymmetry under particle exchange. For example, in the two-electron case, we could expand the wavefunction as

$$\psi(\boldsymbol{e}_1, \boldsymbol{e}_2) = \sum_{i,j} A_{ij} \psi_i(\boldsymbol{e}_1) \psi_j(\boldsymbol{e}_2).$$

The probability of the two electrons occupying the same state is zero, so A_{ii} must vanish. This is true no matter what basis we have expanded the wavefunction into. One can show that if a matrix satisfies $A_{ii} = 0$ in every basis, then it must be antisymmetric, so that $A_{ij} = -A_{ji}$. In the general many-electron case, the corresponding tensor A must be skew-symmetric in every pair of indices; exchanging any pair of particles should cause a change of sign. This is clearly not the case for the Hartree product. Instead, we use the Slater determinant.

$$\psi(\boldsymbol{e}_1, \boldsymbol{e}_2, \ldots, \boldsymbol{e}_n) = |\psi_1 \psi_2 \ldots \psi_n\rangle = \begin{vmatrix} \psi_1(\boldsymbol{e}_1) & \psi_2(\boldsymbol{e}_1) & \cdots & \psi_n(\boldsymbol{e}_1) \\ \psi_1(\boldsymbol{e}_2) & \psi_2(\boldsymbol{e}_2) & \cdots & \psi_n(\boldsymbol{e}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\boldsymbol{e}_n) & \psi_2(\boldsymbol{e}_n) & \cdots & \psi_n(\boldsymbol{e}_n) \end{vmatrix}$$

Since determinants change sign under exchanges of columns, this wavefunction is guaranteed to have the required antisymmetry property. We will use the Slater determinant as our variational wavefunction; the expectation value of its energy will be minimized with respect to the parameters of the individual ψ_i.

5   The Hamiltonian

Before we proceed with minimizing an energy expectation, we need to have a Hamiltonian operator to work with. The Hamiltonian is composed of two main parts: the core Hamiltonian and the two-electron interaction. The core is the sum of the nuclear Coulomb attractions and the kinetic energy of the electrons,

$$H^{\text{core}} = -\sum_{i=1}^{n}\sum_{j=1}^{m}\frac{q_j}{|r_i - r_j|} - \frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 .^{1}$$

This can be written as a sum of operators acting on individual electrons; the core Hamiltonian comprises a series of one-body problems. The two-electron interaction is the source of the challenges of molecular modeling, because it entails the many-body problem.

$$H^{\text{elec}} = \sum_{i=1}^{n}\sum_{j=1}^{n}\frac{1}{r_{ij}}$$

6   The Self-Consistent Field Method

When we add the core Hamiltonian to the electron interaction terms, we obtain the total Hamiltonian operator

$$H = H^{\text{core}} + H^{\text{elec}}.$$

To use the variational method, we have to minimize the expected value of the Hamiltonian operator on the antisymmetrized wavefunction $|\psi_1\psi_2\ldots\psi_n\rangle$. We can write expressions for the expectation of each term in the Hamiltonian; if we consider only the H^{core} terms, then this is relatively simple. However, the H^{elec} terms introduce a complication because of the r_{ij} contribution. These terms depend on two wavefunctions each. In the self-consistent field method, we work around this by fixing one set of wavefunctions, ψ_i^{old}. We then vary the new wavefunctions, ψ_i^{new}, to minimize their energy expectation in the field of the old electrons. With this adjustment, we obtain the Fock operator. It is not a proper Hamiltonian for the system, but it contains only one-electron terms and so we are able to handle it easily. Once we find wavefunctions minimizing our Fock operator, we use them to compute a new Fock operator and repeat the process. After a number of iterations, this method leads to wavefunctions that minimize the actual Hamiltonian operator. This process is depicted in Figure 1.

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[1]Note the use of natural units: physical constants like $\hbar$, $\frac{1}{4\pi\epsilon_0}$ and m_e are scaled to have unit value.
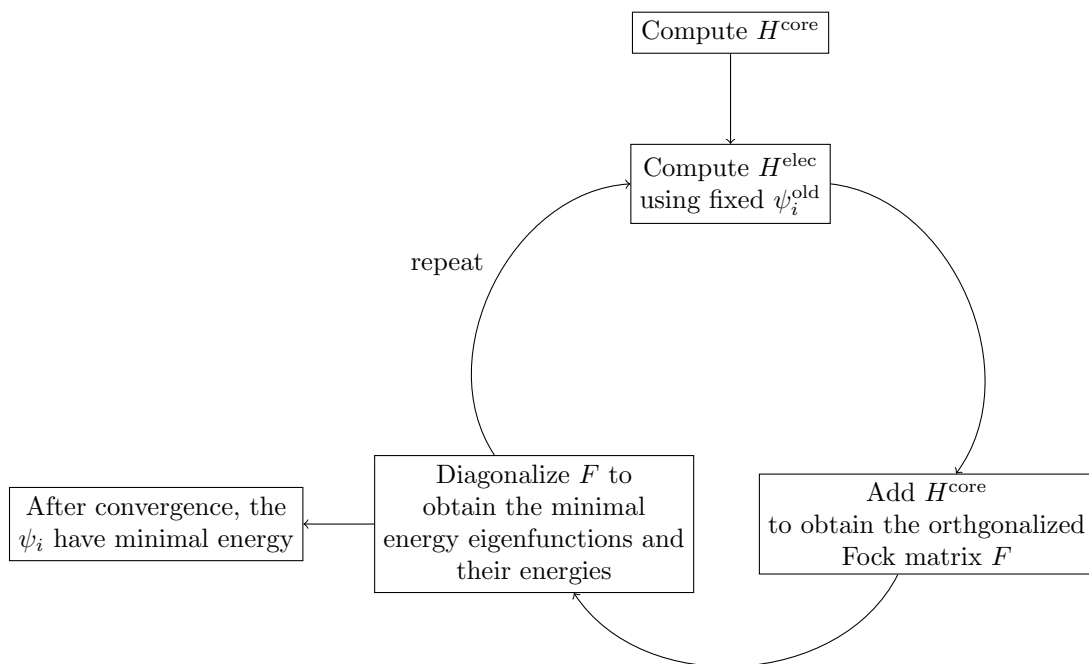
Figure 1: The SCF method for determining the ground state wavefunctions comprising the Slater determinant $|\psi_1 \psi_2 \ldots \psi_n\rangle$.