Hartree-Fock and post-Hartree-Fock methods

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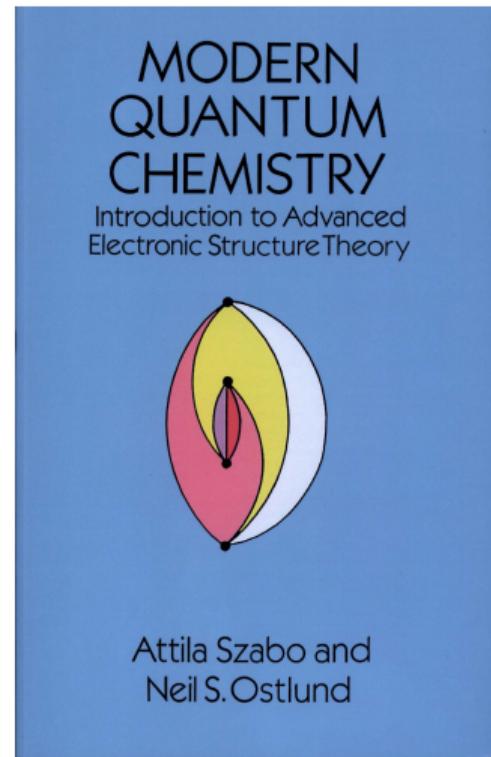
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The SCF algorithm for Hartree-Fock (HF) calculations (p. 146)

1. Specify molecule $\{\boldsymbol{R}_A\}$ 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 $\boldsymbol{S}$ and compute $\boldsymbol{X} = \boldsymbol{S}^{-1/2}$

4. Obtain guess density matrix for $\boldsymbol{P}$
   1. Calculate $\boldsymbol{J}$ and $\boldsymbol{K}$, then $\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{J} + \boldsymbol{K}$
   2. Compute $\boldsymbol{F}' = \boldsymbol{X}^\dagger \cdot \boldsymbol{F} \cdot \boldsymbol{X}$
   3. Diagonalize $\boldsymbol{F}'$ to obtain $\boldsymbol{C}'$ and $\boldsymbol{E}$
   4. Calculate $\boldsymbol{C} = \boldsymbol{X} \cdot \boldsymbol{C}'$
   5. Form a new density matrix $\boldsymbol{P} = \boldsymbol{C} \cdot \boldsymbol{C}^\dagger$
   6. Am I converged? If not go back to 1.

5. Calculate stuff that you want, like E_{HF} for example

MODERN QUANTUM CHEMISTRY
Introduction to Advanced Electronic Structure Theory

Attila Szabo and Neil S. Ostlund

- 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!

In the Schrödinger equation

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

the total Hamiltonian is

$$\boxed{\mathcal{H} = \mathcal{T}_n + \mathcal{T}_e + \mathcal{V}_{ne} + \mathcal{V}_{ee} + \mathcal{V}_{nn}} \tag{2}$$

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

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

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

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

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

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

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

- ∇^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
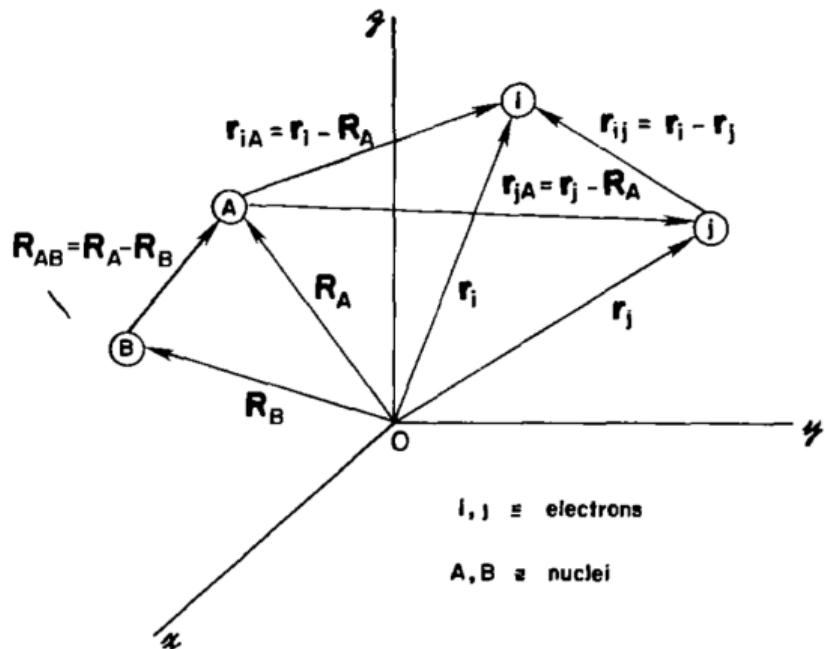
Figure 2.1 A molecular coordinate system i, j = electrons, A, B = nuclei

Born-Oppenheimer approximation = decoupling nuclei and electrons

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

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

Nuclear Hamiltonian

The nuclear Hamiltonian is

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

It describes the vibration, rotation and translation of the molecules

Electronic Hamiltonian

The electronic Hamiltonian is

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

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

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

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

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

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

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

Antisymmetry principle

$$\mathcal{H}_{\text{elec}}\Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \mathcal{E}_{\text{elec}}\Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \tag{9}$$

$$\Phi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_i, \ldots, \boldsymbol{x}_j, \ldots, \boldsymbol{x}_N) = -\Phi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_j, \ldots, \boldsymbol{x}_i, \ldots, \boldsymbol{x}_N) \tag{10}$$

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

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Solution
Indistinguishable particles means

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

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

$$\left| \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) \right|^2 = \left| \Psi(\boldsymbol{x}_2, \boldsymbol{x}_1) \right|^2 \Rightarrow \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \pm \Psi(\boldsymbol{x}_2, \boldsymbol{x}_1) \tag{11}$$

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

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

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

The wave function vanishes!   ⇒   This is called the Fermi hole!

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

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Solution

A possible solution is

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

This has been popularized by Slater:

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

This is called a Slater determinant!

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

A Slater determinant

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

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

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

$$\chi_i(\boldsymbol{x}) = \sigma(\omega)\psi_i(\boldsymbol{r}) = \begin{cases} \alpha(\omega)\,\psi_i(\boldsymbol{r}) \\ \beta(\omega)\,\psi_i(\boldsymbol{r}) \end{cases} \qquad \boxed{\psi_i(\boldsymbol{r}) = \sum_{\mu}^{K} C_{\mu i}\phi_{\mu}(\boldsymbol{r})}$$

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

The spin orbitals are orthogonal

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

The spatial orbitals are orthogonal

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

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

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

Comments

- $\{\phi_\mu | i = 1, \ldots, K\}$ are basis functions or atomic orbitals (AOs)
- $\{\chi_i | i = 1, \ldots, 2K\}$ are the spin orbitals
- $\{\psi_i | i = 1, \ldots, K\}$ 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
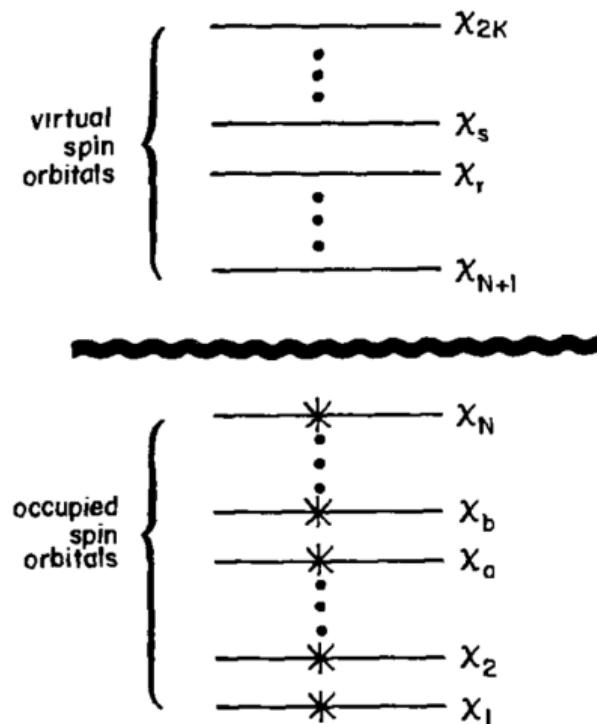
**Figure 2.4** The Hartree-Fock ground state determinant, $|\chi_1 \chi_2 \cdots \chi_a \chi_b \cdots \chi_N\rangle$.

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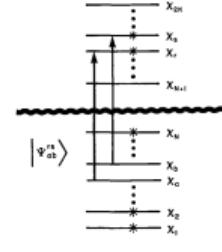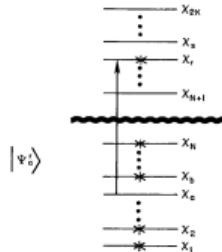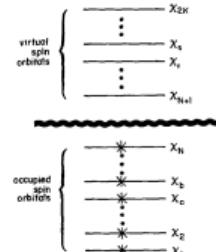
The electrons are in the N lowest orbitals (Aufbau principle): $|\Psi_0\rangle = |\chi_1 \ldots \chi_a \chi_b \ldots \chi_N\rangle$ (16)

Singly-excited determinants

Electron in a promoted in r: $|\Psi_a^r\rangle = |\chi_1 \ldots \chi_r \chi_b \ldots \chi_N\rangle$ (17)

Doubly-excited determinants

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

The HF energy is

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

We define a few quantities:

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

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

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

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

Therefore, we have

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

- Nuclear repulsion:

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

- Core Hamiltonian:

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

- Two-electron Hamiltonian:

$$\langle \Psi_{HF} | \mathcal{O}_2 | \Psi_{HF} \rangle = \sum_{a<b}^{N} \left[\langle \chi_a(1)\chi_b(2) | r_{12}^{-1} | \chi_a(1)\chi_b(2) \rangle - \langle \chi_a(1)\chi_b(2) | r_{12}^{-1} | \chi_b(1)\chi_a(2) \rangle \right]$$

$$= \sum_{a<b}^{N} \left(\underbrace{\mathcal{J}_{ab}}_{\text{Coulomb}} - \underbrace{\mathcal{K}_{ab}}_{\text{Exchange}} \right) = \frac{1}{2} \sum_{a=1}^{N} \sum_{b=1}^{N} (\mathcal{J}_{ab} - \mathcal{K}_{ab}) \quad \text{because} \quad \boxed{\mathcal{J}_{aa} = \mathcal{K}_{aa}}$$

$$(25)$$

- HF energy:

$$\boxed{E_{HF} = \sum_{a=1}^{N} h_a + \sum_{a<b}^{N} (\mathcal{J}_{ab} - \mathcal{K}_{ab}) + V_{nn}} \qquad (26)$$

- Coulomb operator

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

- Coulomb matrix elements

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

- (non-local) Exchange operator

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

- Exchange matrix elements

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

Spin orbitals

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

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

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

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

Spatial orbitals

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

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

Permutation symmetry in physicsts' notations

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

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

Permutation symmetry in chemists' notations

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

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

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

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

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

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

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

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

$$\langle K|\mathcal{O}_1|L\rangle = 0 \tag{44}$$

$$\boxed{\mathcal{O}_2 = \sum_{i<j}^{N} r_{ij}^{-1}} \tag{45}$$

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

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

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

$$\langle K|\mathcal{O}_2|L\rangle = \sum_{n}^{N} \langle mn||pn\rangle \tag{47}$$

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

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

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"

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Solution

$$\Psi_{HF} = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \frac{\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)}{\sqrt{2}}$$

$$\langle \Psi_{HF} | \Psi_{HF} \rangle = \frac{1}{2} \langle \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2) | \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2) \rangle$$

$$= \frac{1}{2} \Big[\langle \chi_1(1)\chi_2(2) | \chi_1(1)\chi_2(2) \rangle - \langle \chi_1(1)\chi_2(2) | \chi_2(1)\chi_1(2) \rangle$$

$$- \langle \chi_2(1)\chi_1(2) | \chi_1(1)\chi_2(2) \rangle + \langle \chi_2(1)\chi_1(2) | \chi_2(1)\chi_1(2) \rangle \Big]$$

$$= \frac{1}{2} \Big[1 - 0 - 0 + 1 \Big] = 1$$

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

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

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

Solution

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

$$\langle \Psi_{HF} | h(1) + h(2) | \Psi_{HF} \rangle$$

$$= \frac{1}{2} \langle \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1) | h(1) + h(2) | \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1) \rangle$$

$$= \frac{1}{2} \Big[\langle \chi_1(1)\chi_2(2) | h(1) + h(2) | \chi_1(1)\chi_2(2) \rangle - \langle \chi_1(1)\chi_2(2) | h(1) + h(2) | \chi_2(1)\chi_1(2) \rangle$$

$$- \langle \chi_2(1)\chi_1(2) | h(1) + h(2) | \chi_1(1)\chi_2(2) \rangle + \langle \chi_2(1)\chi_1(2) | h(1) + h(2) | \chi_2(1)\chi_1(2) \rangle \Big]$$

$$= \frac{1}{2} \Big[h_1 + h_2 - 0 - 0 + h_2 + h_1 \Big] = h_1 + h_2$$

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"

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

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

$$\langle \Psi_{HF} | r_{12}^{-1} | \Psi_{HF} \rangle = \frac{1}{2} \langle \chi_1 \chi_2 - \chi_2 \chi_1 | r_{12}^{-1} | \chi_1 \chi_2 - \chi_2 \chi_1 \rangle$$

$$= \frac{1}{2} \Big[\langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_2 \chi_1 \rangle$$

$$- \langle \chi_2 \chi_1 | r_{12}^{-1} | \chi_1 \chi_2 \rangle + \langle \chi_2 \chi_1 | r_{12}^{-1} | \chi_2 \chi_1 \rangle \Big]$$

$$= \frac{1}{2} \Big[\mathcal{J}_{12} - \mathcal{K}_{12} - \mathcal{K}_{12} + \mathcal{J}_{12} \Big] = \mathcal{J}_{12} - \mathcal{K}_{12}$$

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

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

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

$$\mathcal{O}_1 = h(1) + h(2) + h(3)$$
$$\mathcal{O}_2 = r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}$$

$$\vdots$$

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

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

$$\chi_1 = \alpha\,\psi_1 \qquad \chi_2 = \beta\,\psi_1$$

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

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

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

Triplet $1s2s$ state of the He atom

$$\chi_1 = \alpha\,\psi_1 \qquad \chi_2 = \alpha\,\psi_2$$

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

Singlet-triplet energy splitting

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

Problem: HF energy of the Li atom

"Find the HF energy of the Li atom in terms of the spatial MOs"

Problem: HF energy of the Li atom

"Find the HF energy of the Li atom in terms of the spatial MOs"

Solution:

$$\chi_1 = \alpha \, \psi_1 \qquad \chi_2 = \beta \, \psi_1 \qquad \chi_3 = \alpha \, \psi_2 \qquad \chi_4 = \beta \, \psi_2$$

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

Problem: HF energy of the Li atom

"Find the HF energy of the Li atom in terms of the spatial MOs"

Solution:

$$\chi_1 = \alpha\,\psi_1 \qquad \chi_2 = \beta\,\psi_1 \qquad \chi_3 = \alpha\,\psi_2 \qquad \chi_4 = \beta\,\psi_2$$

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

Problem: HF energy of the B atom

"Find the HF energy of the B atom' in terms of the spatial MOs'

Problem: HF energy of the Li atom
"Find the HF energy of the Li atom in terms of the spatial MOs"

Solution:

$$\chi_1 = \alpha \, \psi_1 \qquad \chi_2 = \beta \, \psi_1 \qquad \chi_3 = \alpha \, \psi_2 \qquad \chi_4 = \beta \, \psi_2$$

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

Problem: HF energy of the B atom
"Find the HF energy of the B atom' in terms of the spatial MOs'

Solution:

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

Two-electron example: H_2 in minimal basis

In the spin orbital basis, we have

$$E_{HF} = \langle \chi_1|h|\chi_1 \rangle + \langle \chi_2|h|\chi_2 \rangle + \langle \chi_1\chi_2|\chi_1\chi_2 \rangle - \langle \chi_1\chi_2|\chi_2\chi_1 \rangle$$
$$= [\chi_1|h|\chi_1] + [\chi_2|h|\chi_2] + [\chi_1\chi_1|\chi_2\chi_2] - [\chi_1\chi_2|\chi_2\chi_1]$$
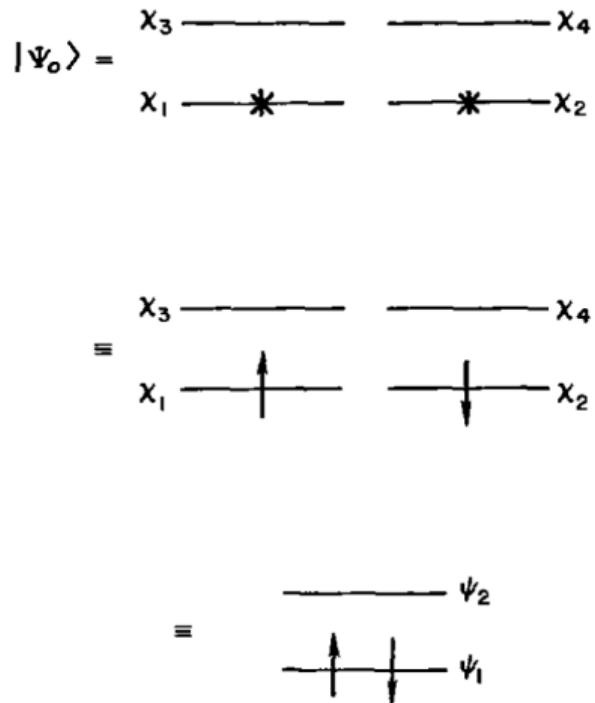
Spin to spatial transformation:

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

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

Therefore, in the spatial orbital basis, we have

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

One-electron terms

$$[\chi_1|h|\chi_1] = \int \chi_1^*(\mathbf{x})h(\mathbf{r})\chi_1(\mathbf{x})d\mathbf{x}$$

$$= \int \alpha^*(\omega)\psi_1^*(\mathbf{r})h(\mathbf{r})\alpha(\omega)\psi_1(\mathbf{r})d\omega d\mathbf{r}$$

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

$$[\chi_2|h|\chi_2] = \int \chi_2^*(\mathbf{x})h(\mathbf{r})\chi_2(\mathbf{x})d\mathbf{x}$$

$$= \int \beta^*(\omega)\psi_1^*(\mathbf{r})h(\mathbf{r})\beta(\omega)\psi_1(\mathbf{r})d\omega d\mathbf{r}$$

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

Two-electron terms

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

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

General expression

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

One- and two-electron terms

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

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

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

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

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)

Problem:
" Find the expression of the matrix elements $f_{ij} = \langle \chi_i | f | \chi_j \rangle$"

Problem:
" Find the expression of the matrix elements $f_{ij} = \langle \chi_i | f | \chi_j \rangle$"

Solution:

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

Problem:
" Deduce the expression of ε_i"

Problem:
" Deduce the expression of ε_i"

Solution:

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

Problem

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

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

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

Problem

"Let's suppose we know all the functions such as $\hat{H}\varphi_i = E_i\varphi_i$, with $E_0 < E_1 < \ldots$ 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

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

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \sum_i c_i\varphi_i \middle| \hat{H} \middle| \sum_j c_j\varphi_j \right\rangle = \sum_{ij} c_i c_j \langle \varphi_i | \hat{H} | \varphi_j \rangle$$

$$= \sum_{ij} c_i c_j E_j \langle \varphi_i | \varphi_j \rangle = \sum_{ij} c_i c_j E_j \delta_{ij} = \sum_i c_i^2 E_i \geq E_0 \sum_i c_i^2 = E_0$$

Ground-state energy of the N-electron system

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

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

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

Ionization potential (IP)

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

Problem:
"Show that Koopmans' theorem applies to electron affinities"

Problem:
"Show that Koopmans' theorem applies to electron affinities"

Solution:

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

Expansion in a basis

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

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

Roothaan-Hall equations

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

Matrix form of the Roothaan-Hall equations

$$\boldsymbol{F} \cdot \boldsymbol{C} = \boldsymbol{S} \cdot \boldsymbol{C} \cdot \boldsymbol{E} \qquad\qquad \Leftrightarrow \qquad\qquad \boldsymbol{F}' \cdot \boldsymbol{C}' = \boldsymbol{C}' \cdot \boldsymbol{E} \qquad (56)$$

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

- 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 $\boldsymbol{C}$ and the orbital energies $\boldsymbol{E}$

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

Self-consistent field (SCF) procedure

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

Problem:

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

Problem:

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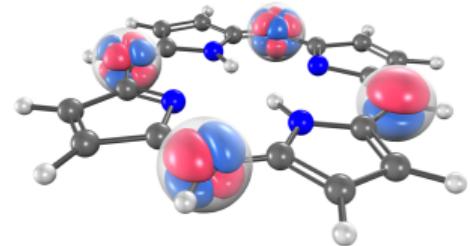
Solution:

$$F_{\mu\nu} = \langle\mu|h + \sum_{a}^{N}(\mathcal{J}_a - \mathcal{K}_a)|\nu\rangle = H_{\mu\nu} + \sum_{a}^{N} \langle\mu|\mathcal{J}_a - \mathcal{K}_a|\nu\rangle$$

$$= H_{\mu\nu} + \sum_{a}^{N}(\langle\mu\chi_a|r_{12}^{-1}|\nu\chi_a\rangle - \langle\mu\chi_a|r_{12}^{-1}|\chi_a\nu\rangle)$$

$$= H_{\mu\nu} + \sum_{a}^{N}\sum_{\lambda\sigma} C_{\lambda a}C_{\sigma a}(\langle\mu\lambda|r_{12}^{-1}|\nu\sigma\rangle - \langle\mu\lambda|r_{12}^{-1}|\sigma\nu\rangle)$$

$$= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\langle\mu\lambda|\nu\sigma\rangle - \langle\mu\lambda|\sigma\nu\rangle) = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \langle\mu\lambda||\nu\sigma\rangle = H_{\mu\nu} + G_{\mu\nu}$$

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

One-electron integrals: overlap & core Hamiltonian

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

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

Chemist/Mulliken notation for two-electron integrals

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

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

Physicist/Dirac notation for two-electron integrals

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

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

Density matrix (closed-shell system)

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

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

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

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

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

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

Problem:

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

Solution:

$$E_{\text{HF}} = \sum_a^N h_a + \frac{1}{2} \sum_{ab}^N (\mathcal{J}_{ab} - \mathcal{K}_{ab}) \quad \text{(cf few slides ago)}$$

$$= \sum_a^N \left\langle \sum_\mu C_{\mu a} \phi_\mu \middle| h \middle| \sum_\nu C_{\nu a} \phi_\nu \right\rangle + \frac{1}{2} \sum_{ab}^N \left\langle \left(\sum_\mu C_{\mu a} \phi_\mu \right) \left(\sum_\lambda C_{\lambda b} \phi_\lambda \right) \middle| \middle| \left(\sum_\nu C_{\nu a} \phi_\nu \right) \left(\sum_\sigma C_{\sigma b} \phi_\sigma \right) \right\rangle$$

$$= \sum_{\mu\nu} P_{\mu\nu} \left[H_{\mu\nu} + \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} \left\langle \mu\lambda || \nu\sigma \right\rangle \right]$$

The SCF algorithm

1. Specify molecule $\{\boldsymbol{R}_A\}$ 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 $\boldsymbol{S}$ and compute $\boldsymbol{X}$
4. Obtain guess density matrix for $\boldsymbol{P}$
   1. Calculate $\boldsymbol{G}$ and then $\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{G}$
   2. Compute $\boldsymbol{F}' = \boldsymbol{X}^\dagger \cdot \boldsymbol{F} \cdot \boldsymbol{X}$
   3. Diagonalize $\boldsymbol{F}'$ to obtain $\boldsymbol{C}'$ and $\boldsymbol{E}$
   4. Calculate $\boldsymbol{C} = \boldsymbol{X} \cdot \boldsymbol{C}'$
   5. Form a new density matrix $\boldsymbol{P} = \boldsymbol{C} \cdot \boldsymbol{C}^\dagger$
   6. Am I converged? If not go back to 1.
5. Calculate stuff that you want, like E_{HF} for example

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

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

Is it working?
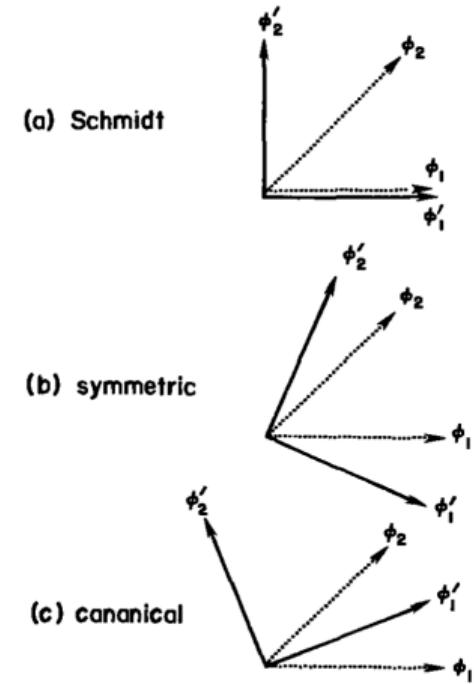
$$X^\dagger \cdot S \cdot X = S^{-1/2} \cdot S \cdot S^{-1/2} = S^{-1/2} \cdot S \cdot S^{-1/2} = I \quad \checkmark \tag{70}$$

Canonical orthogonalization

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

Is it working?

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

(a) Schmidt

(b) symmetric

(c) canonical

Possible initial density matrix

1. We can set $P = 0 \Rightarrow F = H$ (core Hamiltonian approximation):
   $\Rightarrow$ Usually a poor guess but easy to implement

2. Use EHT or semi-empirical methods:
   $\Rightarrow$ Out of fashion

3. Using tabulated atomic densities:
   $\Rightarrow$ "SAD" guess in QChem

4. Read the MOs of a previous calculation:
   $\Rightarrow$ Very common and very useful

Convergence in SCF calculations

❶ You can check the energy and/or the density matrix:
   ⇒ The energy/density **should not** change at convergence

❷ You can check the commutator $F \cdot P \cdot S - S \cdot P \cdot F$:
   ⇒ At convergence, we have $F \cdot P \cdot S - S \cdot P \cdot F = 0$

❸ The DIIS (direct inversion in the iterative subspace) method is usually used to speed up convergence:
   ⇒ Extrapolation of the Fock matrix using previous iterations

$$F_{m+1} = \sum_{i=m-k}^{m} c_i F_i$$

Classical vs Quantum

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

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

Vector components

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

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

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

How to model open-shell systems?
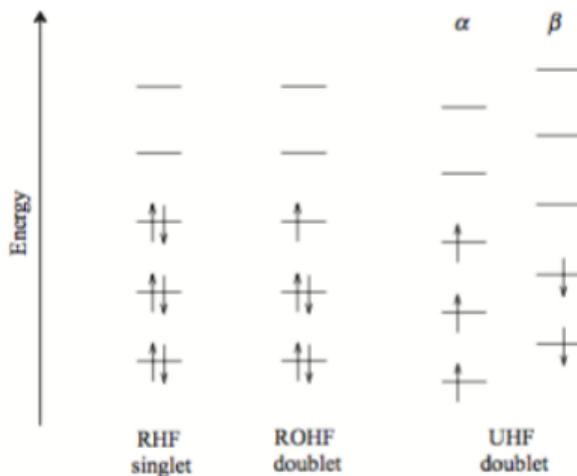
- RHF is made to describe closed-shell systems and we have used restricted spin orbitals:

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

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

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

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

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

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:

$$\boxed{f^\alpha(1)\,\psi_i^\alpha(1) = \varepsilon_i^\alpha\,\psi_j^\alpha(1)} \qquad\qquad \boxed{f^\beta(1)\,\psi_i^\beta(1) = \varepsilon_i^\beta\,\psi_j^\beta(1)} \tag{79}$$

where

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

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

The Coulomb and Exchange operators are

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

UHF energy

The UHF energy is composed by three contributions:

$$E_{\text{UHF}} = E_{\text{UHF}}^{\alpha\alpha} + E_{\text{UHF}}^{\beta\beta} + E_{\text{UHF}}^{\alpha\beta} \tag{83}$$

which yields

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

The matrix elements are given by

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

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

Problem
"Write down the UHF energy of the doublet state of the lithium atom"

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"Write down the UHF energy of the doublet state of the lithium atom"

Solution

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

Expansion of the unrestricted spin orbitals in a basis

$$\psi_i^\alpha(\boldsymbol{r}) = \sum_{\mu=1}^{K} C_{\mu i}^\alpha \phi_\mu(\boldsymbol{r}) \qquad\qquad \psi_i^\beta(\boldsymbol{r}) = \sum_{\mu=1}^{K} C_{\mu i}^\beta \phi_\mu(\boldsymbol{r}) \tag{86}$$

The Pople-Nesbet equations

$$\boldsymbol{F}^\alpha \cdot \boldsymbol{C}^\alpha = \boldsymbol{S} \cdot \boldsymbol{C}^\alpha \cdot \boldsymbol{E}^\alpha \qquad\qquad \boldsymbol{F}^\beta \cdot \boldsymbol{C}^\beta = \boldsymbol{S} \cdot \boldsymbol{C}^\beta \cdot \boldsymbol{E}^\beta \tag{87}$$

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

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

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

Spin-up and spin-down density matrices

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

(90)

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

$$\rho^{\sigma}(\boldsymbol{r}) = \sum_{\mu\nu} \phi_{\mu}(\boldsymbol{r}) P_{\mu\nu}^{\sigma} \phi_{\nu}(\boldsymbol{r}) \qquad\qquad \int \rho^{\sigma}(\boldsymbol{r}) d\boldsymbol{r} = N^{\sigma}$$

(91)

Total and Spin density matrices

$$\underbrace{\boldsymbol{P}^{\mathrm{T}}}_{\text{Charge density}} = \boldsymbol{P}^{\alpha} + \boldsymbol{P}^{\beta} \qquad\qquad \underbrace{\boldsymbol{P}^{\mathrm{S}}}_{\text{Spin density}} = \boldsymbol{P}^{\alpha} - \boldsymbol{P}^{\beta}$$

(92)

The SCF algorithm

1. Specify molecule $\{\boldsymbol{R}_A\}$ 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 $\boldsymbol{S}$ and compute $\boldsymbol{X}$ (same as RHF)

4. Obtain guess density matrix for $\boldsymbol{P}^\alpha$ and $\boldsymbol{P}^\beta$

   1a. Calculate $\boldsymbol{G}^\alpha$ and then $\boldsymbol{F}^\alpha = \boldsymbol{H} + \boldsymbol{G}^\alpha$

   1b. Calculate $\boldsymbol{G}^\beta$ and then $\boldsymbol{F}^\beta = \boldsymbol{H} + \boldsymbol{G}^\beta$

   2. Compute $(\boldsymbol{F}^\alpha)' = \boldsymbol{X}^\dagger \cdot \boldsymbol{F}^\alpha \cdot \boldsymbol{X}$ and $(\boldsymbol{F}^\beta)' = \boldsymbol{X}^\dagger \cdot \boldsymbol{F}^\beta \cdot \boldsymbol{X}$

   3a. Diagonalize $(\boldsymbol{F}^\alpha)'$ to obtain $(\boldsymbol{C}^\alpha)'$ and $\boldsymbol{E}^\alpha$

   3b. Diagonalize $(\boldsymbol{F}^\beta)'$ to obtain $(\boldsymbol{C}^\beta)'$ and $\boldsymbol{E}^\beta$

   4. Calculate $\boldsymbol{C}^\alpha = \boldsymbol{X} \cdot (\boldsymbol{C}^\alpha)'$ and $\boldsymbol{C}^\beta = \boldsymbol{X} \cdot (\boldsymbol{C}^\beta)'$

   5. Form the new new density matrix $\boldsymbol{P}^\alpha$ and $\boldsymbol{P}^\beta$, and compute $\boldsymbol{P}^\mathsf{T} = \boldsymbol{P}^\alpha + \boldsymbol{P}^\beta$

   6. Am I converged? If not go back to 1.

5. Calculate stuff that you want, like E_{UHF} for example

- HF replaces the e-e interaction by an averaged interaction

- The error in the HF method is called the correlation energy

$$E_c = E - E_{\text{HF}}$$
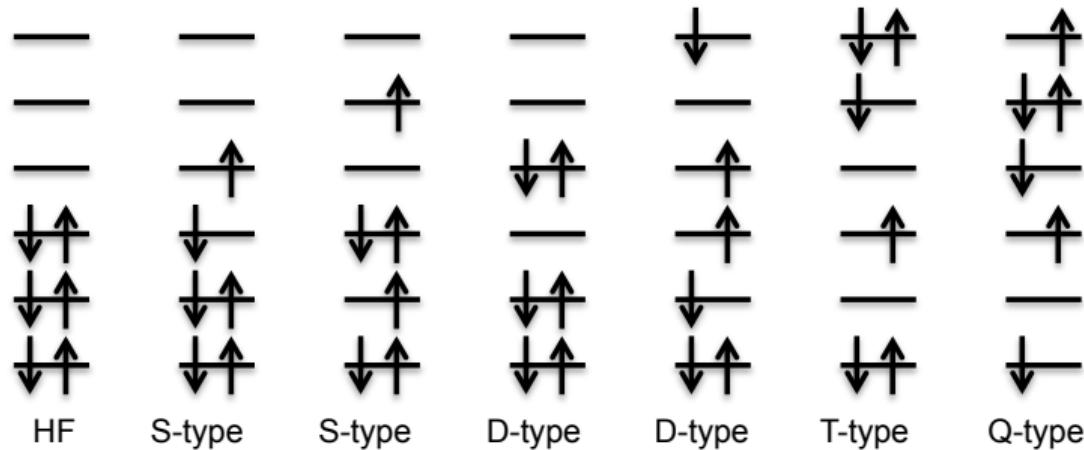
- The correlation energy is small but cannot but neglected!

- HF energy roughly 99% of total but chemistry very sensitive to remaining 1%

- The correlation energy is always negative

- Computing E_c is one of the central problem of quantum chemistry

- In quantum chemistry, we usually "freeze" the core electrons for correlated calculations

1. Configuration Interaction (CID, CIS, CISD, QCISD)

2. Coupled Cluster (CCD, CCSD, CCSD(T), CCSDT)

3. Møller-Plesset perturbation theory (MP2, MP3, MP4)

4. Multireference methods (MCSCF, CASSCF, RASSCF, MRCC, CASPT2)

5. Explicitly correlated F12 methods (MP2-F12, CCSD-F12, CAS-F12)

6. Density-functional theory (DFT, TDDFT)

7. Stochastic Quantum Monte Carlo methods (VMC, DMC, FCIQMC)

- This is the oldest and perhaps the easiest method to understand

- CI is based on the variational principle (like HF)

- The CI wave function is a linear combination of determinants

- CI methods use excited determinants to "improve" the HF wave function

$$|\Phi_0\rangle = c_0 |\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle + \sum_{\substack{i<j<k<l \\ a<b<c<d}} c_{ijkl}^{abcd} |\Psi_{ijkl}^{abcd}\rangle + \cdots \quad (93)$$

Excited determinants

| | HF | S-type | S-type | D-type | D-type | T-type | Q-type |

CI wave function

$$|\Phi_0\rangle = c_0\,|\mathsf{HF}\rangle + c_S\,|\mathsf{S}\rangle + c_D\,|\mathsf{D}\rangle + c_T\,|\mathsf{T}\rangle + c_Q\,|\mathsf{Q}\rangle + \ldots \tag{94}$$

- When $|S\rangle$ (singles) are taken into account: **CIS**

$$|\Phi_{CIS}\rangle = c_0 |HF\rangle + c_S |S\rangle \qquad (95)$$

  NB: CIS is an excited state method
- When $|D\rangle$ (doubles) are taken into account: **CID**

$$|\Phi_{CID}\rangle = c_0 |HF\rangle + c_D |D\rangle \qquad (96)$$

  NB: CID is the cheapest CI method
- When $|S\rangle$ and $|D\rangle$ are taken into account: **CISD**

$$|\Phi_{CISD}\rangle = c_0 |HF\rangle + c_S |S\rangle + c_D |D\rangle \qquad (97)$$

  NB: CISD is the most commonly-used CI method
- When $|S\rangle$, $|D\rangle$ and $|T\rangle$ (triples) are taken into account: **CISDT**

$$|\Phi_{CISDT}\rangle = c_0 |HF\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle \qquad (98)$$

- **CISDTQ**, etc.

- When all possible excitations are taken into account, this is called a Full CI calculation (**FCI**)

$$|\Phi_{FCI}\rangle = c_0|HF\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \ldots \tag{99}$$

- FCI gives the exact solution of the Schrödinger equation within a given basis

- FCI is becoming more and more fashionable these days (e.g. FCIQMC and SCI methods)

- So, why do we care about other methods?

- Because FCI is super computationally expensive!

"Assume we have 10 electrons in 38 spin MOs: 10 are occupied and 28 are empty"

For $N = 10$ and $K = 38$:

- There is C_{10}^k possible ways of selecting k electrons out of the 10 occupied orbitals

$$C_n^k = \frac{n!}{k!(n-k)!}$$

- There is C_{28}^k ways of distributing them out in the 28 virtual orbitals
- For a given excitation level k, there is $C_{10}^k C_{28}^k$ excited determinants
- The total number of possible excited determinant is

$$\sum_{k=0}^{10} C_{10}^k C_{28}^k = C_{38}^{10} = 472,733,756$$

- This is a lot...

k	Num. of excitations
0	1
1	280
2	17,010
3	393,120
4	4,299,750
5	24,766,560
6	79,115,400
7	142,084,800
8	139,864,725
9	69,069,000
10	13,123,110
Tot.	472,733,756

$$|\Phi_0\rangle = c_0|\mathsf{HF}\rangle + c_\mathsf{S}|\mathsf{S}\rangle + c_\mathsf{D}|\mathsf{D}\rangle + c_\mathsf{T}|\mathsf{T}\rangle + c_\mathsf{Q}|\mathsf{Q}\rangle + \ldots$$

Before pruning:

	$|\mathsf{HF}\rangle$	$|\mathsf{S}\rangle$	$|\mathsf{D}\rangle$	$|\mathsf{T}\rangle$	$|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{HF}|$	$\langle\mathsf{HF}|\hat{H}|\mathsf{HF}\rangle$	$\langle\mathsf{HF}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{HF}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{HF}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{HF}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{S}|$	$\langle\mathsf{S}|\hat{H}|\mathsf{HF}\rangle$	$\langle\mathsf{S}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{S}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{S}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{S}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{D}|$	$\langle\mathsf{D}|\hat{H}|\mathsf{HF}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{T}|$	$\langle\mathsf{T}|\hat{H}|\mathsf{HF}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{Q}|$	$\langle\mathsf{Q}|\hat{H}|\mathsf{HF}\rangle$	$\langle\mathsf{Q}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{Q}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{Q}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{Q}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

After pruning:

	$|\mathsf{HF}\rangle$	$|\mathsf{S}\rangle$	$|\mathsf{D}\rangle$	$|\mathsf{T}\rangle$	$|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{HF}|$	$\langle\mathsf{HF}|\hat{H}|\mathsf{HF}\rangle$	0	$\langle\mathsf{HF}|\hat{H}|\mathsf{D}\rangle$	0	0	$\cdots$
$\langle\mathsf{S}|$	0	$\langle\mathsf{S}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{S}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{S}|\hat{H}|\mathsf{T}\rangle$	0	$\cdots$
$\langle\mathsf{D}|$	$\langle\mathsf{D}|\hat{H}|\mathsf{HF}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{D}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{T}|$	0	$\langle\mathsf{T}|\hat{H}|\mathsf{S}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{T}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\langle\mathsf{Q}|$	0	0	$\langle\mathsf{Q}|\hat{H}|\mathsf{D}\rangle$	$\langle\mathsf{Q}|\hat{H}|\mathsf{T}\rangle$	$\langle\mathsf{Q}|\hat{H}|\mathsf{Q}\rangle$	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

❶ No coupling between HF ground state $|HF\rangle$ and single excitations $|S\rangle$
⇒ Brillouin's theorem

$$\langle HF|\hat{H}|S\rangle = 0$$

❷ No coupling between $|HF\rangle$ and triples $|T\rangle$, quadruples $|Q\rangle$, etc.
⇒ Slater-Condon rules

$$\langle HF|\hat{H}|T\rangle = \langle HF|\hat{H}|Q\rangle = \ldots = 0$$

$$\langle S|\hat{H}|Q\rangle = \ldots = 0$$

❸ $|S\rangle$ have small effect but mix indirectly with $|D\rangle$
⇒ CID ≠ CISD

$$\langle HF|\hat{H}|S\rangle = 0 \text{ but } \langle S|\hat{H}|D\rangle \neq 0$$

❹ $|D\rangle$ have large effect and $|Q\rangle$ more important than $|T\rangle$
⇒ CID gives most of the correlation energy

$$\langle HF|\hat{H}|D\rangle \gg \langle HF|\hat{H}|Q\rangle \gg \langle HF|\hat{H}|T\rangle$$

Weights of excited configurations
for Ne

Excit. level	Weight
0	9.6×10^{-1}
1	9.8×10^{-4}
2	3.4×10^{-2}
3	3.7×10^{-4}
4	4.5×10^{-4}
5	1.9×10^{-5}
6	1.7×10^{-6}
7	1.4×10^{-7}
8	1.1×10^{-9}

Correlation energy of Be and Method scaling

Method	ΔE_c	%	Scaling
HF	0	0	K^4
CIS	0	0	K^5
CISD	0.075277	96.05	K^6
CISDT	0.075465	96.29	K^8
CISDTQ	0.078372	100	K^{10}
FCI	0.078372	100	e^K

- Truncated CI methods are size inconsistent i.e.

$$2E_c(\mathrm{H}_2) \neq E_c(\mathrm{H}_2\cdots\mathrm{H}_2)$$

- Size consistent defines for non-interacting fragment

- Size extensivity refers to the scaling of E_c with the number of electrons

- NB: FCI is size consistent and size extensive

Let's assume we want to find Ψ_0 and E_0, such as

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)})\Psi_0 = E_0 \, \Psi_0 \tag{100}$$

and that we know

$$\boxed{\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}, \quad n = 0, 1, 2, \ldots, \infty} \tag{101}$$

Let's expand Ψ_0 and E_0 in term of λ:

$$E_0 = \lambda^0 \, E_0^{(0)} + \lambda^1 \, E_0^{(1)} + \lambda^2 \, E_0^{(2)} + \lambda^3 \, E_0^{(3)} + \ldots \tag{102}$$

$$\Psi_0 = \lambda^0 \, \Psi_0^{(0)} + \lambda^1 \, \Psi_0^{(1)} + \lambda^2 \, \Psi_0^{(2)} + \lambda^3 \, \Psi_0^{(3)} + \ldots \tag{103}$$

such as (intermediate normalization)

$$\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle = 1 \qquad \langle \Psi_0^{(0)} | \Psi_0^{(k)} \rangle = 0, \quad k = 1, 2, \ldots, \infty \tag{104}$$

Gathering terms with respect to the power of λ:

$$\lambda^0: \quad \hat{H}^{(0)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(0)} \tag{105}$$

$$\lambda^1: \quad \hat{H}^{(0)}\Psi_0^{(1)} + \hat{H}^{(1)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)} \tag{106}$$

$$\lambda^2: \quad \hat{H}^{(0)}\Psi_0^{(2)} + \hat{H}^{(1)}\Psi_0^{(1)} = E_0^{(0)}\Psi_0^{(2)} + E_0^{(1)}\Psi_0^{(1)} + E_0^{(2)} \tag{107}$$

$$\lambda^3: \quad \hat{H}^{(0)}\Psi_0^{(3)} + \hat{H}^{(1)}\Psi_0^{(2)} = E_0^{(0)}\Psi_0^{(3)} + E_0^{(1)}\Psi_0^{(2)} + E_0^{(2)}\Psi_0^{(1)} + E_0^{(3)} \tag{108}$$

Using the intermediate normalization, we have

$$\lambda^0: \quad E_0^{(0)} = \langle \Psi_0^{(0)} | \hat{H}^{(0)} | \Psi_0^{(0)} \rangle \tag{109}$$

$$\lambda^1: \quad E_0^{(1)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \tag{110}$$

$$\lambda^2: \quad E_0^{(2)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle \qquad \text{Wigner's (2n+1) rule!} \tag{111}$$

$$\lambda^3: \quad E_0^{(3)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(2)} \rangle = \langle \Psi_0^{(1)} | \hat{H}^{(1)} - E_0^{(1)} | \Psi_0^{(1)} \rangle \tag{112}$$

Expanding $\Psi_0^{(1)}$ in the basis $\Psi_n^{(0)}$ with $n = 0, 1, 2, \ldots, \infty$

$$|\Psi_0^{(1)}\rangle = \sum_n c_n^{(1)} |\Psi_n^{(0)}\rangle \quad \Rightarrow \quad c_n^{(1)} = \langle \Psi_n^{(0)} | \Psi_0^{(1)} \rangle \tag{113}$$

Therefore,

$$|\Psi_0^{(1)}\rangle = \sum_{n \neq 0} |\Psi_n^{(0)}\rangle \langle \Psi_n^{(0)} | \Psi_0^{(1)} \rangle \tag{114}$$

Using results from the previous slide, one can show that

$$E_0^{(2)} = \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{H}_1 | \Psi_n^{(0)} \rangle^2}{E_0^{(0)} - E_n^{(0)}} \tag{115}$$

$$E_0^{(3)} = \sum_{n,m \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{H}_1 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{H}_1 | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{H}_1 | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} - E_0^{(1)} \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{H}_1 | \Psi_n^{(0)} \rangle^2}{(E_0^{(0)} - E_n^{(0)})^2} \tag{116}$$

In Møller-Plesset perturbation theory, the partition is

$$\hat{H}^{(0)} = \sum_{i=1}^{N} f(i) = \sum_{i=1}^{N} [h(i) + v^{\mathrm{HF}}(i)], \qquad \hat{H}^{(1)} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i} v^{\mathrm{HF}}(i) \tag{117}$$

Therefore,

$$E_0^{(0)} = \sum_{i}^{\mathrm{occ}} \varepsilon_i, \qquad E_0^{(1)} = -\frac{1}{2} \sum_{ij}^{\mathrm{occ}} \langle ij||ij\rangle \quad \Rightarrow \quad \boxed{E_{\mathrm{HF}} = E_0^{(0)} + E_0^{(1)}} \tag{118}$$

The first information about the correlation energy is given by the 2nd-order energy

$$\boxed{E_0^{(2)} = \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{virt}} \frac{\langle ij||ab\rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}} \qquad \text{This is the MP2 energy!!} \tag{119}$$

The third-order correction is a bit ugly...

$$
\begin{aligned}
E_0^{(3)} = {} & \frac{1}{8} \sum_{ijkl} \sum_{ab} \frac{\langle ij||ab\rangle\langle kl||ij\rangle\langle ab||kl\rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b)} \\
& + \frac{1}{8} \sum_{ij} \sum_{abcd} \frac{\langle ij||ab\rangle\langle ab||cd\rangle\langle cd||ij\rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_d)} \\
& + \sum_{ijk} \sum_{abc} \frac{\langle ij||ab\rangle\langle kb||cj\rangle\langle ac||ik\rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_c)}
\end{aligned}
$$

NB:
MP2 and MP3 only requires only doubly excited determinants
MP4 does need singly, doubly, triply and quadruply excited determinant!

Correlation energy of Be in a 4s2p basis set

Scaling	Level	ΔE_c	%	Level	ΔE_c	%
K^5	MP2	0.053174	67.85			
K^6	MP3	0.067949	86.70	CISD	0.075277	96.05
K^7	MP4	0.074121	94.58			
K^8	MP5	0.076918	98.15	CISDT	0.075465	96.29
K^9	MP6	0.078090	99.64			
K^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100

- MPn is not a variational method, i.e. you can get an energy lower than the true ground state energy!
- MPn fails for systems with small HOMO-LUMO gap
- The MPn series can oscillate around the exact energy
- MPn is size-consistent!

- **Idea behind CC**
  "Perturbation methods add all types of corrections (S, D, T, Q, etc.) to the reference wave function to a given order (2, 3, 4, etc.). The idea in CC methods is to include all corrections of a given type to infinite order.

- **Excitation operator**

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \ldots + \hat{T}_N \tag{120}$$

- **Action on the HF wave function**

$$\hat{T}_1 \Psi_0 = \sum_{ia} t_i^a \Psi_i^a \qquad \hat{T}_2 \Psi_0 = \sum_{\substack{i<j \\ a<b}} t_{ij}^{ab} \Psi_{ij}^{ab} \tag{121}$$

- **CI wave function**

$$\Psi_{CI} = (\hat{1} + \hat{T})\Psi_0 \tag{122}$$

- **CC wave function**

$$\boxed{\Psi_{CC} = e^{\hat{T}}\Psi_0} \qquad e^{\hat{T}} = \hat{1} + \hat{T} + \frac{\hat{T}^2}{2} + \frac{\hat{T}^3}{6} + \ldots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!} \tag{123}$$

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2} \right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{\hat{T}_1^3}{6} \right) + \left(\hat{T}_4 + \hat{T}_3\hat{T}_1 + \frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2\hat{T}_1^2}{2} + \frac{\hat{T}_1^4}{24} \right) + \dots \qquad (124)$$

- singles = $\hat{T}_1$
- doubles = connected doubles $\hat{T}_2$ + disconnected doubles $\hat{T}_1^2$
- $\hat{T}_4$ = four electrons interacting simultaneously
- $\hat{T}_2^2$ = two non-interacting pairs of interacting electrons
- Compared to CI, CC contains additional terms arising from products of excitations at each excitation level
  $\Rightarrow$ CC is size consistent!! but not variational!
- CISD lacks $\hat{T}_2^2 \Rightarrow$ not size consistent

- Schrödinger equation for CC wave function

$$\hat{H}|\Psi_{CC}\rangle = E_{CC}|\Psi_{CC}\rangle \quad \Rightarrow \quad \hat{H}|e^{\hat{T}}\Psi_0\rangle = E_{CC}|e^{\hat{T}}\Psi_0\rangle \tag{125}$$

- Projection onto Ψ_0

$$\langle\Psi_0|\hat{H}|e^{\hat{T}}\Psi_0\rangle = E_{CC}\langle\Psi_0|e^{\hat{T}}\Psi_0\rangle \tag{126}$$

$$
\begin{aligned}
E_{CC} &= \langle\Psi_0|\hat{H}|e^{\hat{T}}\Psi_0\rangle \\
&= \langle\Psi_0|\hat{H}|\Psi_0\rangle + \langle\Psi_0|\hat{H}|\hat{T}_1\Psi_0\rangle + \langle\Psi_0|\hat{H}|\hat{T}_2\Psi_0\rangle + \frac{1}{2}\langle\Psi_0|\hat{H}|\hat{T}_1^2\Psi_0\rangle \\
&= E_0 + \sum_{ia} t_i^a \langle\Psi_0|\hat{H}|\Psi_i^a\rangle + \sum_{ijab}(t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a)\langle\Psi_0|\hat{H}|\Psi_{ij}^{ab}\rangle \\
&= E_0 + \sum_{ijab}(t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a)\langle ij||ab\rangle
\end{aligned}
\tag{127}
$$

- Projection onto singly, doubly, triply, etc., excited determinants

$$\langle \Psi_i^a | \underbrace{e^{-\hat{T}} \hat{H} e^{\hat{T}}}_{\text{similarity transform}} | \Psi_0 \rangle = 0 \tag{128}$$

$$\langle \Psi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0 \tag{129}$$

$$\langle \Psi_{ijk}^{abc} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0 \tag{130}$$

- $e^{-\hat{T}}$ is a deexcitation operator

$$
\begin{aligned}
e^{-\hat{T}} &= \hat{1} - \hat{T} + \frac{\hat{T}^2}{2} - \frac{\hat{T}^3}{6} + \frac{\hat{T}^4}{24} + \dots \\
&= \sum_{k=0}^{\infty} (-1)^k \frac{\hat{T}^k}{k!}
\end{aligned}
\tag{131}
$$

- CCSD

$$e^{\hat{T}_1+\hat{T}_2} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2}\right) + \left(\hat{T}_2\hat{T}_1 + \frac{\hat{T}_1^3}{6}\right) + \left(\frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2\hat{T}_1^2}{2} + \frac{\hat{T}_1^4}{24}\right) + \dots$$

- How do determine the CCSD amplitudes?

$$\langle\Psi_i^a(\hat{1}-\hat{T}_1)|\hat{H}\left[\hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2}\right) + \left(\hat{T}_2\hat{T}_1 + \frac{\hat{T}_1^3}{6}\right)\right]\Psi_0\rangle = 0 \qquad (132)$$

$$\langle\Psi_{ij}^{ab}\left[\hat{1} - \hat{T}_1 - \left(\hat{T}_2 - \frac{\hat{T}_1^2}{2}\right)\right]|\hat{H}|\left[\hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2}\right) + \left(\hat{T}_2\hat{T}_1 + \frac{\hat{T}_1^3}{6}\right) + \left(\frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2\hat{T}_1^2}{2} + \frac{\hat{T}_1^4}{24}\right)\right]|\Psi_0\rangle = 0$$
$$(133)$$

- All the matrix elements can be evaluated in terms of MO integrals
- Coupled non-linear equations for the singles and doubles amplitudes
- Must be solved iteratively (quartic in the amplitudes)

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2} \right) + \left(\hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{\hat{T}_1^3}{6} \right) + \left(\hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2 \hat{T}_1^2}{2} + \frac{\hat{T}_1^4}{24} \right) + \cdots$$

- Each parenthesis generates all the excited determinants of the given type
- $\hat{T}_1$ is small $\Rightarrow \hat{T}_1^2, \hat{T}_1^3, \hat{T}_1^4, \hat{T}_1 \hat{T}_2 \ldots$ are small
- $\hat{T}_2$ is large, and $\hat{T}_3 \gg \hat{T}_2 \hat{T}_1 \gg \hat{T}_1^3$
- $\hat{T}_2$ is large $\Rightarrow \hat{T}_2^2 > \hat{T}_4$ and the rest is small because $\hat{T}_1 \ll 0$
- $\hat{T}_m$ with $m > 4$ expected to have small effects

- CISD lacks $\hat{T}_2^2 \Rightarrow$ not size consistent
- $\hat{T}_2^2$ becomes large when number of electrons increases $\Rightarrow$ Davidson correction

$$E_c(\text{CISD+Q}) = E_c(\text{CISD}) + (1 - c_0^2) E_c(\text{CISD})$$

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2} \right) + \left(\hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{\hat{T}_1^3}{6} \right) + \left(\hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2 \hat{T}_1^2}{2} + \frac{\hat{T}_1^4}{24} \right) + \cdots$$

- MP2 and MP3 uses only doubles
- MP4 uses singles, doubles, triples ($\hat{T}_3$) and quadruples ($\hat{T}_2^2$)
- CCD $\approx$ MP4(DQ) and CCSD $\approx$ MP4(SDQ)
- MP2, MP3 and MP4(SDQ) can be obtained in 1st CCSD iteration

- CCSD lacks connected triples $\hat{T}_3$
  1. CCSDT but very expensive!
  2. CCSD(T) where triples comes from MP4 (non-iterative)
  3. CCSD(T) = gold standard of quantum chemistry (for ground state and weakly correlated systems)

Correlation energy of Be in a 4s2p basis set

| Scaling	Level	ΔE_c	%	Level	ΔE_c	%	Level	ΔE_c	%
K^5	MP2	0.053174	67.85						
K^6	MP3	0.067949	86.70	CISD	0.075277	96.05	CCSD	0.078176	99.75
K^7	MP4	0.074121	94.58				CCSD(T)	0.078361	99.99
K^8	MP5	0.076918	98.15	CISDT	0.075465	96.29	CCSDT	0.078364	99.99
K^9	MP6	0.078090	99.64						
K^{10}	MP7	0.078493	100.15	CISDTQ	0.078372	100	CCSDTQ	0.078372	100
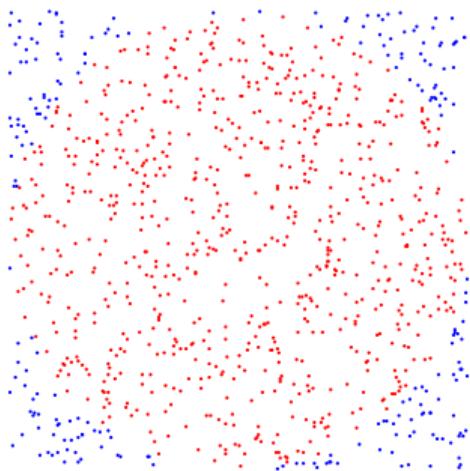
As a rule of thumb:

HF $\ll$ MP2 < CISD < MP4(SDQ) $\sim$ CCSD < MP4 < CCSD(T)
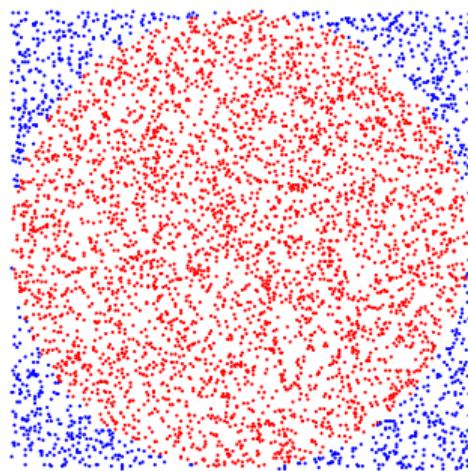
- Monte Carlo is a numerical integration method

- It is used in problems where it is too difficult or impossible to obtain analytical expressions or the dimensionality of the integral is large

- The method consists in repeating random sampling many times to obtain numerical results: $\Rightarrow$ this is a non-deterministic or stochastic method.

- MC converges as $N^{-1/2}$ where N is the number of MC step

- In 1946, **Stanislaw Ulam** was the first mathematician to dignify this approach with a name, in honor of his uncle having a little issue with gambling

- **Nicolas Metropolis** also made important contributions (Metropolis algorithm)
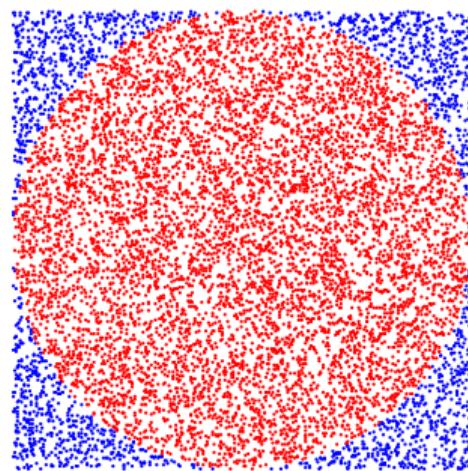
$$\int_{-1}^{1} \int_{-1}^{1} f(x,y)\,dx\,dy = \pi \qquad \text{with} \qquad f(x,y) = \begin{cases} 1, & x^2 + y^2 \leq 1, \\ 0, & \text{otherwise.} \end{cases}$$

$\pi \approx \frac{774}{1000} = 3.096$ $\pi \approx \frac{3962}{5000} = 3.1696$ $\pi \approx \frac{7948}{10000} = 3.1792$

- Within quantum chemistry, VMC is used to obtain expectation values (mainly energies)

- In VMC, the expectation value of the Hamiltonian with respect to a trial wave function Ψ_T is obtained using a stochastic integration technique

- The VMC energy is an upper bound to the exact ground state energy

$$E_{\text{VMC}} = \frac{\int \Psi_T(\boldsymbol{R}) \, \hat{H} \, \Psi_T(\boldsymbol{R}) \, d\boldsymbol{R}}{\int \Psi_T(\boldsymbol{R})^2 \, d\boldsymbol{R}} = \frac{\int \frac{\hat{H}\Psi_T(\boldsymbol{R})}{\Psi_T(\boldsymbol{R})} \Psi_T(\boldsymbol{R})^2 \, d\boldsymbol{R}}{\int \Psi_T(\boldsymbol{R})^2 \, d\boldsymbol{R}} = \frac{\int E_L(\boldsymbol{R})\Psi_T(\boldsymbol{R})^2 \, d\boldsymbol{R}}{\int \Psi_T(\boldsymbol{R})^2 \, d\boldsymbol{R}} \tag{134}$$

where

$$E_L(\boldsymbol{R}) = \frac{\hat{H}\,\Psi_T(\boldsymbol{R})}{\Psi_T(\boldsymbol{R})} \quad \text{is the local energy and } \boldsymbol{R} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n) \tag{135}$$

Time-dependent Schrödinger equation written in imaginary time:

$$\frac{\partial \Phi(\boldsymbol{R}, \tau)}{\partial \tau} = (\hat{H} - S)\Phi(\boldsymbol{R}, \tau) \tag{136}$$

- For $\tau \to \infty$, the solution is the exact ground state wave function $\Phi(\boldsymbol{R})$
- DMC generates **configurations** (or **walkers**) distributed according to the density $\rho(\boldsymbol{R}, \tau) = \Psi_{\mathsf{T}}(\boldsymbol{R})\,\Phi(\boldsymbol{R}, \tau)$
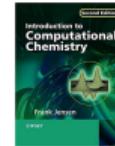
$$\frac{\partial \rho(\boldsymbol{R}, \tau)}{d\tau} = \underbrace{\frac{1}{2}\nabla^2 \rho(\boldsymbol{R}, \tau)}_{\textbf{diffusion}} + \underbrace{\nabla \cdot [F(\boldsymbol{R})\rho(\boldsymbol{R}, \tau)]}_{\textbf{drift}} - \underbrace{[E_{\mathsf{L}}(\boldsymbol{R}) - E_{\mathsf{T}}]\,\rho(\boldsymbol{R}, \tau)}_{\textbf{branching}} \tag{137}$$

where

$$F(\boldsymbol{R}) = \frac{\nabla \Psi_{\mathsf{T}}(\boldsymbol{R})}{\Psi_{\mathsf{T}}(\boldsymbol{R})} \quad \text{is the quantum force} \tag{138}$$

If $\Psi_{\mathsf{T}}(\boldsymbol{R})$ has exact **nodes**, DMC energy = exact energy (fixed-node error)
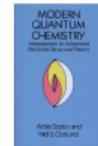
- Introduction to Computational Chemistry (Jensen)

- Essentials of Computational Chemistry (Cramer)

- Modern Quantum Chemistry (Szabo & Ostlund)

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