

The Hartree–Fock Approximation

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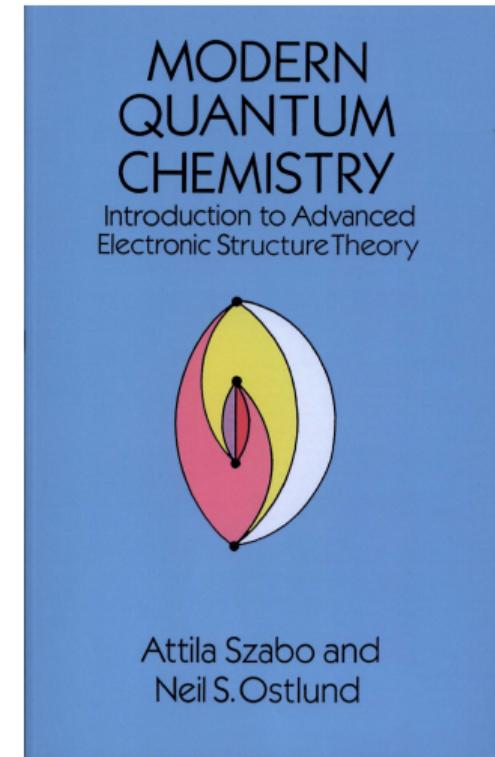
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How to perform a HF calculation in practice?

The SCF algorithm for Hartree-Fock (HF) calculations (p. 146)

- ➊ Specify molecule $\{R_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$
- ➋ Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle \mu\nu | \lambda\sigma \rangle$
- ➌ Diagonalize \mathbf{S} and compute $\mathbf{X} = \mathbf{S}^{-1/2}$
- ➍ Obtain guess density matrix for \mathbf{P}
 1. Calculate \mathbf{J} and \mathbf{K} , then $\mathbf{F} = \mathbf{H} + \mathbf{J} + \mathbf{K}$
 2. Compute $\mathbf{F}' = \mathbf{X}^\dagger \cdot \mathbf{F} \cdot \mathbf{X}$
 3. Diagonalize \mathbf{F}' to obtain \mathbf{C}' and \mathbf{E}
 4. Calculate $\mathbf{C} = \mathbf{X} \cdot \mathbf{C}'$
 5. Form a new density matrix $\mathbf{P} = \mathbf{C} \cdot \mathbf{C}^\dagger$
 6. Am I converged? If not go back to 1.
- ➎ Calculate stuff that you want, like E_{HF} for example



Szabo's and Ostlund's book

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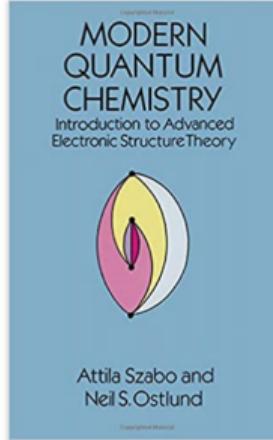
Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory (Dover Books on Chemistry)

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Motivations & Assumptions

- 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**
- HF is an **independent-particle model**, i.e., the motion of one electron **is considered to be independent of the dynamics of all other electrons** ⇒ **interactions are taken into account in an average fashion**
- HF is the starting point of pretty much anything!

The Hamiltonian

In the Schrödinger equation

$$\mathcal{H}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) = \mathcal{E}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) \quad (1)$$

the total Hamiltonian is

$$\mathcal{H} = \mathcal{T}_n + \mathcal{T}_e + \mathcal{V}_{ne} + \mathcal{V}_{ee} + \mathcal{V}_{nn} \quad (2)$$

What are all these terms?

- \mathcal{T}_n is the kinetic energy of the nuclei
- \mathcal{T}_e is the kinetic energy of the electrons
- \mathcal{V}_{ne} is the Coulomb attraction between nuclei and electrons
- \mathcal{V}_{ee} is the Coulomb repulsion between electrons
- \mathcal{V}_{nn} is the Coulomb repulsion between nuclei

The Hamiltonian (Take 2)

In atomic units ($m = e = \hbar = 1$)

$$\mathcal{T}_n = - \sum_{A=1}^M \frac{\nabla_A^2}{2M_A} \quad (3a)$$

$$\mathcal{T}_e = - \sum_{i=1}^N \frac{\nabla_i^2}{2} \quad (3b)$$

$$\mathcal{V}_{ne} = - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{r_{iA}} \quad (3c)$$

$$\mathcal{V}_{ee} = \sum_{i < j}^N \frac{1}{r_{ij}} \quad (3d)$$

$$\mathcal{V}_{nn} = \sum_{A < B}^M \frac{Z_A Z_B}{R_{AB}} \quad (3e)$$

- ∇^2 is the **Laplace operator** (or Laplacian)
- M_A is the **mass** of nucleus A
- Z_A is the **charge** of nucleus A
- r_{iA} is the **distance** between electron i and nucleus A
- r_{ij} is the **distance** between electrons i and j
- R_{AB} is the **distance** between nuclei A and B

Molecular coordinate system

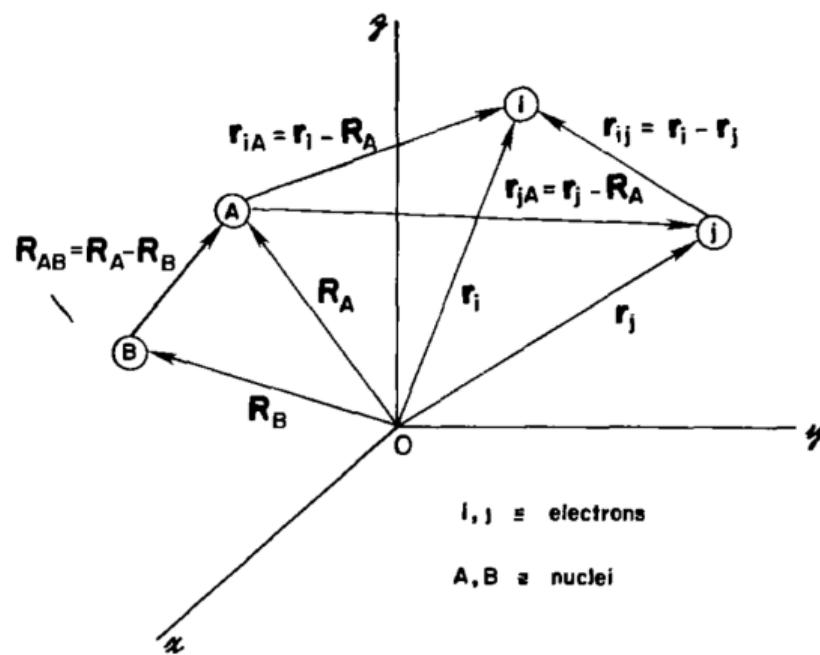


Figure 2.1 A molecular coordinate system $i, j =$ electrons, $A, B =$ nuclei

The Born-Oppenheimer approximation

Born-Oppenheimer approximation = decoupling nuclei and electrons

Because $M_A \gg 1$, the nuclear coordinates are “parameters” \Rightarrow potential energy surface (PES)

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) = \Phi_{\text{nucl}}(\{\mathbf{R}_A\}) \Phi_{\text{elec}}(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) \quad \text{with} \quad \mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{elec}} + \sum_{A < B}^M \frac{Z_A Z_B}{R_{AB}} \quad (4)$$

Nuclear Hamiltonian

The **nuclear Hamiltonian** is

$$\mathcal{H}_{\text{nucl}} \Phi_{\text{nucl}} = \mathcal{E}_{\text{nucl}} \Phi_{\text{nucl}} \quad \text{with} \quad \mathcal{H}_{\text{nucl}} = \mathcal{T}_n + \mathcal{V}_{nn} \quad (5)$$

It describes the vibration, rotation and translation of the molecules

Electronic Hamiltonian

The **electronic Hamiltonian** is

$$\mathcal{H}_{\text{elec}} \Phi_{\text{elec}} = \mathcal{E}_{\text{elec}} \Phi_{\text{elec}} \quad \text{with} \quad \mathcal{H}_{\text{elec}} = \mathcal{T}_e + \mathcal{V}_{ne} + \mathcal{V}_{ee} \quad (6)$$

Separability of the Schrödinger equation

Problem:

“Assuming that $\hat{H} = \hat{H}_A + \hat{H}_B$ with $\hat{H}_A \Psi_A = E_A \Psi_A$ and $\hat{H}_B \Psi_B = E_B \Psi_B$, find the expression of Ψ and E such that $\hat{H}\Psi = E\Psi$ ”

Separability of the Schrödinger equation

Problem:

"Assuming that $\hat{H} = \hat{H}_A + \hat{H}_B$ with $\hat{H}_A \Psi_A = E_A \Psi_A$ and $\hat{H}_B \Psi_B = E_B \Psi_B$, find the expression of Ψ and E such that $\hat{H}\Psi = E\Psi$ "

Solution:

Let's try $\Psi = \Psi_A \Psi_B$ and see if we're lucky.

Then,

$$\begin{aligned}\hat{H}\Psi &= (\hat{H}_A + \hat{H}_B)\Psi_A \Psi_B \\ &= \hat{H}_A \Psi_A \Psi_B + \hat{H}_B \Psi_A \Psi_B \\ &= E_A \Psi_A \Psi_B + E_B \Psi_A \Psi_B \\ &= \underbrace{(E_A + E_B)}_E \underbrace{\Psi_A \Psi_B}_\Psi\end{aligned}$$

Spin of the electron

We are interested by electrons which are fermions \Rightarrow Pauli exclusion principle (cf next slide)

Spin functions: $|\sigma\rangle = |s, m_s\rangle \quad s^2 |s, m_s\rangle = s(s+1) |s, m_s\rangle \quad s_z |s, m_s\rangle = m_s |s, m_s\rangle$

$|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$ spin-up electron $|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$ = spin-down electron

$$\int \alpha^*(\omega) \beta(\omega) d\omega = \int \beta^*(\omega) \alpha(\omega) d\omega = 0 \quad \int \alpha^*(\omega) \alpha(\omega) d\omega = \int \beta^*(\omega) \beta(\omega) d\omega = 1 \quad (7)$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \quad \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \quad (8)$$

The composite variable \mathbf{x} combines spin (ω) and spatial (\mathbf{r}) coordinates: $\mathbf{x} = (\omega, \mathbf{r})$

Antisymmetry principle

$$\mathcal{H}_{\text{elec}} \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \mathcal{E}_{\text{elec}} \Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (9)$$

$$\Phi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = -\Phi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N) \quad (10)$$

Antisymmetry

Problem:

“Show that, for a system of two fermions, the wave function vanishes when they are at the same point in spin-space”

Antisymmetry

Problem:

Show that, for a system of two fermions, the wave function vanishes when they are at the same point in spin-space"

Solution

Indistinguishable particles means

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1)|^2 \Rightarrow \Psi(\mathbf{x}_1, \mathbf{x}_2) = \pm \Psi(\mathbf{x}_2, \mathbf{x}_1) \quad (11)$$

Antisymmetry

Problem:

Show that, for a system of two fermions, the wave function vanishes when they are at the same point in spin-space"

Solution

Indistinguishable particles means

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1)|^2 \Rightarrow \Psi(\mathbf{x}_1, \mathbf{x}_2) = \pm \Psi(\mathbf{x}_2, \mathbf{x}_1) \quad (11)$$

Bosons mean $\Psi(\mathbf{x}_1, \mathbf{x}_2) = \Psi(\mathbf{x}_2, \mathbf{x}_1)$ and Fermions mean $\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$

Let's put them at the same spot, i.e. $\mathbf{x} = \mathbf{x}_1 = \mathbf{x}_2$

$$\text{For Fermions, } \Psi(\mathbf{x}, \mathbf{x}) = -\Psi(\mathbf{x}, \mathbf{x}) \Rightarrow \boxed{\Psi(\mathbf{x}, \mathbf{x}) = 0} \quad (12)$$

The wave function vanishes! \Rightarrow This is called the Fermi hole!

Antisymmetry (Take 2)

Problem:

“Given two one-electron functions $\chi_1(\mathbf{x})$ and $\chi_2(\mathbf{x})$, could you construct a two-electron (fermionic) wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$?”

Antisymmetry (Take 2)

Problem:

"Given two one-electron functions $\chi_1(\mathbf{x})$ and $\chi_2(\mathbf{x})$, could you construct a two-electron (fermionic) wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$?"

Solution

A possible solution is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) \quad (13)$$

This has been popularized by [Slater](#):

$$\boxed{\Psi(\mathbf{x}_1, \mathbf{x}_2) = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix} = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)} \quad (14)$$

This is called a **Slater determinant!**

A wave function of the form $\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)$ is called a **Hartree product**

The HF wave function

A Slater determinant

$$\Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_N(\mathbf{x}_N)\rangle \quad (15)$$
$$= \mathcal{A}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_N(\mathbf{x}_N) = \mathcal{A}\Pi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

- \mathcal{A} is called the **antisymmetrizer**
- $\Pi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is a **Hartree product**
- The many-electron wave function $\Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is an antisymmetrized product of one-electron functions

Spin and spatial orbitals

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

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

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

The spin orbitals are orthogonal

$$\langle \chi_i | \chi_j \rangle = \int \chi_i^*(\mathbf{x}) \chi_j(\mathbf{x}) d\mathbf{x} = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$$

The spatial orbitals are orthogonal

$$\langle \psi_i | \psi_j \rangle = \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} = \text{Kronecker delta}$$

The basis functions (or atomic orbitals) **are, a priori, not** orthogonal

$$\langle \phi_{\mu} | \phi_{\nu} \rangle = \int \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} = S_{\mu\nu} = \text{Overlap matrix}$$

Spin and spatial orbitals (Take 2)

Comments

- $\{\phi_\mu | i = 1, \dots, K\}$ are basis functions or **atomic orbitals (AOs)**
- $\{\chi_i | i = 1, \dots, 2K\}$ are the **spin orbitals**
- $\{\psi_i | i = 1, \dots, K\}$ are the **spatial orbitals** or **molecular orbitals (MOs)**
- With K AOs, one can create K **spatial orbitals** and $2K$ **spin orbitals**
- For the ground state, the first N **spin orbitals** are occupied and the last $2K - N$ are vacant (unoccupied)
- When a system has **2 electrons in each orbital**, it is called a **closed-shell** system, otherwise it is called a **open-shell** system
- For the ground state of a closed shell, the first $N/2$ **spatial orbitals** are doubly-occupied and the last $K - N/2$ are vacant (unoccupied)
- 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**

Ground-state Hartree-Fock determinant

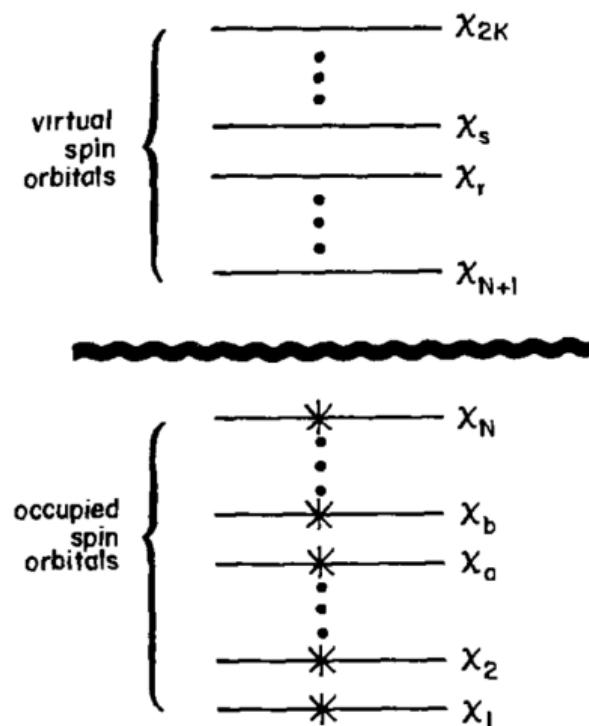


Figure 2.4 The Hartree-Fock ground state determinant, $|\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$.

Excited determinants

Reference determinant

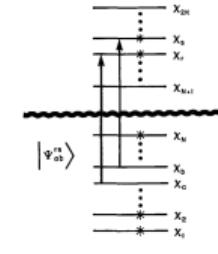
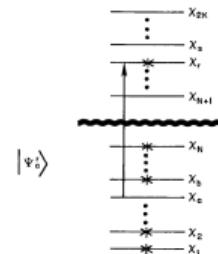
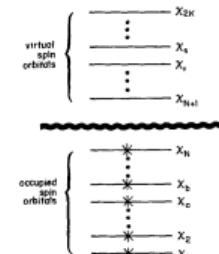
The electrons are in the N lowest orbitals (Aufbau principle): $|\Psi_0\rangle = |\chi_1 \dots \chi_a \chi_b \dots \chi_N\rangle$ (16)

Singly-excited determinants

Electron in a promoted in r : $|\Psi_{\text{a}}^r\rangle = |\chi_1 \dots \chi_r \chi_a \chi_b \dots \chi_N\rangle$ (17)

Doubly-excited determinants

Electrons in a and b promoted in r and s : $|\Psi_{ab}^{rs}\rangle = |\chi_1 \dots \chi_r \chi_s \chi_a \chi_b \dots \chi_N\rangle$ (18)



The Hartree-Fock energy

The HF energy is

$$E_{\text{HF}} = \langle \Psi_{\text{HF}} | \mathcal{H}_{\text{elec}} + \mathcal{V}_{\text{nn}} | \Psi_{\text{HF}} \rangle \quad \text{where} \quad \mathcal{H}_{\text{elec}} = \mathcal{T}_e + \mathcal{V}_{ne} + \mathcal{V}_{ee} \quad (19)$$

We define a few quantities:

- the one-electron Hamiltonian (or core Hamiltonian) = nice guy!

$$\mathcal{O}_1 = \mathcal{T}_e + \mathcal{V}_{ne} = \sum_{i=1}^N h(i) \quad \text{where} \quad h(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad (20)$$

- the two-electron Hamiltonian (electron-electron repulsion) = nasty guy!

$$\mathcal{O}_2 = \mathcal{V}_{ee} = \sum_{i < j}^N \frac{1}{r_{ij}} \quad (21)$$

Therefore, we have

$$\mathcal{H}_{\text{elec}} = \sum_{i=1}^N h(i) + \sum_{i < j}^N \frac{1}{r_{ij}} \quad (22)$$

The Hartree-Fock energy (Take 2)

- Nuclear repulsion:

$$\langle \Psi_{\text{HF}} | \mathcal{V}_{\text{nn}} | \Psi_{\text{HF}} \rangle = V_{\text{nn}} \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle = V_{\text{nn}} \quad (23)$$

- Core Hamiltonian:

$$\langle \Psi_{\text{HF}} | \mathcal{O}_1 | \Psi_{\text{HF}} \rangle = \sum_{a=1}^N \langle \chi_a(1) | h(1) | \chi_a(1) \rangle = \sum_{a=1}^N h_a \quad (24)$$

- Two-electron Hamiltonian:

$$\begin{aligned} \langle \Psi_{\text{HF}} | \mathcal{O}_2 | \Psi_{\text{HF}} \rangle &= \sum_{a < b}^N [\langle \chi_a(1) \chi_b(2) | r_{12}^{-1} | \chi_a(1) \chi_b(2) \rangle - \langle \chi_a(1) \chi_b(2) | r_{12}^{-1} | \chi_b(1) \chi_a(2) \rangle] \\ &= \sum_{a < b}^N \left(\underbrace{\mathcal{J}_{ab}}_{\text{Coulomb}} - \underbrace{\mathcal{K}_{ab}}_{\text{Exchange}} \right) = \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab}) \quad \text{because } \boxed{\mathcal{J}_{aa} = \mathcal{K}_{aa}} \end{aligned} \quad (25)$$

- HF energy:

$$E_{\text{HF}} = \sum_{a=1}^N h_a + \sum_{a < b}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab}) + V_{\text{nn}}$$

(26)

The Hartree-Fock energy (Take 3)

- Coulomb operator

$$\mathcal{J}_j(1) |\chi_i(1)\rangle = \langle \chi_j(2) | r_{12}^{-1} | \chi_j(2) \rangle |\chi_i(1)\rangle = \left[\int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_j(\mathbf{x}_2) \right] |\chi_i(\mathbf{x}_1)\rangle \quad (27)$$

- Coulomb matrix elements

$$\begin{aligned} \mathcal{J}_{ij} &= \langle \chi_i(1) | \mathcal{J}_j(1) | \chi_i(1) \rangle = \langle \chi_i(1) \chi_j(2) | r_{12}^{-1} | \chi_i(1) \chi_j(2) \rangle \\ &= \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (28)$$

- (non-local) Exchange operator

$$\mathcal{K}_j(1) |\chi_i(1)\rangle = \langle \chi_j(2) | r_{12}^{-1} | \chi_i(2) \rangle |\chi_j(1)\rangle = \left[\int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_2) \right] |\chi_j(\mathbf{x}_2)\rangle \quad (29)$$

- Exchange matrix elements

$$\begin{aligned} \mathcal{K}_{ij} &= \langle \chi_i(1) | \mathcal{K}_j(1) | \chi_i(1) \rangle = \langle \chi_i(1) \chi_j(2) | r_{12}^{-1} | \chi_j(1) \chi_i(2) \rangle \\ &= \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (30)$$

Integral notations

Spin orbitals

$$[i|h|j] = \langle i|h|j \rangle = \int \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1) d\mathbf{x}_1 \quad (31)$$

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = [ik|jl] \quad (32)$$

$$[ij|kl] = [\chi_i \chi_j | \chi_k \chi_l] = \iint \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = \langle ik|jl \rangle \quad (33)$$

$$\langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (34)$$

Spatial orbitals

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1) d\mathbf{r}_1 \quad (35)$$

$$(ij|kl) = (\psi_i \psi_j | \psi_k \psi_l) = \iint \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \frac{1}{r_{12}} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (36)$$

Permutation symmetry

Permutation symmetry in physicists' notations

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (37)$$

Complex-valued integrals: $\langle ij|kl \rangle = \langle ji|lk \rangle = \langle kl|ij \rangle^* = \langle lk|ji \rangle^*$ (38)

Permutation symmetry in chemists' notations

$$[ij|kl] = [\chi_i \chi_j | \chi_k \chi_l] = \iint \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (39)$$

Real-valued integrals: $[ij|kl] = [ji|kl] = [ij|lk] = [ji|lk] = [kl|ij] = [lk|ij] = [kl|ji] = [lk|ji]$ (40)

Slater-Condon rules: One-electron operators

$$\mathcal{O}_1 = \sum_i^N h(i) \quad (41)$$

Case 1 = differ by zero spinorbital: $|K\rangle = |\dots mn\dots\rangle$

$$\langle K | \mathcal{O}_1 | K \rangle = \sum_m^N \langle m | h | m \rangle \quad (42)$$

Case 2 = differ by one spinorbital: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pn\dots\rangle$

$$\langle K | \mathcal{O}_1 | L \rangle = \langle m | h | p \rangle \quad (43)$$

Case 3 = differ by two spinorbitals: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pq\dots\rangle$

$$\langle K | \mathcal{O}_1 | L \rangle = 0 \quad (44)$$

Slater-Condon rules: Two-electron operators

$$\mathcal{O}_2 = \sum_{i < j}^N r_{ij}^{-1} \quad (45)$$

Case 1 = differ by zero spinorbital: $|K\rangle = |\dots mn\dots\rangle$

$$\langle K | \mathcal{O}_2 | K \rangle = \frac{1}{2} \sum_{mn}^N \langle mn || mn \rangle \quad (46)$$

Case 2 = differ by one spinorbital: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pn\dots\rangle$

$$\langle K | \mathcal{O}_2 | L \rangle = \sum_n^N \langle mn || pn \rangle \quad (47)$$

Case 3 = differ by two spinorbitals: $|K\rangle = |\dots mn\dots\rangle$ and $|L\rangle = |\dots pq\dots\rangle$

$$\langle K | \mathcal{O}_2 | L \rangle = \langle mn || pq \rangle \quad (48)$$

The Hartree-Fock energy: examples

Problem: Normalization of the HF wave function

"Show that the HF wave function built with two (normalized) spin orbitals χ_1 and χ_2 is normalized"

The Hartree-Fock energy: examples

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Solution

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \frac{\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)}{\sqrt{2}}$$
$$\begin{aligned} \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle &= \frac{1}{2} \langle \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2) | \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2) \rangle \\ &= \frac{1}{2} \left[\langle \chi_1(1)\chi_2(2) | \chi_1(1)\chi_2(2) \rangle - \langle \chi_1(1)\chi_2(2) | \chi_2(1)\chi_1(2) \rangle \right. \\ &\quad \left. - \langle \chi_2(1)\chi_1(2) | \chi_1(1)\chi_2(2) \rangle + \langle \chi_2(1)\chi_1(2) | \chi_2(1)\chi_1(2) \rangle \right] \\ &= \frac{1}{2} [1 - 0 - 0 + 1] = 1 \end{aligned}$$

Remember that $\langle \chi_1(1)\chi_2(2) | \chi_1(1)\chi_2(2) \rangle = \langle \chi_1(1) | \chi_1(1) \rangle \langle \chi_2(2) | \chi_2(2) \rangle$

The Hartree-Fock energy: examples (Take 2)

Problem: Core Hamiltonian

"Show that $\langle \Psi_{HF} | \mathcal{O}_1 | \Psi_{HF} \rangle = \sum_{a=1}^N h_a$ for the same system"

The Hartree-Fock energy: examples (Take 2)

Problem: Core Hamiltonian

Show that $\langle \Psi_{HF} | \mathcal{O}_1 | \Psi_{HF} \rangle = \sum_{a=1}^N h_a$ for the same system"

Solution

$$\mathcal{O}_1 = h(1) + h(2)$$

$$\begin{aligned}\langle \Psi_{HF} | h(1) + h(2) | \Psi_{HF} \rangle &= \frac{1}{2} \langle \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1) | h(1) + h(2) | \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1) \rangle \\ &= \frac{1}{2} \left[\langle \chi_1(1)\chi_2(2) | h(1) + h(2) | \chi_1(1)\chi_2(2) \rangle - \langle \chi_1(1)\chi_2(2) | h(1) + h(2) | \chi_2(1)\chi_1(2) \rangle \right. \\ &\quad \left. - \langle \chi_2(1)\chi_1(2) | h(1) + h(2) | \chi_1(1)\chi_2(2) \rangle + \langle \chi_2(1)\chi_1(2) | h(1) + h(2) | \chi_2(1)\chi_1(2) \rangle \right] \\ &= \frac{1}{2} [h_1 + h_2 - 0 - 0 + h_2 + h_1] = h_1 + h_2\end{aligned}$$

The Hartree-Fock energy: examples (Take 3)

Problem: Two-electron Hamiltonian

“Show that $\langle \Psi_{HF} | \mathcal{O}_2 | \Psi_{HF} \rangle = \sum_{a < b}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab})$ for the same system and write down the HF energy”

The Hartree-Fock energy: examples (Take 3)

Problem: Two-electron Hamiltonian

“Show that $\langle \Psi_{HF} | \mathcal{O}_2 | \Psi_{HF} \rangle = \sum_{a < b}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab})$ for the same system and write down the HF energy”

Solution

$$\begin{aligned}\mathcal{O}_2 &= r_{12}^{-1} \\ \langle \Psi_{HF} | r_{12}^{-1} | \Psi_{HF} \rangle &= \frac{1}{2} \langle \chi_1 \chi_2 - \chi_2 \chi_1 | r_{12}^{-1} | \chi_1 \chi_2 - \chi_2 \chi_1 \rangle \\ &= \frac{1}{2} \left[\langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_2 \chi_1 \rangle \right. \\ &\quad \left. - \langle \chi_2 \chi_1 | r_{12}^{-1} | \chi_1 \chi_2 \rangle + \langle \chi_2 \chi_1 | r_{12}^{-1} | \chi_2 \chi_1 \rangle \right] \\ &= \frac{1}{2} [\mathcal{J}_{12} - \mathcal{K}_{12} - \mathcal{K}_{12} + \mathcal{J}_{12}] = \mathcal{J}_{12} - \mathcal{K}_{12}\end{aligned}$$

Remember that $\langle \chi_2 \chi_1 | r_{12}^{-1} | \chi_2 \chi_1 \rangle = \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_1 \chi_2 \rangle$

$$E_{HF} = h_1 + h_2 + \mathcal{J}_{12} - \mathcal{K}_{12}$$

The Hartree-Fock energy: examples (Take 4)

Three-electron system

“Find the HF energy of a three-electron system composed by the spin orbitals χ_1, χ_2 and χ_3 ”

Solution

$$\mathcal{O}_1 = h(1) + h(2) + h(3)$$

$$\mathcal{O}_2 = r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}$$

⋮

$$E_{\text{HF}} = h_1 + h_2 + h_3 + \mathcal{J}_{12} + \mathcal{J}_{13} + \mathcal{J}_{23} - \mathcal{K}_{12} - \mathcal{K}_{13} - \mathcal{K}_{23}$$

HF energy of He

Singlet $1s^2$ state of the He atom

$$\chi_1 = \alpha \psi_1 \quad \chi_2 = \beta \psi_1$$

$$E_{\text{HF}}(\text{singlet}) = h_1 + h_2 + \mathcal{J}_{12} - \mathcal{K}_{12} = 2h_1 + J_{11}$$

$$\begin{aligned}\mathcal{J}_{12} &= \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle \\ &= \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle \langle \psi_1 \psi_1 | \psi_1 \psi_1 \rangle = J_{11}\end{aligned}$$

$$\begin{aligned}\mathcal{K}_{12} &= \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle \\ &= \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle \langle \psi_1 \psi_1 | \psi_1 \psi_1 \rangle = 0\end{aligned}$$

Triplet $1s2s$ state of the He atom

$$\chi_1 = \alpha \psi_1 \quad \chi_2 = \alpha \psi_2$$

$$E_{\text{HF}}(\text{triplet}) = h_1 + h_2 + \mathcal{J}_{12} - \mathcal{K}_{12} = h_1 + h_2 + J_{12} - K_{12}$$

Singlet-triplet energy splitting

$$\begin{aligned}\Delta E_{\text{HF}} &= E_{\text{HF}}(\text{triplet}) - E_{\text{HF}}(\text{singlet}) \\ &= \underbrace{(h_2 - h_1)}_{>0} + \underbrace{(J_{12} - J_{11})}_{<0} - K_{12}\end{aligned}$$

HF Energy of Atoms

Problem: HF energy of the Li atom

“Find the HF energy of the Li atom in terms of the spatial MOs”

HF Energy of Atoms

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Solution:

$$\chi_1 = \alpha \psi_1 \quad \chi_2 = \beta \psi_1 \quad \chi_3 = \alpha \psi_2 \quad \chi_4 = \beta \psi_2$$

$$E_{\text{HF}} = 2h_1 + h_2 + J_{11} + 2J_{12} - K_{12}$$

HF Energy of Atoms

Problem: HF energy of the Li atom

“Find the HF energy of the Li atom in terms of the spatial MOs”

Solution:

$$\chi_1 = \alpha \psi_1 \quad \chi_2 = \beta \psi_1 \quad \chi_3 = \alpha \psi_2 \quad \chi_4 = \beta \psi_2$$

$$E_{\text{HF}} = 2h_1 + h_2 + J_{11} + 2J_{12} - K_{12}$$

Problem: HF energy of the B atom

“Find the HF energy of the B atom’ in terms of the spatial MOs’

HF Energy of Atoms

Problem: HF energy of the Li atom

“Find the HF energy of the Li atom in terms of the spatial MOs”

Solution:

$$\chi_1 = \alpha \psi_1 \quad \chi_2 = \beta \psi_1 \quad \chi_3 = \alpha \psi_2 \quad \chi_4 = \beta \psi_2$$

$$E_{\text{HF}} = 2h_1 + h_2 + J_{11} + 2J_{12} - K_{12}$$

Problem: HF energy of the B atom

“Find the HF energy of the B atom’ in terms of the spatial MOs’

Solution:

$$E_{\text{HF}} = 2h_1 + 2h_2 + h_3 + J_{11} + 4J_{12} + J_{22} - 2K_{12} + 2J_{13} + 2J_{23} - K_{13} - K_{23}$$

From spin to spatial orbitals

Two-electron example: H_2 in minimal basis

In the spin orbital basis, we have

$$\begin{aligned} E_{HF} &= \langle \chi_1 | h | \chi_1 \rangle + \langle \chi_2 | h | \chi_2 \rangle + \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle \\ &= [\chi_1 | h | \chi_1] + [\chi_2 | h | \chi_2] + [\chi_1 \chi_2 | \chi_2 \chi_2] - [\chi_1 \chi_2 | \chi_2 \chi_1] \end{aligned}$$

Spin to spatial transformation:

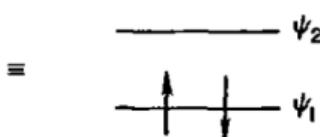
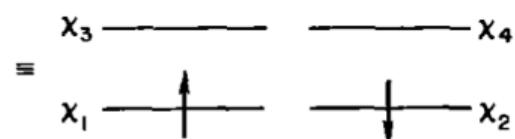
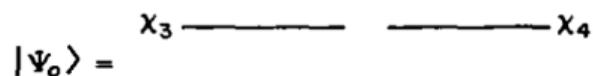
$$\chi_1(\mathbf{x}) \equiv \psi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2(\mathbf{x}) \equiv \bar{\psi}_1(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega)$$

$$E_{HF} = [\psi_1 | h | \psi_1] + [\bar{\psi}_1 | h | \bar{\psi}_1] + [\psi_1 \psi_1 | \bar{\psi}_1 \bar{\psi}_1] - [\psi_1 \bar{\psi}_1 | \bar{\psi}_1 \psi_1]$$

Therefore, in the spatial orbital basis, we have

$$E_{HF} = 2(\psi_1 | h | \psi_1) + (\psi_1 \psi_1 | \psi_1 \psi_1) = 2(1 | h | 1) + (11 | 11)$$



From spin to spatial orbitals (Take 2)

One-electron terms

$$\begin{aligned}
 [\chi_1 | h | \chi_1] &= \int \chi_1^*(\mathbf{x}) h(\mathbf{r}) \chi_1(\mathbf{x}) d\mathbf{x} \\
 &= \int \alpha^*(\omega) \psi_1^*(\mathbf{r}) h(\mathbf{r}) \alpha(\omega) \psi_1(\mathbf{r}) d\omega d\mathbf{r} \\
 &= \underbrace{\left[\int \alpha^*(\omega) \alpha(\omega) d\omega \right]}_{=1} \underbrace{\left[\int \psi_1^*(\mathbf{r}) h(\mathbf{r}) \psi_1(\mathbf{r}) d\mathbf{r} \right]}_{(\psi_1 | h | \psi_1)}
 \end{aligned}$$

$$\begin{aligned}
 [\chi_2 | h | \chi_2] &= \int \chi_2^*(\mathbf{x}) h(\mathbf{r}) \chi_2(\mathbf{x}) d\mathbf{x} \\
 &= \int \beta^*(\omega) \psi_1^*(\mathbf{r}) h(\mathbf{r}) \beta(\omega) \psi_1(\mathbf{r}) d\omega d\mathbf{r} \\
 &= \underbrace{\left[\int \beta^*(\omega) \beta(\omega) d\omega \right]}_{=1} \underbrace{\left[\int \psi_1^*(\mathbf{r}) h(\mathbf{r}) \psi_1(\mathbf{r}) d\mathbf{r} \right]}_{(\psi_1 | h | \psi_1)}
 \end{aligned}$$

From spin to spatial orbitals (Take 3)

Two-electron terms

$$\begin{aligned}
 [\chi_1\chi_1|\chi_2\chi_2] &= \iint \chi_1^*(\mathbf{x}_1)\chi_1(\mathbf{x}_1)r_{12}^{-1}\chi_2^*(\mathbf{x}_2)\chi_2(\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2 \\
 &= \iint \alpha^*(\omega_1)\psi_1^*(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_1)r_{12}^{-1}\beta^*(\omega_2)\psi_1^*(\mathbf{r}_2)\beta(\omega_2)\psi_1(\mathbf{r}_2)d\omega_1d\mathbf{r}_1d\omega_2d\mathbf{r}_2 \\
 &= \underbrace{\left[\int \alpha^*(\omega_1)\alpha(\omega_1)d\omega_1 \right]}_{=1} \underbrace{\left[\int \beta^*(\omega_2)\beta(\omega_2)d\omega_2 \right]}_{=1} \underbrace{\left[\iint \psi_1^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1)r_{12}^{-1}\psi_1^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \right]}_{(\psi_1\psi_1|\psi_1\psi_1)}
 \end{aligned}$$

$$\begin{aligned}
 [\chi_1\chi_2|\chi_2\chi_1] &= \iint \chi_1^*(\mathbf{x}_1)\chi_2(\mathbf{x}_1)r_{12}^{-1}\chi_2^*(\mathbf{x}_2)\chi_1(\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2 \\
 &= \iint \alpha^*(\omega_1)\psi_1^*(\mathbf{r}_1)\beta(\omega_1)\psi_1(\mathbf{r}_1)r_{12}^{-1}\beta^*(\omega_2)\psi_1^*(\mathbf{r}_2)\alpha(\omega_2)\psi_1(\mathbf{r}_2)d\omega_1d\mathbf{r}_1d\omega_2d\mathbf{r}_2 \\
 &= \underbrace{\left[\int \alpha^*(\omega_1)\beta(\omega_1)d\omega_1 \right]}_{=0} \underbrace{\left[\int \beta^*(\omega_2)\alpha(\omega_2)d\omega_2 \right]}_{=0} \underbrace{\left[\iint \psi_1^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1)r_{12}^{-1}\psi_1^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \right]}_{(\psi_1\psi_1|\psi_1\psi_1)}
 \end{aligned}$$

From spin to spatial orbitals (Take 4)

General expression

$$E_{\text{HF}} = \sum_a^N [a|h|a] + \frac{1}{2} \sum_a^N \sum_b^N ([aa|bb] - [ab|ba]) = 2 \sum_a^{N/2} (a|h|a) + \sum_a^{N/2} \sum_b^{N/2} [2(aa|bb) - (ab|ba)] \quad (49)$$

One- and two-electron terms

$$\sum_a^N [a|h|a] = \sum_a^{N/2} [a|h|a] + \sum_a^{N/2} [\bar{a}|h|\bar{a}] = 2 \sum_a^{N/2} [a|h|a] \quad (50)$$

$$\begin{aligned} \frac{1}{2} \sum_a^N \sum_b^N ([aa|bb] - [ab|ba]) &= \frac{1}{2} \left\{ \sum_a^{N/2} \sum_b^{N/2} ([aa|bb] - [ab|ba]) + \sum_a^{N/2} \sum_b^{N/2} ([aa|\bar{b}\bar{b}] - [a\bar{b}|\bar{b}a]) \right. \\ &\quad \left. + \sum_a^{N/2} \sum_b^{N/2} ([\bar{a}\bar{a}|bb] - [\bar{a}b|b\bar{a}]) + \sum_a^{N/2} \sum_b^{N/2} ([\bar{a}\bar{a}|\bar{b}\bar{b}] - [\bar{a}\bar{b}|\bar{b}\bar{a}]) \right\} \end{aligned} \quad (51)$$

$$= \sum_a^{N/2} \sum_b^{N/2} [2(aa|bb) - (ab|ba)]$$

The Fock matrix

Using the **variational principle**, one can show that, to minimise the energy, the MOs need to diagonalise the **one-electron Fock operator**

$$f(1) = h(1) + \underbrace{\sum_a^N [\mathcal{J}_a(1) - \mathcal{K}_a(1)]}_{\nu^{\text{HF}}(1) = \text{Hartree-Fock potential}}$$

For a **closed-shell system** (i.e. two electrons in each orbital)

$$f(1) = h(1) + \sum_a^{N/2} [2J_a(1) - K_a(1)] \quad (\text{closed shell})$$

These orbitals are called **canonical molecular orbitals** (= eigenvectors):

$$f(1) \psi_i(1) = \varepsilon_i \psi_i(1)$$

and ε_i are called the **MO energies** (= eigenvalues)

Fock matrix elements in the MO basis

Problem:

“ Find the expression of the matrix elements $f_{ij} = \langle \chi_i | f | \chi_j \rangle$ ”

Fock matrix elements in the MO basis

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“ Find the expression of the matrix elements $f_{ij} = \langle \chi_i | f | \chi_j \rangle$ ”

Solution:

$$\begin{aligned}\langle \chi_i | f | \chi_j \rangle &= \langle \chi_i | h + \sum_a (\mathcal{J}_a - \mathcal{K}_a) | \chi_j \rangle \\&= \langle \chi_i | h | \chi_j \rangle + \sum_a (\langle \chi_i | \mathcal{J}_a | \chi_j \rangle - \langle \chi_i | \mathcal{K}_a | \chi_j \rangle) \\&= \langle i | h | j \rangle + \sum_a [\langle ia | ja \rangle - \langle ia | aj \rangle] \\&= \langle i | h | j \rangle + \sum_a \langle ia || ja \rangle\end{aligned}$$

MO energies in the MO basis

Problem:

“Deduce the expression of ε_i ”

MO energies in the MO basis

Problem:

“Deduce the expression of ε_i ”

Solution:

$$\begin{aligned} f |\chi_i\rangle = \varepsilon_i |\chi_i\rangle &\Rightarrow \langle \chi_i | f | \chi_i \rangle = \varepsilon_i \langle \chi_i | \chi_i \rangle = \varepsilon_i \\ &\Rightarrow \varepsilon_i = \langle i | h | i \rangle + \sum_a [\langle ia | ia \rangle - \langle ia | ai \rangle] \\ &\Rightarrow \varepsilon_i = \langle i | h | i \rangle + \sum_a \langle ia || ia \rangle \end{aligned}$$

The variational principle

Problem

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

The variational principle

Problem

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

Solution

We expand Ψ in a clever basis

$$\Psi = \sum_i^{\infty} c_i \varphi_i \quad \text{with} \quad \sum_i^{\infty} c_i^2 = 1$$

The variational principle

Problem

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

Solution

We expand Ψ in a clever basis

$$\Psi = \sum_i^{\infty} c_i \varphi_i \quad \text{with} \quad \sum_i^{\infty} c_i^2 = 1$$

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \sum_i c_i \varphi_i \middle| \hat{H} \middle| \sum_j c_j \varphi_j \right\rangle = \sum_{ij} c_i c_j \langle \varphi_i | \hat{H} | \varphi_j \rangle \\ &= \sum_{ij} c_i c_j E_j \langle \varphi_i | \varphi_j \rangle = \sum_{ij} c_i c_j E_j \delta_{ij} = \sum_i c_i^2 E_i \geq E_0 \sum_i c_i^2 = E_0 \end{aligned}$$

Koopmans' theorem

Ground-state energy of the N -electron system

$${}^N E_0 = \sum_a h_a + \frac{1}{2} \sum_{ab} \langle ab || ab \rangle \quad (52)$$

Energy of the $(N - 1)$ -electron system (cation)

$${}^{N-1} E_c = \sum_{a \neq c} h_a + \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \langle ab || ab \rangle \quad (53)$$

Ionization potential (IP)

$$\begin{aligned} \text{IP} &= {}^{N-1} E_c - {}^N E_0 \\ &= -\langle c | h | c \rangle - \frac{1}{2} \sum_a \langle ac || ac \rangle - \frac{1}{2} \sum_b \langle cb || cb \rangle \\ &= -\langle c | h | c \rangle - \sum_a \langle ac || ac \rangle = -\varepsilon_c \end{aligned} \quad (54)$$

Koopmans' theorem for electron affinity (EA)

Problem:

“Show that Koopmans’ theorem applies to electron affinities”

Koopmans' theorem for electron affinity (EA)

Problem:

“Show that Koopmans’ theorem applies to electron affinities”

Solution:

$$\begin{aligned} \text{EA} &= {}^N E_0 - {}^{N+1} E^r \\ &= -\langle r | h | r \rangle - \sum_a \langle ra | | ra \rangle \\ &= -\varepsilon_r \end{aligned} \tag{55}$$

Roothaan-Hall equations: introduction of a basis

Expansion in a basis

$$\psi_i(\mathbf{r}) = \sum_{\mu}^K C_{\mu i} \phi_{\mu}(\mathbf{r}) \quad \equiv \quad |i\rangle = \sum_{\mu}^K C_{\mu i} |\mu\rangle$$

K AOs gives K MOs: $N/2$ are occupied MOs and $K - N/2$ are vacant/virtual MOs

Roothaan-Hall equations

$$\begin{aligned} f|i\rangle = \varepsilon_i |i\rangle &\Rightarrow f \sum_{\nu} C_{\nu i} |\nu\rangle = \varepsilon_i \sum_{\nu} C_{\nu i} |\nu\rangle \\ &\Rightarrow \langle \mu | f \sum_{\nu} C_{\nu i} | \nu \rangle = \varepsilon_i \langle \mu | \sum_{\nu} C_{\nu i} | \nu \rangle \\ &\Rightarrow \sum_{\nu} C_{\nu i} \langle \mu | f | \nu \rangle = \sum_{\nu} C_{\nu i} \varepsilon_i \langle \mu | \nu \rangle \\ &\Rightarrow \boxed{\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\nu} S_{\mu\nu} C_{\nu i} \varepsilon_i} \end{aligned}$$

Introduction of a basis (Take 2)

Matrix form of the Roothaan-Hall equations

$$\mathbf{F} \cdot \mathbf{C} = \mathbf{S} \cdot \mathbf{C} \cdot \mathbf{E} \quad \Leftrightarrow \quad \mathbf{F}' \cdot \mathbf{C}' = \mathbf{C}' \cdot \mathbf{E} \quad (56)$$

$$\mathbf{F}' = \mathbf{X}^\dagger \cdot \mathbf{F} \cdot \mathbf{X} \quad \mathbf{C} = \mathbf{X} \cdot \mathbf{C}' \quad \mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{I} \quad (57)$$

- Fock matrix $F_{\mu\nu} = \langle \mu | f | \nu \rangle$ and Overlap matrix $S_{\mu\nu} = \langle \mu | \nu \rangle$
- We need to determine the coefficient matrix \mathbf{C} and the orbital energies \mathbf{E}

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \quad \mathbf{E} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon_K \end{pmatrix} \quad (58)$$

Self-consistent field (SCF) procedure

$$\mathbf{F}(\mathbf{C}) \cdot \mathbf{C} = \mathbf{S} \cdot \mathbf{C} \cdot \mathbf{E} \quad \text{How do we solve these HF equations?} \quad (59)$$

Expression of the Fock matrix

Problem:

“Find the expression of the Fock matrix in terms of the one- and two-electron integrals”

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Solution:

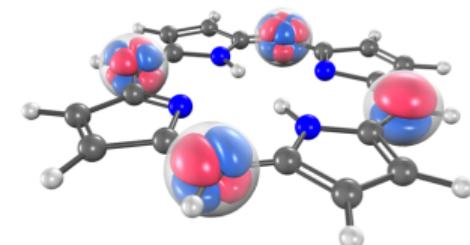
$$\begin{aligned}
 F_{\mu\nu} &= \langle \mu | h + \sum_a^N (\mathcal{J}_a - \mathcal{K}_a) | \nu \rangle = H_{\mu\nu} + \sum_a^N \langle \mu | \mathcal{J}_a - \mathcal{K}_a | \nu \rangle \\
 &= H_{\mu\nu} + \sum_a^N (\langle \mu \chi_a | r_{12}^{-1} | \nu \chi_a \rangle - \langle \mu \chi_a | r_{12}^{-1} | \chi_a \nu \rangle) \\
 &= H_{\mu\nu} + \sum_a^N \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a} (\langle \mu \lambda | r_{12}^{-1} | \nu \sigma \rangle - \langle \mu \lambda | r_{12}^{-1} | \sigma \nu \rangle) \\
 &= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu \lambda | \nu \sigma \rangle - \langle \mu \lambda | \sigma \nu \rangle) = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu \lambda | | \nu \sigma \rangle = H_{\mu\nu} + G_{\mu\nu} \\
 F_{\mu\nu} &= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu \lambda | \nu \sigma \rangle - \frac{1}{2} \langle \mu \lambda | \sigma \nu \rangle) \quad (\text{closed shell})
 \end{aligned}$$

One- and two-electron integrals (Appendix A)

One-electron integrals: overlap & core Hamiltonian

$$S_{\mu\nu} = \langle \mu | \nu \rangle = \int \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (60)$$

$$H_{\mu\nu} = \langle \mu | \hat{H}^c | \nu \rangle = \int \phi_{\mu}^*(\mathbf{r}) \hat{H}^c(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (61)$$



Chemist/Mulliken notation for two-electron integrals

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}^*(\mathbf{r}_1) \phi_{\nu}(\mathbf{r}_1) \frac{1}{r_{12}} \phi_{\lambda}^*(\mathbf{r}_2) \phi_{\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (62)$$

$$(\mu\nu||\lambda\sigma) = (\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu) \quad (63)$$

Physicist/Dirac notation for two-electron integrals

$$\langle \mu\nu|\lambda\sigma \rangle = \iint \phi_{\mu}^*(\mathbf{r}_1) \phi_{\nu}^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{\lambda}(\mathbf{r}_1) \phi_{\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (64)$$

$$\langle \mu\nu||\lambda\sigma \rangle = \langle \mu\nu|\lambda\sigma \rangle - \langle \mu\nu|\sigma\lambda \rangle \quad (65)$$

Computation of the Fock matrix and energy

Density matrix (closed-shell system)

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a} \quad \text{or} \quad \boxed{\mathbf{P} = 2 \mathbf{C} \cdot \mathbf{C}^\dagger} \quad (66)$$

Fock matrix in the AO basis (closed-shell system)

$$F_{\mu\nu} = H_{\mu\nu} + \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma)}_{J_{\mu\nu} = \text{Coulomb}} - \frac{1}{2} \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\sigma|\lambda\nu)}_{K_{\mu\nu} = \text{exchange}} \quad (67)$$

HF energy in the AO basis (closed-shell system)

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma} \quad \text{or} \quad \boxed{E_{\text{HF}} = \frac{1}{2} \text{Tr}[\mathbf{P} \cdot (\mathbf{H} + \mathbf{F})]} \quad (68)$$

Expression of the HF energy

Problem:

“Find the expression of the HF energy in terms of the one- and two-electron integrals”

Expression of the HF energy

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“Find the expression of the HF energy in terms of the one- and two-electron integrals”

Solution:

$$\begin{aligned} E_{\text{HF}} &= \sum_a^N h_a + \frac{1}{2} \sum_{ab}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab}) \quad (\text{cf few slides ago}) \\ &= \sum_a^N \left\langle \sum_\mu C_{\mu a} \phi_\mu \middle| h \left| \sum_\nu C_{\nu a} \phi_\nu \right. \right\rangle + \frac{1}{2} \sum_{ab}^N \left\langle \left(\sum_\mu C_{\mu a} \phi_\mu \right) \left(\sum_\lambda C_{\lambda b} \phi_\lambda \right) \middle| \left(\sum_\nu C_{\nu a} \phi_\nu \right) \left(\sum_\sigma C_{\sigma b} \phi_\sigma \right) \right\rangle \\ &= \sum_{\mu\nu} P_{\mu\nu} \left[H_{\mu\nu} + \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda | | \nu\sigma \rangle \right] \end{aligned}$$

How to perform a HF calculation in practice?

The SCF algorithm

- ① Specify molecule $\{R_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$
- ② Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle \mu\nu | \lambda\sigma \rangle$
- ③ Diagonalize \mathbf{S} and compute \mathbf{X}
- ④ Obtain guess density matrix for \mathbf{P}
 1. Calculate \mathbf{G} and then $\mathbf{F} = \mathbf{H} + \mathbf{G}$
 2. Compute $\mathbf{F}' = \mathbf{X}^\dagger \cdot \mathbf{F} \cdot \mathbf{X}$
 3. Diagonalize \mathbf{F}' to obtain \mathbf{C}' and \mathbf{E}
 4. Calculate $\mathbf{C} = \mathbf{X} \cdot \mathbf{C}'$
 5. Form a new density matrix $\mathbf{P} = \mathbf{C} \cdot \mathbf{C}^\dagger$
 6. Am I converged? If not go back to 1.
- ⑤ Calculate stuff that you want, like E_{HF} for example

Orthogonalization matrix

We are looking for a matrix in order to orthogonalize the AO basis, i.e. $\mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{I}$

Symmetric (or Löwdin) orthogonalization

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U} \cdot \mathbf{s}^{-1/2} \cdot \mathbf{U}^\dagger \text{ is one solution...} \quad (69)$$

Is it working?

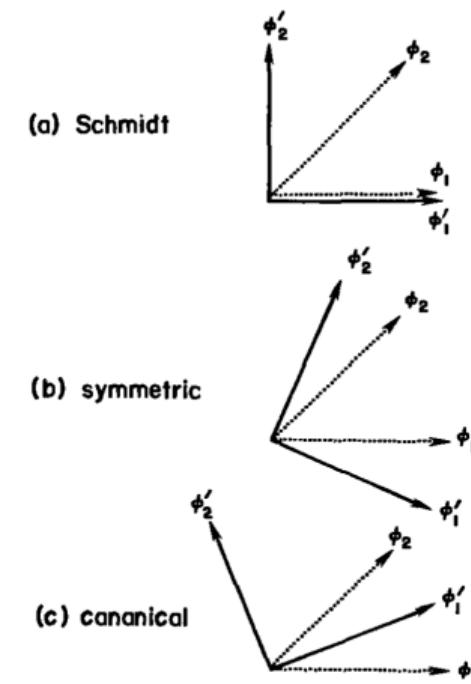
$$\mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{S}^{-1/2} \cdot \mathbf{S} \cdot \mathbf{S}^{-1/2} = \mathbf{S}^{-1/2} \cdot \mathbf{S} \cdot \mathbf{S}^{-1/2} = \mathbf{I} \quad \checkmark \quad (70)$$

Canonical orthogonalization

$$\mathbf{X} = \mathbf{U} \cdot \mathbf{s}^{-1/2} \text{ is another solution (when you have linear dependencies)...} \quad (71)$$

Is it working?

$$\mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{s}^{-1/2} \cdot \underbrace{\mathbf{U}^\dagger \cdot \mathbf{S} \cdot \mathbf{U}}_s \cdot \mathbf{s}^{-1/2} = \mathbf{I} \quad \checkmark \quad (72)$$



How to obtain a good guess for the MOs or density matrix?

Possible initial density matrix

- ➊ We can set $P = \mathbf{0} \Rightarrow F = H$ (core Hamiltonian approximation):
⇒ Usually a poor guess but easy to implement
- ➋ Use EHT or semi-empirical methods:
⇒ Out of fashion
- ➌ Using tabulated atomic densities:
⇒ “SAD” guess in QChem
- ➍ Read the MOs of a previous calculation:
⇒ Very common and very useful

How do I know I have converged (or not)?

Convergence in SCF calculations

- ① You can check the **energy and/or the density matrix**:
⇒ The energy/density **should not** change at convergence
- ② You can check the commutator $\mathbf{F} \cdot \mathbf{P} \cdot \mathbf{S} - \mathbf{S} \cdot \mathbf{P} \cdot \mathbf{F}$:
⇒ At convergence, we have $\mathbf{F} \cdot \mathbf{P} \cdot \mathbf{S} - \mathbf{S} \cdot \mathbf{P} \cdot \mathbf{F} = 0$
- ③ The **DIIS (direct inversion in the iterative subspace) method** is usually used to speed up convergence:
⇒ **Extrapolation of the Fock matrix** using previous iterations

$$\mathbf{F}_{m+1} = \sum_{i=m-k}^m c_i \mathbf{F}_i$$

Dipole moments

Classical vs Quantum

$$\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z) = \underbrace{\sum_i q_i \mathbf{r}_i}_{\text{classical definition}} \quad (73)$$

$$\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z) = \underbrace{\langle \Psi_0 | - \sum_i^N \mathbf{r}_i | \Psi_0 \rangle}_{\text{electrons}} + \underbrace{\sum_A^M Z_A \mathbf{R}_A}_{\text{nuclei}} = - \sum_{\mu\nu} P_{\mu\nu}(\nu | \mathbf{r} | \mu) + \sum_A^M Z_A \mathbf{R}_A \quad (74)$$

Vector components

$$\mu_x = - \sum_{\mu\nu} P_{\mu\nu}(\nu | x | \mu) + \sum_A^M Z_A X_A \quad \text{with} \quad \underbrace{(\nu | x | \mu)}_{\text{one-electron integrals}} = \int \phi_\nu^*(\mathbf{r}) \times \phi_\mu(\mathbf{r}) d\mathbf{r} \quad (75)$$

Charge analysis

Electron density

$$\rho(\mathbf{r}) = \sum_{\mu\nu} \phi_\mu(\mathbf{r}) P_{\mu\nu} \phi_\nu(\mathbf{r}) \quad \text{with} \quad \int \rho(\mathbf{r}) d\mathbf{r} = N \Rightarrow N = \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu} (\mathbf{P} \cdot \mathbf{S})_{\mu\mu} = \text{Tr}(\mathbf{P} \cdot \mathbf{S}) \quad (76)$$

Mulliken population analysis

Assuming that the basis functions are atom-centered

$$\underbrace{q_A^{\text{Mulliken}}}_{\text{net charge on } A} = Z_A - \sum_{\mu \in A} (\mathbf{P} \cdot \mathbf{S})_{\mu\mu} \quad (77)$$

Löwdin population analysis

Because $\text{Tr}(\mathbf{A} \cdot \mathbf{B}) = \text{Tr}(\mathbf{B} \cdot \mathbf{A})$, we have, for any α , $N = \sum_{\mu} (\mathbf{S}^{\alpha} \cdot \mathbf{P} \cdot \mathbf{S}^{1-\alpha})_{\mu\mu}$

$$\text{For } \alpha = 1/2, \text{ we get: } N = \sum_{\mu} (\mathbf{S}^{1/2} \cdot \mathbf{P} \cdot \mathbf{S}^{1/2})_{\mu\mu} \Rightarrow q_A^{\text{Löwdin}} = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2} \cdot \mathbf{P} \cdot \mathbf{S}^{1/2})_{\mu\mu} \quad (78)$$

Unrestricted HF (UHF)

How to model open-shell systems?

- RHF is made to describe **closed-shell systems** and we have used **restricted spin orbitals**:

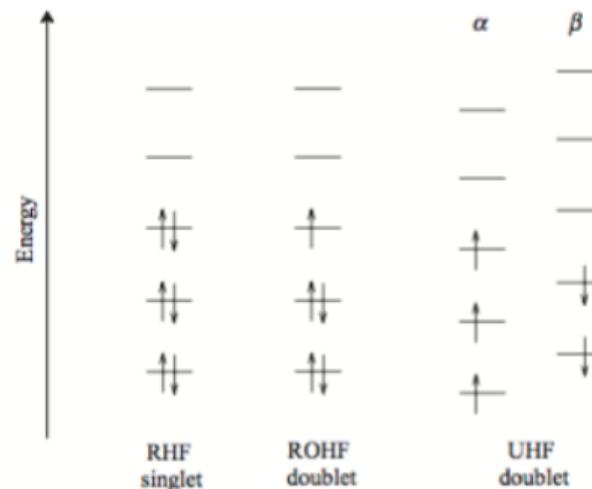
$$\chi_i^{\text{RHF}}(\mathbf{x}) = \begin{cases} \alpha(\omega) \psi_i(\mathbf{r}) \\ \beta(\omega) \psi_i(\mathbf{r}) \end{cases}$$

- It does **not** describe **open-shell systems**
- For open-shell systems we can use **unrestricted spin orbitals**

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

- RHF = **Restricted Hartree-Fock** \leftrightarrow **Roothaan-Hall equations**
- UHF = **Unrestricted Hartree-Fock** \leftrightarrow **Pople-Nesbet equations**
- Restricted Open-shell Hartree-Fock (ROHF)** do exist but we won't talk about it

RHF, ROHF and UHF



- RHF = Restricted Hartree-Fock
- UHF = Unrestricted Hartree-Fock
- ROHF = Restricted Open-shell Hartree-Fock

Unrestricted Hartree-Fock equations

UHF equations for unrestricted spin orbitals

To minimize the UHF energy, the unrestricted spin orbitals must be eigenvalues of the α and β Fock operators:

$$f^\alpha(1) \psi_i^\alpha(1) = \varepsilon_i^\alpha \psi_j^\alpha(1) \quad f^\beta(1) \psi_i^\beta(1) = \varepsilon_i^\beta \psi_j^\beta(1) \quad (79)$$

where

$$f^\alpha(1) = h(1) + \sum_a^{N^\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N^\beta} J_a^\beta(1) \quad (80)$$

$$f^\beta(1) = h(1) + \sum_a^{N^\beta} [J_a^\beta(1) - K_a^\beta(1)] + \sum_a^{N^\alpha} J_a^\alpha(1) \quad (81)$$

The Coulomb and Exchange operators are

$$J_i^\sigma(1) = \int \psi_i^\sigma(2) r_{12}^{-1} \psi_i^\sigma(2) d\mathbf{r}_2 \quad K_i^\sigma(1) \psi_j^\sigma(1) = \left[\int \psi_i^\sigma(2) r_{12}^{-1} \psi_j^\sigma(2) d\mathbf{r}_2 \right] \psi_i^\sigma(1) \quad (82)$$

Unrestricted Hartree-Fock equations (Take 2)

UHF energy

The UHF energy is composed by three contributions:

$$E_{\text{UHF}} = E_{\text{UHF}}^{\alpha\alpha} + E_{\text{UHF}}^{\beta\beta} + E_{\text{UHF}}^{\alpha\beta} \quad (83)$$

which yields

$$E_{\text{UHF}} = \sum_a^{N^\alpha} h_i^\alpha + \frac{1}{2} \sum_{ab}^{N^\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \sum_a^{N^\beta} h_a^\beta + \frac{1}{2} \sum_{ab}^{N^\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta} \quad (84)$$

The matrix elements are given by

$$h_i^\sigma = \langle \psi_i^\sigma | h | \psi_i^\sigma \rangle \quad J_{ij}^{\sigma\sigma'} = \left\langle \psi_i^\sigma \psi_j^{\sigma'} \middle| \psi_i^\sigma \psi_j^{\sigma'} \right\rangle \quad K_{ij}^{\sigma\sigma} = \left\langle \psi_i^\sigma \psi_j^\sigma \middle| \psi_j^\sigma \psi_i^\sigma \right\rangle \quad (85)$$

Note that $K_{ij}^{\alpha\beta} = 0 \Leftrightarrow$ there is no exchange between opposite-spin electrons

UHF energy of the Li atom

Problem

“Write down the UHF energy of the doublet state of the lithium atom”

UHF energy of the Li atom

Problem

“Write down the UHF energy of the doublet state of the lithium atom”

Solution

$$E_{\text{UHF}} = h_1^\alpha + h_1^\beta + h_2^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}$$

The Pople-Nesbet Equations

Expansion of the unrestricted spin orbitals in a basis

$$\psi_i^\alpha(\mathbf{r}) = \sum_{\mu=1}^K \textcolor{blue}{C}_{\mu i}^\alpha \phi_\mu(\mathbf{r}) \quad \psi_i^\beta(\mathbf{r}) = \sum_{\mu=1}^K \textcolor{purple}{C}_{\mu i}^\beta \phi_\mu(\mathbf{r}) \quad (86)$$

The Pople-Nesbet equations

$$\textcolor{orange}{F}^\alpha \cdot \textcolor{blue}{C}^\alpha = \mathbf{S} \cdot \textcolor{blue}{C}^\alpha \cdot \textcolor{red}{E}^\alpha \quad \textcolor{red}{F}^\beta \cdot \textcolor{purple}{C}^\beta = \mathbf{S} \cdot \textcolor{purple}{C}^\beta \cdot \textcolor{red}{E}^\beta \quad (87)$$

$$F_{\mu\nu}^\alpha = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}^\alpha [(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_{\lambda\sigma} P_{\lambda\sigma}^\beta (\mu\nu|\sigma\lambda) \quad (88)$$

$$F_{\mu\nu}^\beta = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}^\beta [(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_{\lambda\sigma} P_{\lambda\sigma}^\alpha (\mu\nu|\sigma\lambda) \quad (89)$$

$\textcolor{orange}{F}^\alpha$ and $\textcolor{red}{F}^\beta$ are both functions of $\textcolor{blue}{C}^\alpha$ and $\textcolor{purple}{C}^\beta$ \Rightarrow There's a coupling between α and β MOs!

Unrestricted Density Matrices

Spin-up and spin-down density matrices

$$P_{\mu\nu}^{\alpha} = \sum_{a=1}^{N^{\alpha}} C_{\mu a}^{\alpha} C_{\nu a}^{\alpha} \Leftrightarrow \textcolor{orange}{P}^{\alpha}$$

$$P_{\mu\nu}^{\beta} = \sum_{a=1}^{N^{\beta}} C_{\mu a}^{\beta} C_{\nu a}^{\beta} \Leftrightarrow \textcolor{red}{P}^{\beta} \quad (90)$$

Properties of the density ($\sigma = \alpha$ or β)

$$\rho^{\sigma}(\mathbf{r}) = \sum_{\mu\nu} \phi_{\mu}(\mathbf{r}) P_{\mu\nu}^{\sigma} \phi_{\nu}(\mathbf{r}) \quad \int \rho^{\sigma}(\mathbf{r}) d\mathbf{r} = N^{\sigma} \quad (91)$$

Total and Spin density matrices

$$\underbrace{P^T}_{\text{Charge density}} = \textcolor{orange}{P}^{\alpha} + \textcolor{red}{P}^{\beta} \quad \underbrace{P^S}_{\text{Spin density}} = \textcolor{orange}{P}^{\alpha} - \textcolor{red}{P}^{\beta} \quad (92)$$

How to perform a UHF calculation in practice?

The SCF algorithm

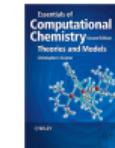
- ① Specify molecule $\{R_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$ (same as RHF)
- ② Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle \mu\nu | \lambda\sigma \rangle$ (same as RHF)
- ③ Diagonalize \mathbf{S} and compute \mathbf{X} (same as RHF)
- ④ Obtain guess density matrix for \mathbf{P}^α and \mathbf{P}^β
 - 1a. Calculate \mathbf{G}^α and then $\mathbf{F}^\alpha = \mathbf{H} + \mathbf{G}^\alpha$
 - 1b. Calculate \mathbf{G}^β and then $\mathbf{F}^\beta = \mathbf{H} + \mathbf{G}^\beta$
 2. Compute $(\mathbf{F}^\alpha)' = \mathbf{X}^\dagger \cdot \mathbf{F}^\alpha \cdot \mathbf{X}$ and $(\mathbf{F}^\beta)' = \mathbf{X}^\dagger \cdot \mathbf{F}^\beta \cdot \mathbf{X}$
 - 3a. Diagonalize $(\mathbf{F}^\alpha)'$ to obtain $(\mathbf{C}^\alpha)'$ and \mathbf{E}^α
 - 3b. Diagonalize $(\mathbf{F}^\beta)'$ to obtain $(\mathbf{C}^\beta)'$ and \mathbf{E}^β
 4. Calculate $\mathbf{C}^\alpha = \mathbf{X} \cdot (\mathbf{C}^\alpha)'$ and $\mathbf{C}^\beta = \mathbf{X} \cdot (\mathbf{C}^\beta)'$
 5. Form the new new density matrix \mathbf{P}^α and \mathbf{P}^β , and compute $\mathbf{P}^T = \mathbf{P}^\alpha + \mathbf{P}^\beta$
 6. Am I converged? If not go back to 1.
- ⑤ Calculate stuff that you want, like E_{UHF} for example

Good books

- Introduction to Computational Chemistry (Jensen)



- Essentials of Computational Chemistry (Cramer)



- Modern Quantum Chemistry (Szabo & Ostlund)



- Molecular Electronic Structure Theory (Helgaker, Jorgensen & Olsen)

