

# The Hartree–Fock Approximation

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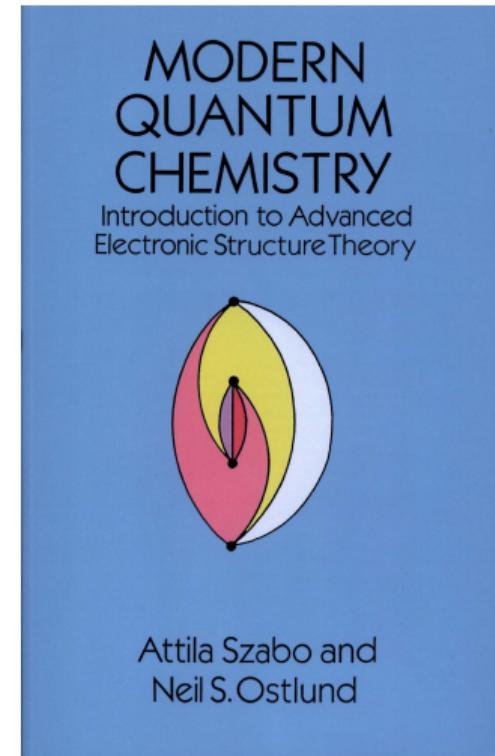
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# How to perform a HF calculation in practice?

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

- 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  $\mathbf{X} = \mathbf{S}^{-1/2}$
- ④ 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.
- ⑤ Calculate stuff that you want, like  $E_{HF}$  for example



# Szabo's and Ostlund's book

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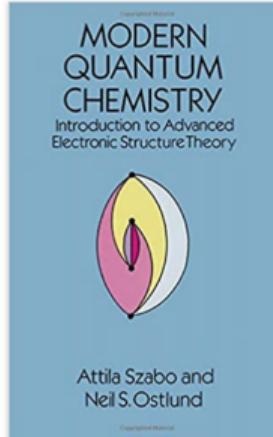
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# Motivations & Assumptions

- 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**  $\Rightarrow$  **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 ( $m = e = \hbar = 1$ )

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

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

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

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

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

- $\nabla^2$  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

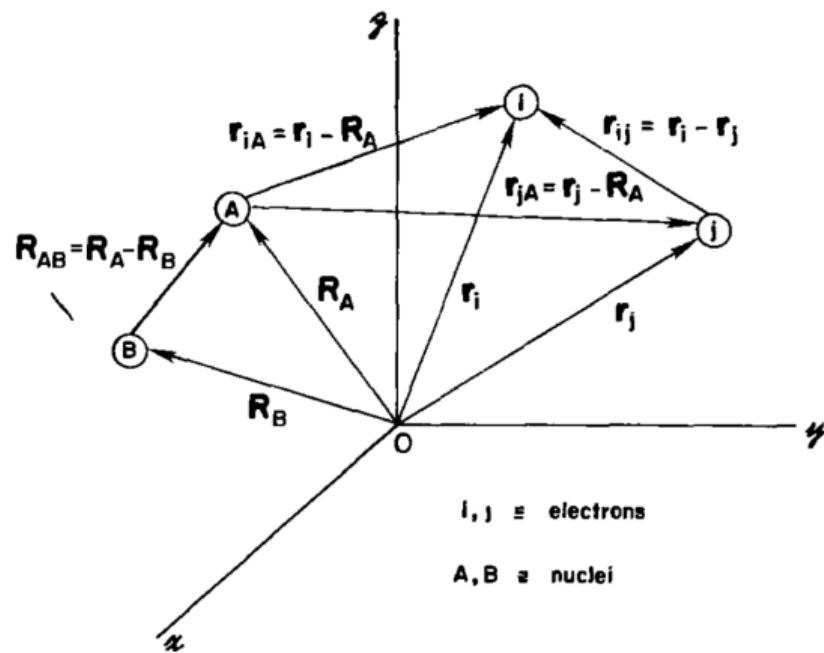


Figure 2.1 A molecular coordinate system  $i, j = \text{electrons}, A, B = \text{nuclei}$

# 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

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

It describes the vibration, rotation and translation of the molecules

## Electronic Hamiltonian

The **electronic Hamiltonian** is

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



# 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  $\Psi$  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  $\Psi$  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 ( $\omega$ ) and spatial ( $\mathbf{r}$ ) coordinates:  $\boxed{\mathbf{x} = (\omega, \mathbf{r})}$

## Antisymmetry principle

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

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

# 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

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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

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

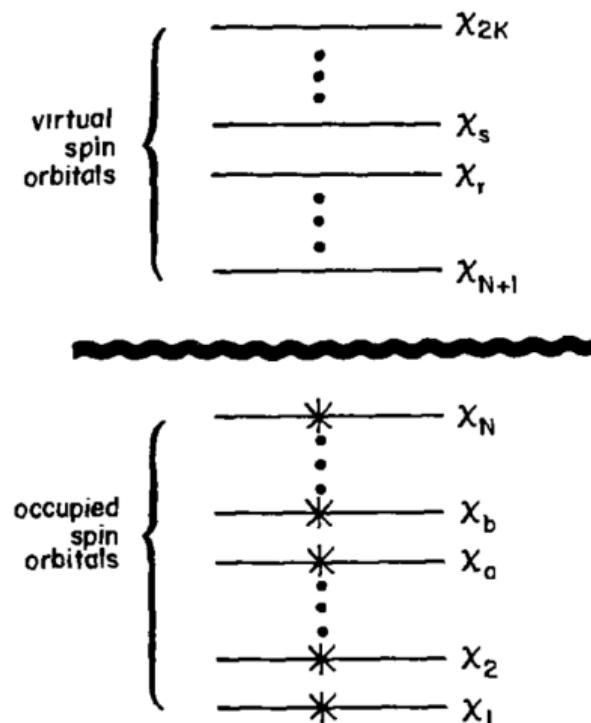


# Spin and spatial orbitals (Take 2)

## 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

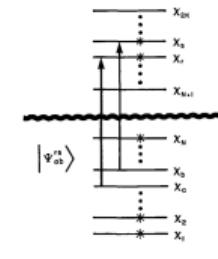
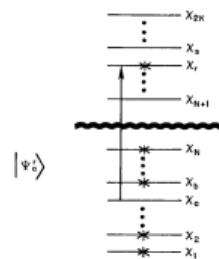
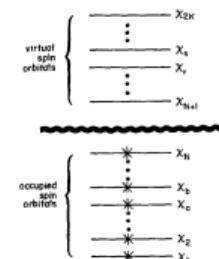
The electrons are in the  $N$  lowest orbitals (Aufbau principle):  $|\Psi_0\rangle = |\chi_1 \dots \chi_a \chi_b \dots \chi_N\rangle$  (16)

## Singly-excited determinants

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

## Doubly-excited determinants

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



# The Hartree-Fock energy

The HF energy is

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

We define a few quantities:

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

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

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

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

Therefore, we have

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

# 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  $\chi_1$  and  $\chi_2$  is normalized”*

# The Hartree-Fock energy: examples

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*"Show that the HF wave function built with two (normalized) spin orbitals  $\chi_1$  and  $\chi_2$  is normalized"*

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)

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“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  $\chi_1$ ,  $\chi_2$  and  $\chi_3$ "*

## Solution

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

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

$$\vdots$$

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

# 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”

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

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

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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:

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

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<sub>2</sub> in minimal basis

In the spin orbital basis, we have

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

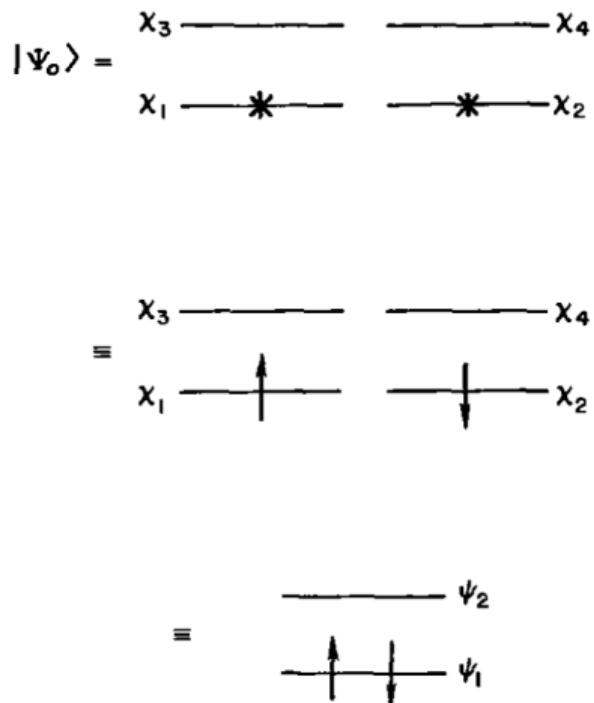
Spin to spatial transformation:

$$\begin{aligned} \chi_1(\mathbf{x}) &\equiv \psi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega) \\ \chi_2(\mathbf{x}) &\equiv \bar{\psi}_1(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega) \end{aligned}$$

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

Therefore, in the spatial orbital basis, we have

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



# 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

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

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

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

# 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**

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

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

$$f(1) = h(1) + \sum_a^{N/2} [2\mathcal{J}_a(1) - \mathcal{K}_a(1)] \quad (\text{closed shell})$$

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

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

and  $\varepsilon_i$  are called the **MO energies** (= eigenvalues)

# Fock matrix elements in the MO basis

Problem:

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

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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  $\varepsilon_i$ ”

# MO energies in the MO basis

Problem:

“Deduce the expression of  $\varepsilon_i$ ”

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  $\Psi$ , we have  $E = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$ ”*

# The variational principle

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## Solution

We expand  $\Psi$  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  $\Psi$ , we have  $E = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$ "

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We expand  $\Psi$  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”*

# Expression of the Fock matrix

Problem:

*"Find the expression of the Fock matrix in terms of the one- and two-electron integrals"*

Solution:

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

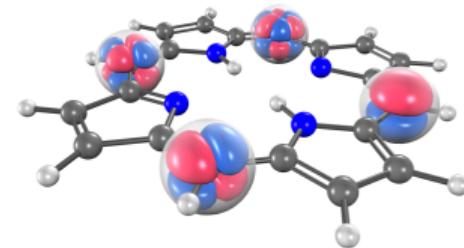


# One- and two-electron integrals (Appendix A)

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"*

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*"Find the expression of the HF energy in terms of the one- and two-electron integrals"*

Solution:

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

# 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.  $X^\dagger \cdot S \cdot X = I$

## Symmetric (or Löwdin) orthogonalization

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

Is it working?

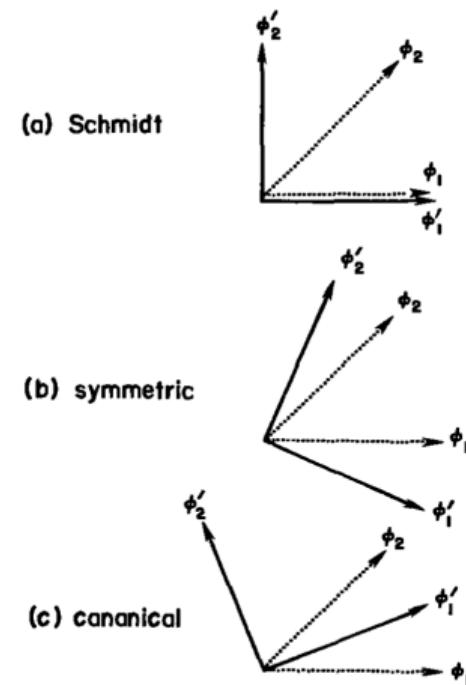
$$X^\dagger \cdot S \cdot X = S^{-1/2} \cdot S \cdot S^{-1/2} = S^{-1/2} \cdot S \cdot S^{-1/2} = I \quad \checkmark \quad (70)$$

## Canonical orthogonalization

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

Is it working?

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



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

## Possible initial density matrix

- ① We can set  $P = \mathbf{0} \Rightarrow F = H$  (core Hamiltonian approximation):  
⇒ Usually a poor guess but easy to implement
- ② Use EHT or semi-empirical methods:  
⇒ Out of fashion
- ③ Using tabulated atomic densities:  
⇒ “SAD” guess in QChem
- ④ 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  $\mathbf{F} \cdot \mathbf{P} \cdot \mathbf{S} - \mathbf{S} \cdot \mathbf{P} \cdot \mathbf{F} = \mathbf{0}$
- 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

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

## 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  $\alpha$ ,  $N = \sum_{\mu} (\mathbf{S}^{\alpha} \cdot \mathbf{P} \cdot \mathbf{S}^{1-\alpha})_{\mu\mu}$

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

# Unrestricted HF (UHF)

How to model open-shell systems?

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

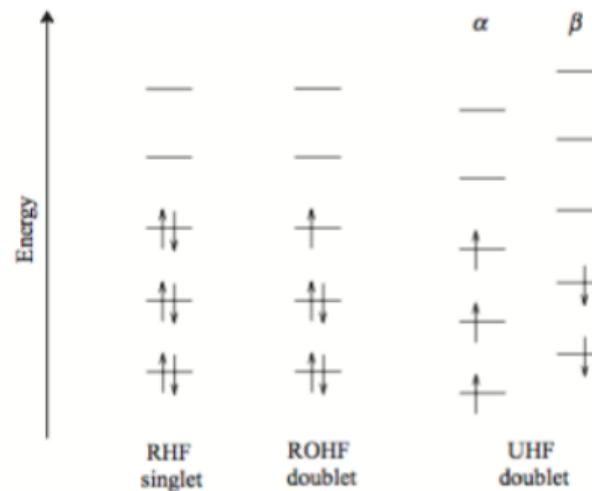
$$\chi_i^{\text{RHF}}(\mathbf{x}) = \begin{cases} \alpha(\omega) \psi_i(\mathbf{r}) \\ \beta(\omega) \psi_i(\mathbf{r}) \end{cases}$$

- 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  $\alpha$  and  $\beta$  Fock operators:

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

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

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

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

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

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

The Pople-Nesbet equations

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

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

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

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

# Unrestricted Density Matrices

Spin-up and spin-down density matrices

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

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

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

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

Total and Spin density matrices

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

# How to perform a UHF calculation in practice?

## The SCF algorithm

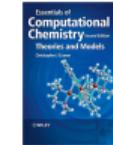
- ① Specify molecule  $\{R_A\}$  and  $\{Z_A\}$  and basis set  $\{\phi_\mu\}$  (same as RHF)
- ② Calculate integrals  $S_{\mu\nu}$ ,  $H_{\mu\nu}$  and  $\langle \mu\nu | \lambda\sigma \rangle$  (same as RHF)
- ③ Diagonalize  $\mathbf{S}$  and compute  $\mathbf{X}$  (same as RHF)
- ④ Obtain guess density matrix for  $\mathbf{P}^\alpha$  and  $\mathbf{P}^\beta$ 
  - 1a. Calculate  $\mathbf{G}^\alpha$  and then  $\mathbf{F}^\alpha = \mathbf{H} + \mathbf{G}^\alpha$
  - 1b. Calculate  $\mathbf{G}^\beta$  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  $\mathbf{E}^\alpha$
  - 3b. Diagonalize  $(\mathbf{F}^\beta)'$  to obtain  $(\mathbf{C}^\beta)'$  and  $\mathbf{E}^\beta$
  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  $\mathbf{P}^\alpha$  and  $\mathbf{P}^\beta$ , 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  $E_{\text{UHF}}$  for example

# Good books

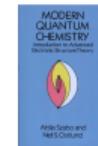
- Introduction to Computational Chemistry (Jensen)



- Essentials of Computational Chemistry (Cramer)



- Modern Quantum Chemistry (Szabo & Ostlund)



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

