

Chem3208 Lectures 5–9

Hartree-Fock Theory

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The Hartree-Fock (HF) Method

- We consider the **time-independent** Schrödinger equation
- HF is an **ab initio method** i.e there's no parameter
- We don't care about **relativistic effects**
- We decouple nuclei and electrons \Rightarrow **Born-Oppenheimer approximation**
- Electronic part is solved with the nuclear positions as parameters \Rightarrow **potential energy surface (PES)**
- HF is an **independent-particle model** \Rightarrow **interactions are taken into account in an average fashion**
- the motion of one electron **is considered to be independent of the dynamics of all other electrons**
- We are interested by **electrons** which are **fermions** \Rightarrow **Pauli exclusion principle**
 $|\alpha\rangle =$ **spin-up** electron and $|\beta\rangle =$ **spin-down** electron

$$\langle\alpha|\beta\rangle = 0 \quad \langle\alpha|\alpha\rangle = 1 \quad \langle\beta|\beta\rangle = 1$$

- HF is the starting point of pretty much anything!

Antisymmetry

Pauli Exclusion Principle

“For a system of two fermions, the wave function vanishes when they are at the same point in space”

Indistinguishable particles means

$$|\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2 \Rightarrow \Psi(x_1, x_2) = \pm \Psi(x_2, x_1)$$

Bosons mean $\Psi(x_1, x_2) = \Psi(x_2, x_1)$ and Fermions mean $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$

Let's put them at the same spot, i.e. $x = x_1 = x_2$

$$\text{For Fermions, } \Psi(x, x) = -\Psi(x, x) \Rightarrow \boxed{\Psi(x, x) = 0}$$

The wave function vanishes!

Antisymmetry (Take 2)

Problem: Fermionic wave function

“Given two one-electron functions $\chi_1(x)$ and $\chi_2(x)$, could you construct a two-electron (fermionic) wave function $\Psi(x_1, x_2)$?”

Antisymmetry (Take 2)

Problem: Fermionic wave function

“Given two one-electron functions $\chi_1(x)$ and $\chi_2(x)$, could you construct a two-electron (fermionic) wave function $\Psi(x_1, x_2)$?”

Solution

A possible solution is

$$\Psi(x_1, x_2) = \chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)$$

This has been popularized by Slater:

$$\Psi(x_1, x_2) = \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) \\ \chi_1(x_2) & \chi_2(x_2) \end{vmatrix} = \chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)$$

This is called a Slater determinant!

A wave function of the form $\Psi(x_1, x_2) = \chi_1(x_1)\chi_2(x_2)$ is called a **Hartree product**

The Hartree-Fock Wave Function

A Slater determinant

$$\begin{aligned}
 \mathbf{x} = (\mathbf{r}, \omega) \quad \Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \\
 &= \mathcal{A} \chi_1(\mathbf{r}_1) \chi_2(\mathbf{r}_2) \cdots \chi_N(\mathbf{r}_N) \\
 &= \mathcal{A} \Pi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)
 \end{aligned}$$

- The variable \mathbf{x} combines **spin** (ω) and **spatial** (\mathbf{r}) coordinates
- \mathcal{A} is called the **antisymetrizer**
- $\Pi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is a **Hartree product**
- Ψ_{HF} is an antisymmetrized product of one-electron functions

The Hartree-Fock Wave Function (Take 2)

Molecular orbitals (MO)

$$\chi_i(\mathbf{x}) = \sigma(\omega)\psi_i(\mathbf{r}) = \begin{cases} \alpha(\omega)\psi_i(\mathbf{r}) \\ \beta(\omega)\psi_i(\mathbf{r}) \end{cases}$$

$$\psi_i(\mathbf{r}) = \sum_{\mu}^K c_{\mu i} \phi_{\mu}(\mathbf{r})$$

These are **restricted spin orbitals** \Rightarrow Restricted Hartree-Fock = **RHF**

The spin orbitals are orthogonal

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$$

The spatial orbitals are orthogonal

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} = \text{Kronecker delta}$$

The atomic orbitals **are not** orthogonal

$$\langle \phi_{\mu} | \phi_{\nu} \rangle = S_{\mu\nu} = \text{Overlap matrix}$$

The Hartree-Fock Wave Function (Take 3)

Comments

- $\phi_\mu(\mathbf{r})$ is called an **atomic orbital (AO)**
- $\chi_i(\mathbf{x})$ is a **spin orbital = MO**
- $\psi_i(\mathbf{r})$ is a **spatial orbital = MO**
- $\sigma = \alpha$ for **spin-up electrons** and $\sigma = \beta$ for **spin-down electrons**
- With K AOs, we can create K **spatial orbitals** and $2K$ **spin orbitals**
- When a system has **2 electrons in each orbital**, it is called a **closed-shell system**
- The **spatial orbitals** and the **spin orbitals** form orthogonal bases
- The AOs are not orthogonal to each other
- The MOs are build by **linear combination of AOs (LCAO)**
- The coefficient $C_{\mu i}$ are determined via the **HF equations** based on **variational principle**

The Variational Principle

Problem

“Let’s suppose we know all the functions such as $\mathbf{H}\varphi_i = E_i\varphi_i$, with $E_0 < E_1 < \dots$ and $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$. Show that, for any normalized Ψ , we have $E = \langle \Psi | \mathbf{H} | \Psi \rangle \geq E_0$ ”