

# The Hartree–Fock Approximation

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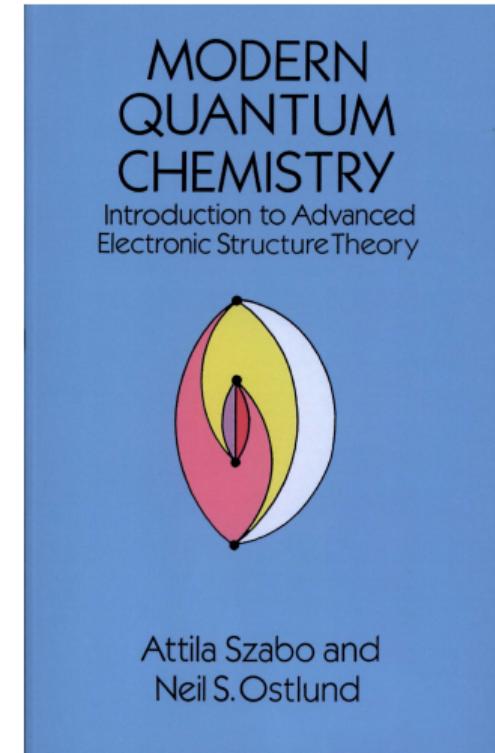
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# How to perform a HF calculation in practice?

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



Attila Szabo and  
Neil S. Ostlund

# 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 ( $m = e = \hbar = 1$ )

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

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

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

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

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

- $\nabla^2$  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

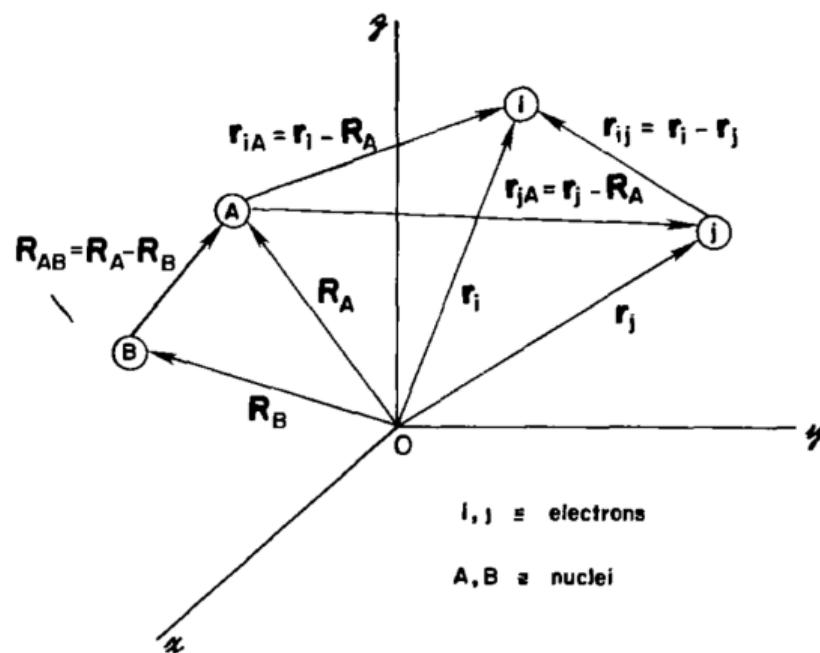


Figure 2.1 A molecular coordinate system  $i, j =$  electrons,  $A, B =$  nuclei

# 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

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

It describes the vibration, rotation and translation of the molecules

## Electronic Hamiltonian

The **electronic Hamiltonian** is

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

# The HF wave function

## A Slater determinant

$$\Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_N(\mathbf{x}_N)\rangle \quad (7)$$

$$= \mathcal{A} \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_N(\mathbf{x}_N) = \mathcal{A} \Pi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

- $\mathcal{A}$  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

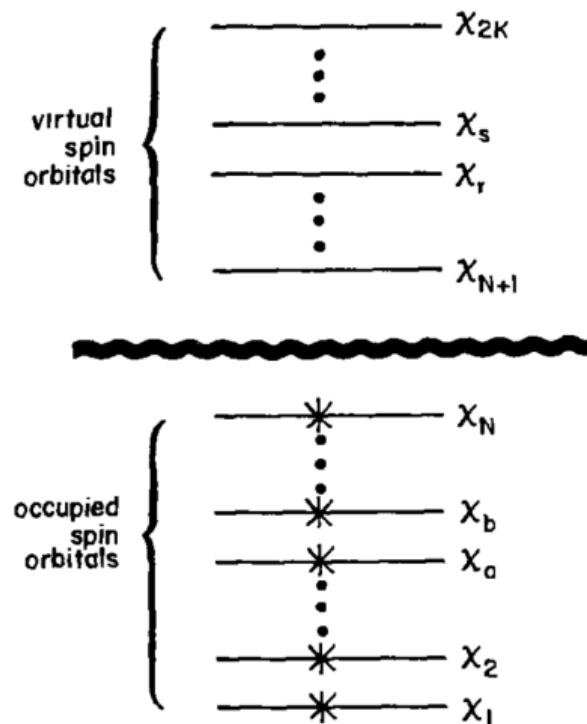
$$\langle \phi_{\mu} | \phi_{\nu} \rangle = \int \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} = S_{\mu\nu} = \text{Overlap matrix}$$

# 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

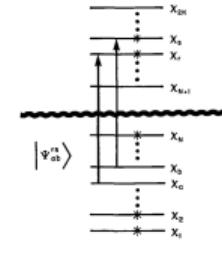
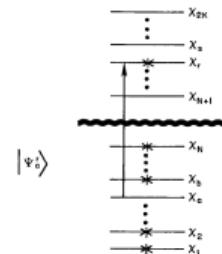
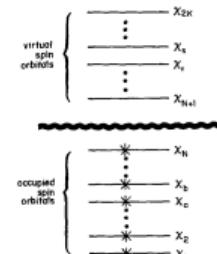
The electrons are in the  $N$  lowest orbitals (Aufbau principle):  $|\Psi_0\rangle = |\chi_1 \dots \chi_a \chi_b \dots \chi_N\rangle$  (8)

## Singly-excited determinants

Electron in  $a$  promoted in  $r$ :  $|\Psi_{\text{a}}^r\rangle = |\chi_1 \dots \chi_r \chi_a \chi_b \dots \chi_N\rangle$  (9)

## Doubly-excited determinants

Electrons in  $a$  and  $b$  promoted in  $r$  and  $s$ :  $|\Psi_{ab}^{rs}\rangle = |\chi_1 \dots \chi_r \chi_s \chi_a \chi_b \dots \chi_N\rangle$  (10)



# The Hartree-Fock energy

The HF energy is

$$E_{\text{HF}} = \langle \Psi_{\text{HF}} | \mathcal{H}_{\text{elec}} + \mathcal{V}_{\text{nn}} | \Psi_{\text{HF}} \rangle \quad \text{where} \quad \mathcal{H}_{\text{elec}} = \mathcal{T}_{\text{e}} + \mathcal{V}_{\text{ne}} + \mathcal{V}_{\text{ee}} \quad (11)$$

We define a few quantities:

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

$$\mathcal{O}_1 = \mathcal{T}_{\text{e}} + \mathcal{V}_{\text{ne}} = \sum_{i=1}^N h(i) \quad \text{where} \quad h(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad (12)$$

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

$$\mathcal{O}_2 = \mathcal{V}_{\text{ee}} = \sum_{i < j}^N \frac{1}{r_{ij}} \quad (13)$$

Therefore, we have

$$\mathcal{H}_{\text{elec}} = \sum_{i=1}^N h(i) + \sum_{i < j}^N \frac{1}{r_{ij}} \quad (14)$$

# The Hartree-Fock energy (Take 2)

- Nuclear repulsion:

$$\langle \Psi_{\text{HF}} | \mathcal{V}_{\text{nn}} | \Psi_{\text{HF}} \rangle = V_{\text{nn}} \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle = V_{\text{nn}} \quad (15)$$

- Core Hamiltonian:

$$\langle \Psi_{\text{HF}} | \mathcal{O}_1 | \Psi_{\text{HF}} \rangle = \sum_{a=1}^N \langle \chi_a(1) | h(1) | \chi_a(1) \rangle = \sum_{a=1}^N h_a \quad (16)$$

- Two-electron Hamiltonian:

$$\begin{aligned} \langle \Psi_{\text{HF}} | \mathcal{O}_2 | \Psi_{\text{HF}} \rangle &= \sum_{a < b}^N [ \langle \chi_a(1) \chi_b(2) | r_{12}^{-1} | \chi_a(1) \chi_b(2) \rangle - \langle \chi_a(1) \chi_b(2) | r_{12}^{-1} | \chi_b(1) \chi_a(2) \rangle ] \\ &= \sum_{a < b}^N \left( \underbrace{\mathcal{J}_{ab}}_{\text{Coulomb}} - \underbrace{\mathcal{K}_{ab}}_{\text{Exchange}} \right) = \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab}) \quad \text{because } \boxed{\mathcal{J}_{aa} = \mathcal{K}_{aa}} \end{aligned} \quad (17)$$

- HF energy:

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

(18)

# The Hartree-Fock energy (Take 3)

- Coulomb operator

$$\mathcal{J}_j(1) |\chi_i(1)\rangle = \langle \chi_j(2) | r_{12}^{-1} | \chi_j(2) \rangle |\chi_i(1)\rangle = \left[ \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_j(\mathbf{x}_2) \right] |\chi_i(\mathbf{x}_1)\rangle \quad (19)$$

- Coulomb matrix elements

$$\begin{aligned} \mathcal{J}_{ij} &= \langle \chi_i(1) | \mathcal{J}_j(1) | \chi_i(1) \rangle = \langle \chi_i(1) \chi_j(2) | r_{12}^{-1} | \chi_i(1) \chi_j(2) \rangle \\ &= \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (20)$$

- (non-local) Exchange operator

$$\mathcal{K}_j(1) |\chi_i(1)\rangle = \langle \chi_j(2) | r_{12}^{-1} | \chi_i(2) \rangle |\chi_j(1)\rangle = \left[ \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_2) \right] |\chi_j(\mathbf{x}_2)\rangle \quad (21)$$

- Exchange matrix elements

$$\begin{aligned} \mathcal{K}_{ij} &= \langle \chi_i(1) | \mathcal{K}_j(1) | \chi_i(1) \rangle = \langle \chi_i(1) \chi_j(2) | r_{12}^{-1} | \chi_j(1) \chi_i(2) \rangle \\ &= \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (22)$$

# Integral notations

## Spin orbitals

$$(i|h|j) = \langle i|h|j \rangle = \int \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1) d\mathbf{x}_1 \quad (23)$$

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (24)$$

$$\langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (25)$$

## Spatial orbitals

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1) d\mathbf{r}_1 \quad (26)$$

$$(ij|kl) = (\psi_i \psi_j | \psi_k \psi_l) = \iint \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \frac{1}{r_{12}} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (27)$$

# Permutation symmetry

## Permutation symmetry in physicists' notations

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \iint \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (28)$$

**Complex-valued integrals:**  $\langle ij|kl \rangle = \langle ji|lk \rangle = \langle kl|ij \rangle^* = \langle lk|ji \rangle^*$  (29)

## Permutation symmetry in chemists' notations

$$(ij|kl) = (\chi_i \chi_j | \chi_k \chi_l) = \iint \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (30)$$

**Real-valued integrals:**  $(ij|kl) = (ji|kl) = (ij|lk) = (ji|lk) = (kl|ij) = (lk|ji) = (kl|ji) = (lk|ji)$  (31)

# Slater-Condon rules: One-electron operators

$$\mathcal{O}_1 = \sum_i^N h(i) \quad (32)$$

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

$$\langle K | \mathcal{O}_1 | K \rangle = \sum_m^N \langle m | h | m \rangle \quad (33)$$

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

$$\langle K | \mathcal{O}_1 | L \rangle = \langle m | h | p \rangle \quad (34)$$

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

$$\langle K | \mathcal{O}_1 | L \rangle = 0 \quad (35)$$

## Slater-Condon rules: Two-electron operators

$$\mathcal{O}_2 = \sum_{i < j}^N r_{ij}^{-1} \quad (36)$$

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

$$\langle K | \mathcal{O}_2 | K \rangle = \frac{1}{2} \sum_{mn}^N \langle mn | | mn \rangle \quad (37)$$

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

$$\langle K | \mathcal{O}_2 | L \rangle = \sum_n^N \langle mn | | pn \rangle \quad (38)$$

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

$$\langle K | \mathcal{O}_2 | L \rangle = \langle mn | | pq \rangle \quad (39)$$

# 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)

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

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

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

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

# 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

$$\mathbf{F} \cdot \mathbf{C} = \mathbf{S} \cdot \mathbf{C} \cdot \mathbf{E} \quad \Leftrightarrow \quad \mathbf{F}' \cdot \mathbf{C}' = \mathbf{C}' \cdot \mathbf{E} \quad (40)$$

$$\mathbf{F}' = \mathbf{X}^\dagger \cdot \mathbf{F} \cdot \mathbf{X} \quad \mathbf{C} = \mathbf{X} \cdot \mathbf{C}' \quad \mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = \mathbf{I} \quad (41)$$

- 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  $\mathbf{E}$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \quad \mathbf{E} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon_K \end{pmatrix} \quad (42)$$

### Self-consistent field (SCF) procedure

$$\mathbf{F}(\mathbf{C}) \cdot \mathbf{C} = \mathbf{S} \cdot \mathbf{C} \cdot \mathbf{E} \quad \text{How do we solve these HF equations?} \quad (43)$$

# Expression of the Fock matrix

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

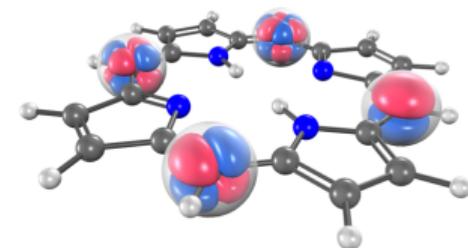
$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu \lambda | \nu \sigma \rangle - \frac{1}{2} \langle \mu \lambda | \sigma \nu \rangle) \quad (\text{closed shell})$$

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

One-electron integrals: overlap & core Hamiltonian

$$S_{\mu\nu} = \langle \mu | \nu \rangle = \int \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (44)$$

$$H_{\mu\nu} = \langle \mu | \hat{H}^c | \nu \rangle = \int \phi_{\mu}^*(\mathbf{r}) \hat{H}^c(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (45)$$



Chemist/Mulliken notation for two-electron integrals

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}^*(\mathbf{r}_1) \phi_{\nu}(\mathbf{r}_1) \frac{1}{r_{12}} \phi_{\lambda}^*(\mathbf{r}_2) \phi_{\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (46)$$

$$(\mu\nu||\lambda\sigma) = (\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu) \quad (47)$$

Physicist/Dirac notation for two-electron integrals

$$\langle \mu\nu|\lambda\sigma \rangle = \iint \phi_{\mu}^*(\mathbf{r}_1) \phi_{\nu}^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{\lambda}(\mathbf{r}_1) \phi_{\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (48)$$

$$\langle \mu\nu||\lambda\sigma \rangle = \langle \mu\nu|\lambda\sigma \rangle - \langle \mu\nu|\sigma\lambda \rangle \quad (49)$$

# Computation of the Fock matrix and energy

## Density matrix (closed-shell system)

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a} \quad \text{or} \quad \boxed{\mathbf{P} = 2 \mathbf{C} \cdot \mathbf{C}^\dagger} \quad (50)$$

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

$$F_{\mu\nu} = H_{\mu\nu} + \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma)}_{J_{\mu\nu} = \text{Coulomb}} - \frac{1}{2} \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\sigma|\lambda\nu)}_{K_{\mu\nu} = \text{exchange}} \quad (51)$$

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

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} \left[ (\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma} \quad \text{or} \quad \boxed{E_{\text{HF}} = \frac{1}{2} \text{Tr}[\mathbf{P} \cdot (\mathbf{H} + \mathbf{F})]} \quad (52)$$

# Expression of the HF energy

## He energy in the AO basis

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

# How to perform a HF calculation in practice?

## The SCF algorithm

- 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  $\mathbf{X}$
- ➍ 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.
- ➎ 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

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U} \cdot \mathbf{s}^{-1/2} \cdot \mathbf{U}^\dagger \text{ is one solution...} \quad (53)$$

## Is it working?

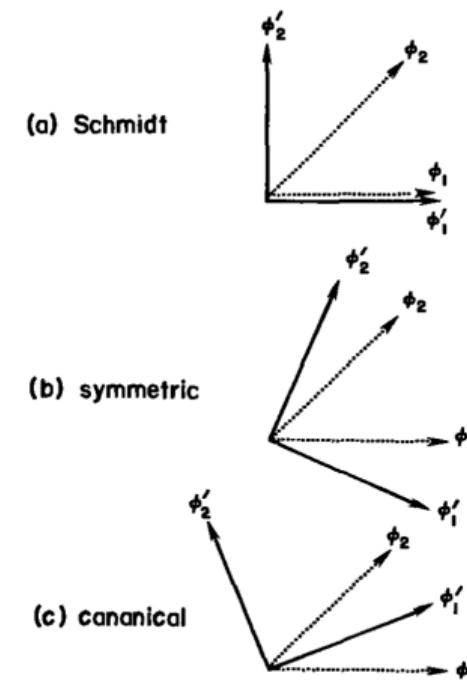
$$X^\dagger \cdot S \cdot X = S^{-1/2} \cdot S \cdot S^{-1/2} = S^{-1/2} \cdot S \cdot S^{-1/2} = I \quad \checkmark \quad (54)$$

## Canonical orthogonalization

$\mathbf{X} = \mathbf{U} \cdot \mathbf{s}^{-1/2}$  is another solution (when you have linear dependencies)... (55)

## Is it working?

$$\mathbf{X}^\dagger \cdot \mathbf{S} \cdot \mathbf{X} = s^{-1/2} \cdot \underbrace{\mathbf{U}^\dagger \cdot \mathbf{S} \cdot \mathbf{U}}_s \cdot s^{-1/2} = \mathbf{I} \quad \checkmark \quad (56)$$



# 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  $\mathbf{F} \cdot \mathbf{P} \cdot \mathbf{S} - \mathbf{S} \cdot \mathbf{P} \cdot \mathbf{F} = \mathbf{0}$
- 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

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

## Practical information

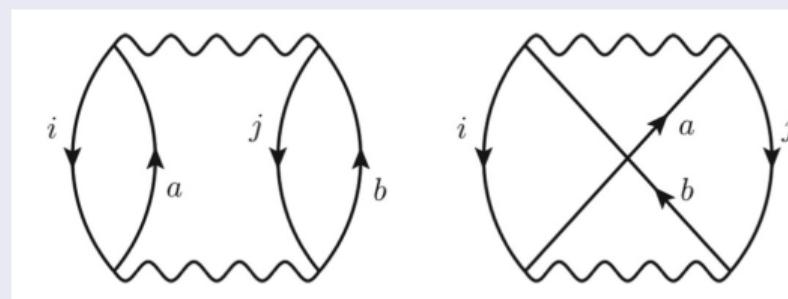
I'm lost, please help me...

- ➊ In directory xHF/src: exercices in xHF.f90 and RHF.f90, tools in utils.f90 and wrap\_lapack.f90
- ➋ In xHF.f90: build matrix X (subroutine orthogonalisation\_matrix.90)
- ➌ in RHF.f90: self-consistent procedure (subroutines hartree\_potential.f90 and exchange\_potential.f90) and final data
- ➍ To compile the program: make
- ➎ To test the program: ./GoHF At Basis (for instance ./GoHF Be VDZ)
- ➏ NB: overlap (S), two-electron integrals (ERI) and core Hamiltonian (Hc) matrix elements are already computed.

# MP2 correlation energy

MP2 is the simplest way of catching a good chunk of correlation:

$$\begin{aligned}
 E_c^{(2)} &= \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij | ab \rangle (2 \langle ij | ab \rangle - \langle ij | ba \rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\
 &= \underbrace{2 \sum_{ij} \sum_{ab} \frac{\langle ij | ab \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{direct part}} - \underbrace{\sum_{ij} \sum_{ab} \frac{\langle ij | ab \rangle \langle ij | ba \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}_{\text{exchange part}}
 \end{aligned} \tag{57}$$



# Computation of the MP2 correlation energy

- Expression of the MP2 correlation energy

$$E_c^{(2)} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle (2\langle ab|ij\rangle - \langle ab|ji\rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- $(i, j)$  are occupied MOs,  $(a, b)$  are virtual (unoccupied) MOs
- The  $\epsilon_p$ 's are the MO one-electron energies (provided by HF program)
- AO to MO integral transformation:

$$\langle pq|rs\rangle = \sum_{\mu\nu\lambda\sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} \langle \mu\nu|\lambda\sigma\rangle$$

- $\langle \mu\nu|\lambda\sigma\rangle$  are ERIs in the AO basis
- $\langle pq|rs\rangle$  are ERIs in the MO basis

## MP2 in practice

- Write a subroutine computing the two-electron integrals in the MO basis using the expressions in the AO basis.
- Check the value of the RHF energy in the MO basis

$$E_{\text{HF}} = 2 \sum_i^{\text{occ}} h_i + \sum_{ij}^{\text{occ}} (2J_{ij} - K_{ij})$$

$$J_{ij} = \langle ij | ij \rangle$$

$$K_{ij} = \langle ij | ji \rangle$$

$$h_i = \sum_{\mu\nu} c_{\mu i} c_{\nu i} \langle \mu | H^c | \nu \rangle$$

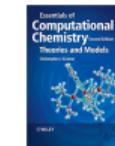
- Write a subroutine computing  $E_c^{(2)}$
- NB: Call the new subroutines from xHF.f90, **not** RHF.f90

# Good books

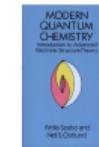
- Introduction to Computational Chemistry (Jensen)



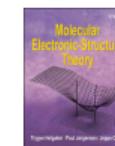
- Essentials of Computational Chemistry (Cramer)



- Modern Quantum Chemistry (Szabo & Ostlund)



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



# Computation of the Fock matrix and energy

## Density matrix (closed-shell system)

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i} \quad \text{or} \quad \boxed{\mathbf{P} = \mathbf{C} \cdot \mathbf{C}^\dagger} \quad (58)$$

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

$$F_{\mu\nu} = H_{\mu\nu} + \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma)}_{J_{\mu\nu} = \text{Coulomb}} - \frac{1}{2} \underbrace{\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\sigma|\lambda\nu)}_{K_{\mu\nu} = \text{exchange}} \quad (59)$$

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

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} \left[ (\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma} \quad \text{or} \quad \boxed{E_{\text{HF}} = \frac{1}{2} \text{Tr}[\mathbf{P} \cdot (\mathbf{H} + \mathbf{F})]} \quad (60)$$

# Computation of the Fock matrix and energy

**procedure** COMPUTING THE COULOMB MATRIX

**for**  $\mu = 1, N$  **do**

**for**  $\nu = 1, N$  **do**

$J_{\mu\nu} = 0$

        ▷ Initialization of the array

**for**  $\lambda = 1, N$  **do**

**for**  $\sigma = 1, N$  **do**

$J_{\mu\nu} = J_{\mu\nu} + P_{\lambda\sigma}(\mu\nu|\lambda\sigma)$

        ▷ Accumulation step

**end for**

**end for**

**end for**

**end for**

**end procedure**

▷ This is a  $\mathcal{O}(N^4)$  algorithm as it involves four loops

# Computation of exact exchange

**procedure** COMPUTING THE EXCHANGE MATRIX

**for**  $\mu = 1, N$  **do**

**for**  $\nu = 1, N$  **do**

$K_{\mu\nu} = 0$

        ▷ Initialization of the array

**for**  $\lambda = 1, N$  **do**

**for**  $\sigma = 1, N$  **do**

$K_{\mu\nu} = K_{\mu\nu} + P_{\lambda\sigma}(\mu\sigma|\lambda\nu)$

        ▷ Accumulation step

**end for**

**end for**

**end for**

**end for**

**end procedure**

# Computing the MP2 correlation energy

How much does it cost to compute the MP2 correlation energy?

**procedure** MP2 CORRELATION ENERGY

```

 $E_c^{(2)} = 0$ 
for  $i = 1, O$  do
    for  $j = 1, O$  do
        for  $a = 1, V$  do
            for  $b = 1, V$  do
                 $\Delta = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$ 
                 $E_c^{(2)} = E_c^{(2)} + (2 \langle ij | ab \rangle^2 - \langle ij | ab \rangle \langle ij | ba \rangle) / \Delta$ 
            end for
        end for
    end for
end procedure
```

▷  $\mathcal{O}(N^4)$  because there are four loops!

# AO to MO transformation (Take 1)

The naive way...

$$\underbrace{(pq|rs)}_{\text{MO integrals}} = \sum_{\mu\nu\lambda\sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} \underbrace{(\mu\nu|\lambda\sigma)}_{\text{AO integrals}} \quad (61)$$

```

procedure AO-TO-MO TRANSFORMATION
  for p = 1, N do
    for q = 1, N do
      for r = 1, N do
        for s = 1, N do
          (pq|rs) = 0
          for μ = 1, N do
            for ν = 1, N do
              for λ = 1, N do
                for σ = 1, N do
                  (pq|rs) = (pq|rs) + cμp cνq cλr cσs (μν|λσ)
                end for
              end for
            end for
          end for
        end for
      end for
    end for
  end for
end procedure

```

▷ Initialization of the array

▷ Accumulation step

▷ This is a  $\mathcal{O}(N^8)$  algorithm! You won't do much quantum chemistry with this...

## AO to MO transformation (Take 2)

Semi-direct algorithm...

$$(pq|rs) = \sum_{\mu p} c_{\mu p} \left\{ \sum_{\nu q} c_{\nu q} \left[ \sum_{\lambda r} c_{\lambda r} \left( \underbrace{\sum_{\sigma s} c_{\sigma s} (\mu \nu | \lambda \sigma)}_{\text{Step #1}} \right) \right] \right\}$$

\_\_\_\_\_  
 Step #2  
 \_\_\_\_\_  
 Step #3  
 \_\_\_\_\_  
 Step #4

(62)

# Semi-direct algorithm

Semi-direct algorithm... Step #1

**procedure** SEMI-DIRECT ALGORITHM (STEP #1)

    Allocate temporary array  $I$  of size  $N^4$

**for**  $\mu = 1, N$  **do**

**for**  $\nu = 1, N$  **do**

**for**  $\lambda = 1, N$  **do**

**for**  $\sigma = 1, N$  **do**

**for**  $s = 1, N$  **do**

$$I_{\mu\nu\lambda s} = I_{\mu\nu\lambda s} + c_{\sigma s}(\mu\nu|\lambda\sigma)$$

**end for**

**end for**

**end for**

**end for**

**end for**

**end procedure**

▷ Step #1 costs  $\mathcal{O}(N^5)$  and  $\mathcal{O}(N^4)$  storage

# Semi-direct algorithm

## Semi-direct algorithm... Step #2

```

procedure SEMI-DIRECT ALGORITHM (STEP #2)
    Allocate temporary array  $J$  of size  $N^4$ 
    for  $\mu = 1, N$  do
        for  $\nu = 1, N$  do
            for  $\lambda = 1, N$  do
                for  $r = 1, N$  do
                    for  $s = 1, N$  do
                         $J_{\mu\nu rs} = J_{\mu\nu rs} + c_{\lambda r} I_{\mu\nu\lambda s}$ 
                    end for
                end for
            end for
        end for
    end for
end procedure

```

▷ Step #2 costs  $\mathcal{O}(N^5)$  and  $\mathcal{O}(N^4)$  storage

# Semi-direct algorithm

Semi-direct algorithm... Step #3

```
procedure SEMI-DIRECT ALGORITHM (STEP #3)
    for  $\mu$  = 1,  $N$  do
        for  $\nu$  = 1,  $N$  do
            for  $q$  = 1,  $N$  do
                for  $r$  = 1,  $N$  do
                    for  $s$  = 1,  $N$  do
                         $I_{\mu q r s} = I_{\mu q r s} + c_{\nu q} J_{\mu \nu r s}$ 
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #3 costs  $\mathcal{O}(N^5)$  and no new storage

# Semi-direct algorithm

Semi-direct algorithm... Step #4

```
procedure SEMI-DIRECT ALGORITHM (STEP #4)
    for  $\mu$  = 1,  $N$  do
        for  $p$  = 1,  $N$  do
            for  $q$  = 1,  $N$  do
                for  $r$  = 1,  $N$  do
                    for  $s$  = 1,  $N$  do
                         $(pq|rs) = (pq|rs) + c_{\mu p} I_{\mu qrs}$ 
                    end for
                end for
            end for
        end for
    end for
end procedure
```

▷ Step #4 costs  $\mathcal{O}(N^5)$  and no new storage