

Outline

1. Recap of the intro. of EST
 2. Formal derivation of HF method: 1st and 2nd quantization
 3. Simplified version of HF method with a He atom.
- Python : https://github.com/HHChuang/HartreeFockPractice/blob/master/src/He_atom.ipynb
 - reference
 1. A.Szabo, Modern Quantum Chemistry, Ch 3.
 2. J. Olsen, Molecular Electronic Structure Theory
 3. C.D. Sherrill's note
<http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.html>
 4. Am. J. Phys. 2021, 89, 426.

1. Recap of the intro. of EST

- Solve molecular TISE, $\hat{H} |\Psi\rangle = E |\Psi\rangle$
remove tran. & rot. BH rep.
 $d.o.f. = 3N - 5/6$.
 $\rightarrow \hat{H} = \hat{H}^0 + \hat{T}_N(\mathbf{R}) + \hat{H}''$ $|\Psi(\vec{r}, \vec{R})\rangle = \sum_j \Phi_j(\vec{r}; \vec{R}) \cdot X_j(\vec{R})$
internal motion ; electrons are coupled with nuclei
- exact $[\hat{E}_i - \frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + \hat{H}_{ii} - E] \chi_i = \sum_{j \neq i} C_{ij} \chi_j$
- B.O. approx. (decouple ele. and nuclei) $\hat{H}_{ii} = C_{ii} = 0$
 $[-\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + \hat{E}_i] \chi_i = E \chi_i$
get this eigenvalue by EST : $\hat{f}_{te} |\Phi\rangle_e = E |\Phi\rangle_e$

- Standard methods in EST

	$ \Phi\rangle_e$ d.o.f. = $3Ne$	$\rho = \Phi ^2$, d.o.f. = 3.
MR	$ \Phi\rangle = \sum_i C_i \Phi_{CSF}\rangle$	
	CC $\hat{T} = \hat{T}_1 + \hat{T}_2 \dots \Phi\rangle = e^{\hat{T}} \Phi\rangle_0$ MBPT $\hat{H} = \hat{H}^0 + \hat{V}$, $ \Phi\rangle = \Phi\rangle_0 + \lambda^{(1)} \Phi^{(1)}\rangle + \dots$	Jacobi's ladder vir. $\sum \Phi_i \xi$ Generalized Ex Σ hyper-GGA ∇_n^2 ∇_n meta-GGA ∇_n n GGA n LSD
SR	CI $ \Phi\rangle = \Phi\rangle_0 + \sum_{i,a} C_i^a \Phi_i^a\rangle + \dots$ HF $ \Phi\rangle = \Phi\rangle_0 = \Phi_1, \Phi_2, \dots\rangle$	$HK-1, HK-2, KS$

2. Formal derivation of HF method: 1st and 2nd quantization

- 1st quantization
 - observable → operator
 - state → function
 - 2nd quantization
 - observable → operator
 - state → operator
- e.g. Creation operator
- $$|a\rangle = \hat{a}^\dagger |0\rangle$$
- wavefunction vacuum state
- c.f. J. Olsen
Molecular Electronic Structure Theory.

→ The Standard derivation of Hartree-Fock method uses the 1st quantization, which needs some pre-required background also leads to complex algebra.
useful and some well-known resources are

1. Szabo, Modern Quantum Chemistry
Ch3.2 Derivation of the Hartree-Fock Equations.
2. C.D. Sherrill, Detail formal derivation
notes <http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.pdf>

YT <https://youtu.be/6XF0F8-QkAM>

3. L. Pielas, Ideas of Quantum Chemistry
Ch8. Electronic motion in the mean field:
atoms and molecules

→ use more understandable language

→ But, we don't use them, instead, focus on this paper.

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A first encounter with the Hartree-Fock self-consistent-field method

American Journal of Physics 89, 426 (2021); <https://doi.org/10.1119/10.0002644>

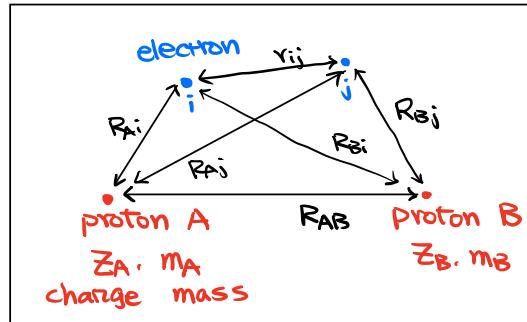
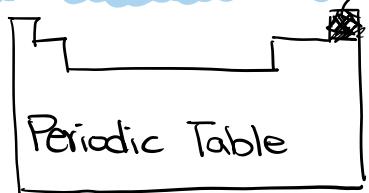
Robin Santra and Michael Obermeyer

3. Simplified version of HF method with a He atom.

ref. Am. J. Phys. 2021, 89, 426.

Python: https://github.com/HHChuang/HartreeFockPractice/blob/master/src/He_atom.ipynb

- Helium atom: He_2^{4+}



- Hamiltonian

$$R_{AB} = 0 \rightarrow \text{He atom.}$$

$$\hat{H} = \underbrace{\hat{T}_N}_{\text{o}} + \hat{T}_e + \cancel{\hat{V}_{NN}} + \hat{V}_{Ne} + \hat{V}_{ee}$$

const.

$$\xrightarrow{\substack{\text{B.O.} \\ \text{approx.}}} \hat{H}_{\text{He}} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}$$

$$\xrightarrow{\text{TISE}}$$

$$\begin{aligned} \underbrace{\hat{H}_{\text{He}}}_{\hat{H}(\vec{x}_1, \vec{x}_2)} |\Psi\rangle &= E \underbrace{|\Psi\rangle}_{\text{spatial}} \underbrace{|\Psi\rangle}_{\text{spin}} \\ &= \hat{T}_{ei} + \hat{V}_{Naei} + \hat{V}_{Nbej} \quad \text{one-electron term, } \hat{n} \\ &\quad + \hat{T}_{ej} + \hat{V}_{NAej} + \hat{V}_{NBcj} \\ &\quad + \hat{V}_{eeij} \quad \text{two-electron term} \\ &= \hat{h}_1 + \hat{h}_2 + \hat{V}_{12} \end{aligned}$$

total spin=0 multiplicity
 ↓ $2S+1$
 closed shell $[\text{He}]$

$$\rightarrow E = \langle \Psi | \hat{H}_{\text{He}} | \Psi \rangle = 2 \langle \psi_1 | \hat{h}_1 | \psi_1 \rangle + \langle \psi_2 | \hat{h}_2 | \psi_2 \rangle$$

→ Hartree-Fock energy

$$E^{\text{HF}} = \min_{\Psi} \langle \Psi | \hat{H}_{\text{He}} | \Psi \rangle$$

changing Ψ in order to find the minimum energy (i.e. variational)

* But $\langle \Psi | \Psi \rangle = 1$, we cannot freely change Ψ

→ constraint optimization → Lagrange undetermined multiplier

* In this simplified version, we ignore the formal derivation, jargon..., and express the electronic wavefunction in a truncated basis.
to write code later

Basis-set expansion

Use a completed basis-set, $\{X_i\}$, and then

$$\Psi = \sum_{i=1}^{\infty} C_i \cdot X_i \quad |\Psi\rangle = \begin{pmatrix} \langle X_1 | \Psi \rangle \\ \langle X_2 | \Psi \rangle \\ \vdots \\ \langle X_n | \Psi \rangle \end{pmatrix} = \begin{pmatrix} C_1 & \xrightarrow{\text{finite}} & \langle X_1 | \Psi \rangle \\ C_2 & \xrightarrow{\text{finite}} & \langle X_2 | \Psi \rangle \\ \vdots & & \vdots \\ C_n & \xrightarrow{\text{finite}} & \langle X_n | \Psi \rangle \end{pmatrix}$$

Practically, we need to truncated the basis expansion (ie. $\sum_{i=1}^{\infty} \rightarrow \sum_{i=1}^n$).

Here, we use two basis functions to express the wavefunction.

$$\Psi \approx \sum_{i=1}^2 C_i X_i = C_1 \cdot \underbrace{X_1}_{\text{1s orbital}} + C_2 \cdot \underbrace{X_2}_{\text{2s orbital}}$$

H-atom like  

$$X_2 \rightarrow \chi_2 = 0 \rightarrow \frac{r}{a_0} = \frac{2}{Z}$$

→ Now, we can calculate the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$

① one-electron term

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle C_1 X_1 + C_2 X_2 | \hat{H} | C_1 X_1 + C_2 X_2 \rangle = C_1^2 \underbrace{\langle X_1 | \hat{H} | X_1 \rangle}_{\langle X_i | X_j \rangle = \delta_{ij}, C_1, C_2 \in \mathbb{R}} + C_2^2 \langle X_2 | \hat{H} | X_2 \rangle$$

② two-electron term

$$\langle \Psi | \hat{V}_{12} | \Psi \rangle = \langle ij | \hat{V}_{12} | ij \rangle - \langle ij | ji \rangle$$

$$\begin{aligned} \langle \Psi | \hat{V}_{12} | \Psi \rangle &= [\underbrace{\langle i i | j j \rangle}_{\text{coulomb}} - \langle i j | j i \rangle] = J_{ij} - K_{ij} \\ &= \langle [C_1 X_1(X_1) + C_2 X_2(X_1)] \cdot [C_1 X_1(X_2) + C_2 X_2(X_2)] \cdot \hat{V}_{12} \cdot [C_1 X_1(X_1) + C_2 X_2(X_1)] \cdot [C_1 X_1(X_2) + C_2 X_2(X_2)] \rangle \\ &\quad \text{coulomb Exchange} \end{aligned}$$

* Dirac notation

$$\langle ij | \hat{V}_{12} | kl \rangle = \int d^3x_1 d^3x_2 \cdot X_i^*(x_1) X_j^*(x_2) \cdot \frac{1}{r_{12}} \cdot X_k(x_1) X_l(x_2)$$

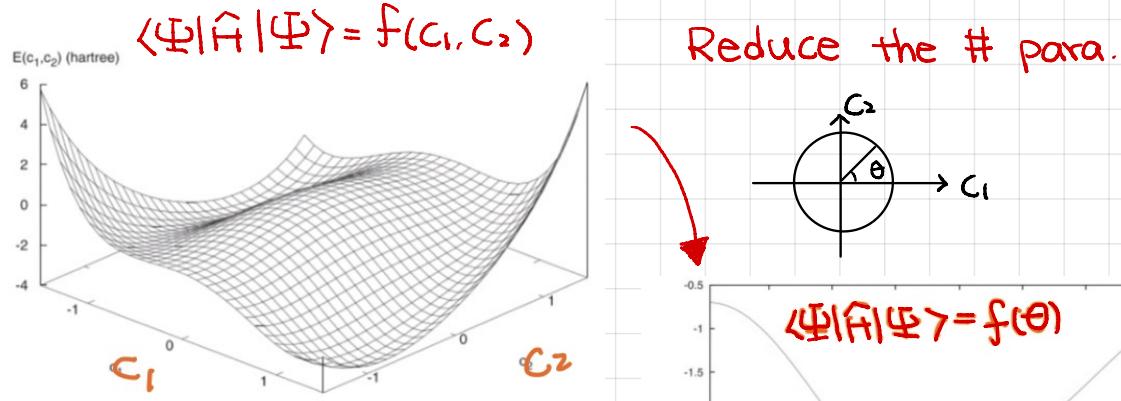
* How many terms? $2 \times 2 \cdot 2 \times 2 = 16$ terms

$$\begin{aligned} \rightarrow \langle 1111 \rangle & C_1^4 \times 1 & \langle X_1(X_1) \cdot X_1(X_2) | X_2(X_1) \cdot X_2(X_2) \rangle \\ \langle 2222 \rangle & C_2^4 \times 1 & \langle X_2(X_2) \cdot X_2(X_1) | X_1(X_2) \cdot X_1(X_1) \rangle \\ \langle 11112 \rangle & C_1^3 C_2 \times 4 & \langle X_1(X_1) \cdot X_1(X_2) | X_2(X_2) \cdot X_2(X_1) \rangle \\ \langle 22212 \rangle & C_1 C_2^3 \times 4 & \langle X_2(X_1) \cdot X_2(X_2) | X_1(X_1) \cdot X_1(X_2) \rangle \\ \cancel{\star} \langle 11122 \rangle & C_1^2 C_2^2 \times 4 & \cancel{\langle X_2(X_2) \cdot X_2(X_1) | X_1(X_2) \cdot X_1(X_1) \rangle} \\ \cancel{\star} \langle 12112 \rangle & C_1^2 C_2^2 \times 2 & \cancel{\langle X_1(X_2) \cdot X_2(X_1) | X_1(X_2) \cdot X_2(X_1) \rangle} \# \\ \rightarrow \text{Evaluated these integrals analytically (cf. Table 1).} \end{aligned}$$

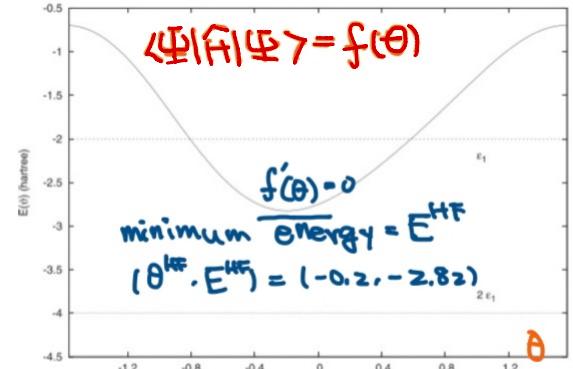
Now, for $Z=2$, the expectation value is

$$\langle \Psi | \hat{H} | \Psi \rangle = f(C_1, C_2)$$

, and the constraint is $C_1^2 + C_2^2 = 1$



Reduce the # para.



How to find Hartree-Fock energy?

* cheat sheet: $\langle \Psi | \hat{H} | \Psi \rangle \rightarrow$ Fock egn. \rightarrow SCF $\rightarrow E^{HF}$

→ Finding the Hartree-Fock energy is equal to this math problem

"Finding extreme with a constraint"

tool → Lagrange undetermine multiplier

Brief review

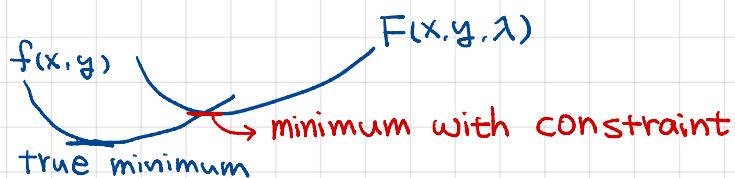
$f(x, y)$ with constraint $g(x, y) = k$

→ Build a new function λ $\downarrow g(x, y) - k = 0$

$$F(x, y, \lambda) = f(x, y) - \lambda [g(x, y) - k]$$

→ Solve:

$$\begin{cases} \frac{\partial F}{\partial x} = F_x = 0 \\ F_y = 0 \\ F_\lambda = 0 \end{cases}$$



→ Back to He2 case.

$$f(x, y) \rightarrow \langle \Psi | \hat{H} | \Psi \rangle = \tilde{f}(c_1, c_2)$$

$$g(x, y) \rightarrow \langle \Psi | \Psi \rangle = c_1^2 + c_2^2 = 1$$

i.e. Normalized one e- WF

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle &= 2(\varepsilon_1 c_1^2 + \varepsilon_2 c_2^2) \\ &+ \langle 11|11\rangle c_1^4 + 4\langle 11|12\rangle c_1^3 c_2 \\ &+ 2(2\langle 11|22\rangle + \langle 12|12\rangle) c_1^2 c_2^2 \\ &+ 4\langle 12|22\rangle c_1 c_2^3 + \langle 22|22\rangle c_2^4, \end{aligned}$$

$$\rightarrow \tilde{F}(c_1, c_2, \lambda) = \langle \Psi | \hat{H} | \Psi \rangle - 2\lambda(c_1^2 + c_2^2 - 1)$$

$\lambda \rightarrow 2\lambda$; for the next step.

Solve ①, ②, ③:

$$\begin{aligned} ① \quad \tilde{F}_{c_1} &= \frac{\partial \tilde{F}}{\partial c_1} = 4\varepsilon_1 c_1 + 4\langle 11|11\rangle c_1^3 + 12\langle 11|12\rangle c_1^2 c_2 \\ &+ 4(2\langle 11|22\rangle + \langle 12|12\rangle) c_1 c_2^2 \\ &+ 4\langle 12|22\rangle c_2^3 \\ &- 4\lambda c_1 = 0 \end{aligned}$$

$$\textcircled{2} \quad \tilde{F}_{C_2} = \frac{\partial \tilde{E}}{\partial C_2} = 4\varepsilon_2 C_2 + 4\langle 11|12 \rangle C_1^3 \\ + 4(2\langle 11|22 \rangle + \langle 12|22 \rangle) C_1^2 C_2 \\ + 12\langle 12|22 \rangle C_1 C_2^2 + 4\langle 22|22 \rangle C_2^3 \\ - 4\lambda C_2 = 0$$

$$\textcircled{3} \quad \tilde{F}_\lambda = \frac{\partial \tilde{E}}{\partial \lambda} = 1 - C_1^2 - C_2^2 = 0 \quad \#$$

From above three equations, we can solve this problem (i.e. solve $Ax = 0$, and then get exact value of C_1 , C_2 and λ). But here we want see the general procedure of Hartree-Fock method, so we factorize \tilde{F}_{C_1} and \tilde{F}_{C_2} in order to transform linear equation problem into eigenvalue problem.

$$Ax = 0 \xrightarrow[\substack{\tilde{F}_{C_1}, \tilde{F}_{C_2} \\ \text{factorize}}]{\substack{A_x = \alpha x, A_{2x2}, A^T = A \\ \text{real-symmetric matrix}}} Ax = \alpha x$$

→ This equation is called Fock equation :

$$F_{i+1}(C_i) \cdot C_{i+1} = \varepsilon_{i+1} \cdot C_{i+1}$$

Finding the matrix elements by factorizing \tilde{F}_{C_1} and \tilde{F}_{C_2}

$$\begin{aligned} \tilde{F}_{C_1} &= 4 [C_1 (\varepsilon_1 - \lambda + \langle 11|11 \rangle C_1^2) \\ &\quad + C_1 C_2 (3\langle 11|12 \rangle C_1 + 2\langle 11|22 \rangle C_2 + \langle 12|12 \rangle C_2) \\ &\quad + \langle 12|22 \rangle C_2^3] = 0 \quad \text{trick: some terms go to} \\ \tilde{F}_{C_2} &= 4 [C_2 (\varepsilon_2 - \lambda + \langle 22|22 \rangle C_2^2) \\ &\quad + C_1 C_2 (3\langle 12|22 \rangle C_2 + 2\langle 11|22 \rangle C_1 + \langle 12|12 \rangle C_1) \\ &\quad + \langle 11|12 \rangle C_1^3] = 0 \quad \text{the off-diagonal part} \end{aligned}$$

$$\Rightarrow \tilde{F}_{C_1} = (F_{11} \ F_{12}) \cdot \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad \text{and} \quad \tilde{F}_{C_2} = (F_{21} \ F_{22}) \cdot \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$F_{11} = \varepsilon_1 - \lambda + \langle 11|11 \rangle C_1^2 + 2\langle 11|12 \rangle C_1 C_2 + \langle 12|12 \rangle C_2^2$$

$$F_{12} = \langle 11|12 \rangle C_1^2 + 2\langle 11|22 \rangle C_1 C_2 + \langle 12|22 \rangle C_2^2$$

$$F_{21} = \langle 12|22 \rangle C_2^2 + 2\langle 11|22 \rangle C_1 C_2 + \langle 11|12 \rangle C_1^2$$

$$F_{22} = \varepsilon_2 - \lambda + \langle 22|22 \rangle C_2^2 + 2\langle 12|22 \rangle C_1 C_2 + \langle 12|12 \rangle C_1^2$$

$$\rightarrow \begin{pmatrix} F_{11} - \lambda & F_{12} \\ F_{21} & F_{22} - \lambda \end{pmatrix} \cdot \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

and let $\lambda = \varepsilon$

$$\rightarrow \underbrace{F_{i+1}(C_i)}_{\text{Fock matrix}} \cdot C_{i+1} = \varepsilon_{i+1} C_{i+1} \quad \#$$

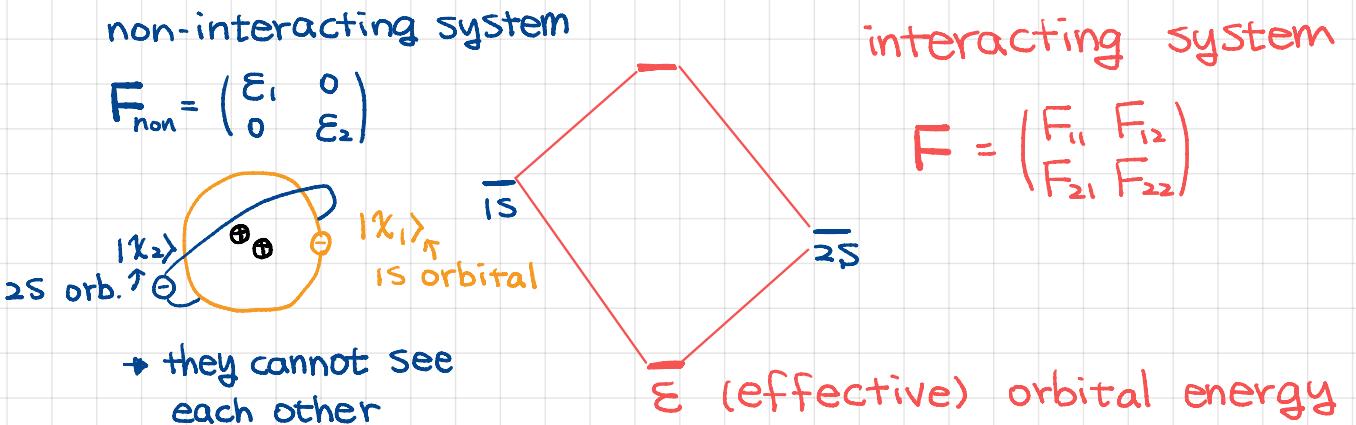
$$\text{c.f. } F_{11}(c) = \varepsilon_1 + \langle 11|11 \rangle c_1^2 + 2\langle 11|12 \rangle c_1 c_2 + \langle 12|12 \rangle c_2^2, \quad (23)$$

$$F_{12}(c) = \langle 11|12 \rangle c_1^2 + 2\langle 11|22 \rangle c_1 c_2 + \langle 12|22 \rangle c_2^2, \quad (24)$$

$$F_{21}(c) = F_{12}(c), \quad (25)$$

$$F_{22}(c) = \varepsilon_2 + \langle 12|12 \rangle c_1^2 + 2\langle 12|22 \rangle c_1 c_2 + \langle 22|22 \rangle c_2^2.$$

* Interpretation of the Fock equation:



2. Algorithm and Python code

• Pseudo-code of the main part

Using He^4 atom to Demonstrate Hartree-Fock SCF Method

Expectation value for neutral Helium atom; He^4

$$\langle \psi | \hat{H} | \psi \rangle = 2 \langle \psi | \hat{h}_1 | \psi \rangle + \langle \psi | \hat{V}_{12} | \psi \rangle$$

Hartree-Fock energy:

$$E^{HF} = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle$$

• Reference:

Am. J. Phys. 2021, 89, 426. "A first encounter with the Hartree-Fock self-consistent-field method"

Pseudo-code:

1. Import libraries
2. Parameters setting
3. Main part: HF-SCF iteration
4. Plot results

1. Initial guess

$$C^{(0)} = 1 \cdot x_1 + 0 \cdot x_2 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \xrightarrow{x_1} \begin{pmatrix} \cos(0) \\ \sin(0) \end{pmatrix} \rightarrow \begin{pmatrix} C_2 \\ C_1 \end{pmatrix} \quad \theta^{(0)} = 0$$

2. Construct the Fock matrix

$$\begin{aligned} F^{(0)} &= F(C^{(0)}) \xrightarrow{\text{more general}} F^{(i+1)} = F(C^{(i)}) \\ &= F(\theta^{(0)}) \xrightarrow{\text{more general}} F^{(i+1)} = F(\theta^{(i)}) \end{aligned}$$

3. Solve eigenvalue problem

$$F_{2 \times 2}^{(i)} \cdot C^{(i)} = \varepsilon^{(i)} \cdot C^{(i)}$$

$$\varepsilon^{(i)} = \frac{1}{2} (F_{11} + F_{22}) - \sqrt{\frac{1}{4} (F_{11} - F_{22})^2 + F_{12}^2}$$

$$\det(F^{(i)} - \varepsilon I) = 0$$

$$\begin{vmatrix} F_{11} - \varepsilon & F_{12} \\ F_{12} & F_{22} - \varepsilon \end{vmatrix} = (F_{11} - \varepsilon)(F_{22} - \varepsilon) - F_{12}^2 = 0$$

$$\varepsilon^2 - (F_{11} + F_{22}) + F_{11}F_{22} - F_{12}^2 = 0 \quad \lambda_{\pm} = \frac{1}{2} (-b \pm \sqrt{b^2 - 4ac})$$

$$\varepsilon = \frac{1}{2} [(F_{11} + F_{22}) - \sqrt{(F_{11} + F_{22})^2 - 4(F_{11}F_{22} - F_{12}^2)}]$$

take the lower one

$$= \frac{1}{2} (F_{11} + F_{22}) - \frac{1}{2} \sqrt{(F_{11} - F_{22})^2 + 4F_{12}^2}$$

4. Calc. θ for the next loop.

$$\theta^{(i)} = \tan^{-1} \left[\frac{\varepsilon^{(i)} - F_{11}^{(i)}}{F_{12}^{(i)}} \right]$$

5. Convergence.

$$\varepsilon^{(i+1)} \approx \varepsilon^{(i)}$$

Criteria?

$$\begin{pmatrix} F_{11}^{(i)} - \varepsilon^{(i)} & F_{12}^{(i)} \\ F_{12}^{(i)} & F_{22}^{(i)} - \varepsilon^{(i)} \end{pmatrix} \cdot \begin{pmatrix} C_1^{(i)} \\ C_2^{(i)} \end{pmatrix} = 0$$

$$[F_{11}^{(i)} - \varepsilon^{(i)}] C_1^{(i)} + F_{12}^{(i)} C_2^{(i)} = 0$$

$$\frac{C_2^{(i)}}{C_1^{(i)}} = \frac{\varepsilon^{(i)} - F_{11}^{(i)}}{F_{12}^{(i)}} = \tan(\theta^{(i)})$$

• Python code

```
# Loop for carrying out the iterative SCF procedure:
for i in range(num_iter):
    c_1 = np.cos(theta) # Eq.(16)
    c_2 = np.sin(theta) # Eq.(17)
    # print(c_1,c_2)

    # Calculation of the two-electron energy [Eq.(13)]:
    total_energy = 2 * ( eps_1 * c_1**2 + eps_2 * c_2**2 ) \
+ I_1111 * c_1**4 + 4 * I_1112 * c_1**3 * c_2 \
+ 2 * ( 2 * I_1122 + I_1212 ) * c_1**2 * c_2**2 \
+ 4 * I_1222 * c_1 * c_2**3 \
+ I_2222 * c_2**4
f_total_energy.append([i,total_energy])
```

3. Solve eigenvalue problem

→ get ϵ

```
# Calculation of the matrix elements of the Fock matrix:
# Eq.(23)
F_11 = eps_1 + I_1111 * c_1**2 \
+ 2 * I_1112 * c_1 * c_2 + I_1212 * c_2**2
# Eq.(24)
F_12 = I_1112 * c_1**2 + 2 * I_1122 * c_1*c_2 \
+ I_1222 * c_2**2
# Eq.(25)
F_21 = F_12
# Eq.(26)
F_22 = eps_2 + I_1212 * c_1**2 \
+ 2 * I_1222 * c_1 * c_2 + I_2222 * c_2**2
```

4. Calc. θ for the next loop

→ get θ

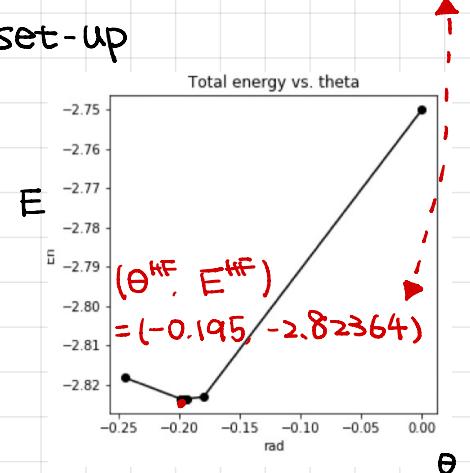
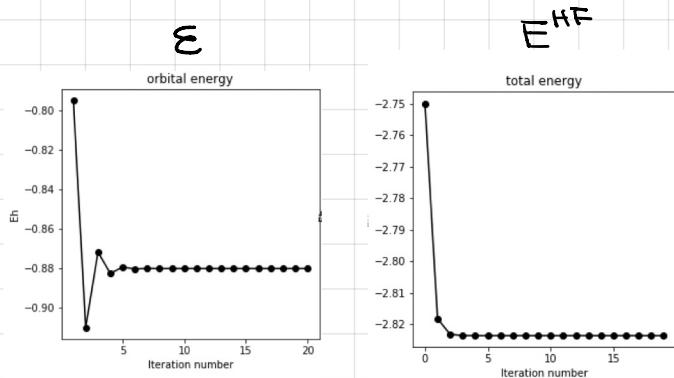
```
orbital_energy = 0.5*(F_11 + F_22) \
- np.sqrt( 0.25*(F_11 - F_22)**2 + F_12**2 )
f_orbital_energy.append([i+1, orbital_energy])

> ...
...
theta = np.arctan ((orbital_energy - F_11)/F_12)
f_theta.append([i+1, theta])
```

3. Numerical results and physical insight

• HF-SCF

- Energy for helium atom from experiment: -2.90372 Hartree
- Numerical result from the current set-up



- Limitation in HF-SCF and comparison to post-HF method.

EST program
: G16 A.03

	Hartree	Accuracy	$\frac{E_{\text{calc.}}}{E_{\text{Expt.}}} \times 100\%$
Expt.	-2.90372		
HF/2WF <small>current method</small>	-2.82364	97.24%	
HF/STO-3G	-2.80778	96.70%	
HF/6-31G	-2.85516	98.33%	
HF/CBS	-2.86168	98.55%	
MP2/6-31G	-2.86636	98.71%	
CCSD/6-31G	-2.87016	98.84%	

$\frac{E_{\text{calc.}}}{E_{\text{Expt.}}} \times 100\%$

different basis-set

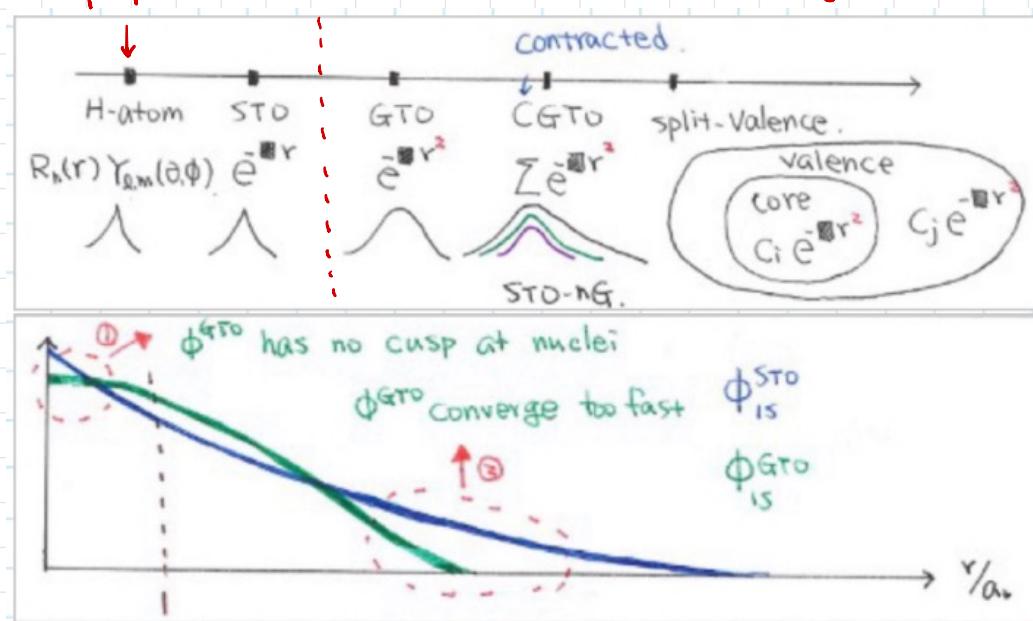
consider electronic correlation

- Brief review of basis-set development in EST

in this paper $\text{STO} \rightarrow \text{GTO} \therefore \text{easier to integrate}$

STO: slater-type

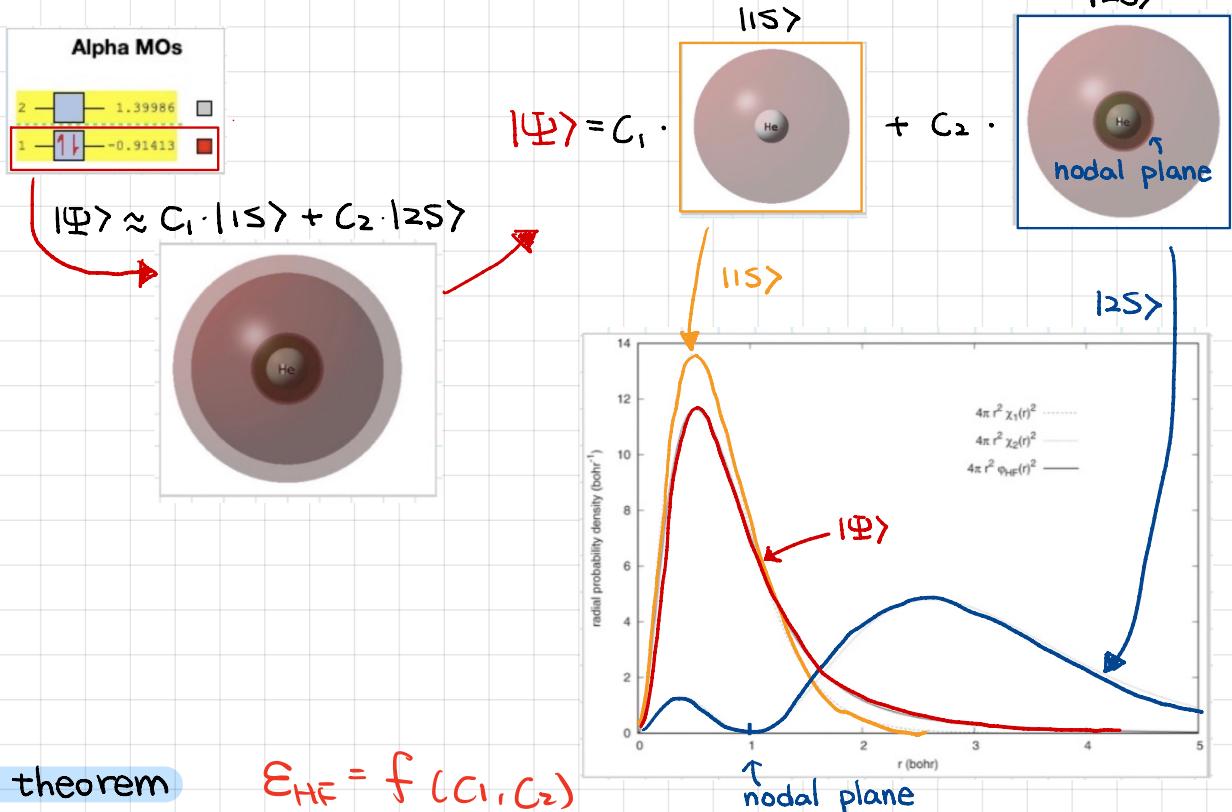
• no radial node



- History of methodology development

wavefunction	parameters	energy
$e^{-Z(r_1+r_2)}$	$Z = 2$	-2.75
$e^{-\alpha(r_1+r_2)}$	$\alpha = 1.6875$	-2.84765
$\psi(r_1)\psi(r_2)$	<small>HF/CBS</small> best $\psi(r)$	-2.86168
$e^{-\alpha(r_1+r_2)}(1 + cr_{12})$	best α, c	-2.89112
Hylleraas (1929)	10 parameters	-2.90363
Pekeris (1959)	1078 parameters	-2.90372

- Visualize orbital
 - Level of theory : HF/6-31G
 - Configuration :



Koopman's theorem

$$\mathbf{E}_{\text{HF}} = f(C_1, C_2)$$

$$\mathbf{F} \mathbf{C} = \mathbf{E}_{\text{HF}} \mathbf{C}$$

$$\mathbf{C}^T \mathbf{F} \mathbf{C} = \mathbf{C}^T \mathbf{E}_{\text{HF}} \mathbf{C} = \underbrace{\mathbf{E}_{\text{HF}} \mathbf{C}^T \mathbf{C}}_1 = \mathbf{E}_{\text{HF}}$$

$$\rightarrow \mathbf{E}_{\text{HF}} = \mathbf{C}^T \mathbf{F} \mathbf{C}$$

$$F_{11}(c) = \varepsilon_1 + \langle 11|11 \rangle c_1^2 + 2\langle 11|12 \rangle c_1 c_2 + \langle 12|12 \rangle c_2^2, \quad (23)$$

$$= (C_1 \ C_2) \cdot \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \cdot \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$F_{12}(c) = \langle 11|12 \rangle c_1^2 + 2\langle 11|22 \rangle c_1 c_2 + \langle 12|22 \rangle c_2^2, \quad (24)$$

$$F_{21}(c) = F_{12}(c), \quad (25)$$

$$F_{22}(c) = \varepsilon_2 + \langle 12|12 \rangle c_1^2 + 2\langle 12|22 \rangle c_1 c_2 + \langle 22|22 \rangle c_2^2.$$

$$= F_{11} C_1^2 + 2F_{12} C_1 C_2 + F_{22} C_2^2$$

$$= \varepsilon_1 C_1^2 + \varepsilon_2 C_2^2$$

$$+ \langle 11|11 \rangle C_1^4 + \langle 12|12 \rangle C_1^2 C_2^2 + 4\langle 11|22 \rangle C_1^2 C_2^2 + \langle 12|12 \rangle C_1^2 C_2^2 + \langle 22|22 \rangle C_2^4$$

$$+ 2\langle 11|11 \rangle C_1^3 C_2 + 2\langle 11|12 \rangle C_1^3 C_2 + 2\langle 12|22 \rangle C_1 C_2^3 + 2\langle 12|22 \rangle C_1 C_2^3$$

$$= \varepsilon_1 C_1^2 + \varepsilon_2 C_2^2 \rightarrow \langle \Psi | \hat{H} | \Psi \rangle$$

$$+ \langle 11|11 \rangle C_1^4 + \langle 22|22 \rangle C_2^4$$

$$+ 4\langle 11|22 \rangle C_1^2 C_2^2 + 2\langle 12|12 \rangle C_1^2 C_2^2$$

$$+ 4\langle 11|22 \rangle C_1^3 C_2 + 4\langle 12|22 \rangle C_1 C_2^3$$

C.F.

$$\langle \Psi | \hat{H} | \Psi \rangle = 2(\varepsilon_1 c_1^2 + \varepsilon_2 c_2^2)$$

$$+ \langle 11|11 \rangle C_1^4 + 4\langle 11|12 \rangle C_1^3 C_2 + 2(2\langle 11|22 \rangle + \langle 12|12 \rangle) C_1^2 C_2^2 + 4\langle 12|22 \rangle C_1 C_2^3 + \langle 22|22 \rangle C_2^4,$$

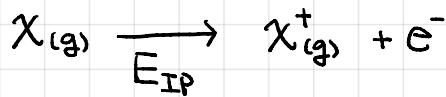
$$= \langle \Psi | \hat{H} | \Psi \rangle - (\varepsilon_1 C_1^2 + \varepsilon_2 C_2^2)$$

total WF

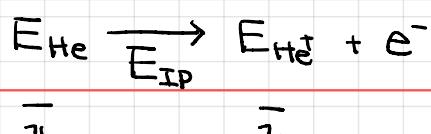
$$= \underbrace{\langle \Psi | \hat{A} | \Psi \rangle}_{2e^- \text{ WF}} - \underbrace{\langle \varphi | \hat{h} | \varphi \rangle}_{1e^- \text{ WF}}$$

$$\rightarrow \Sigma_{HF} = \langle \Psi | \hat{A} | \Psi \rangle - \langle \varphi | \hat{h} | \varphi \rangle \dots \textcircled{1}$$

* Ionization potential (IP)



$E_{IP} \equiv$ energy to remove an e^- within an atom/molecule.



$$\langle \Psi_{HF} | \hat{A} | \Psi_{HF} \rangle - \langle \varphi_{HF} | \hat{h} | \varphi_{HF} \rangle$$

$$\langle \Psi_{HF} | \hat{A} | \Psi_{HF} \rangle + E_{IP} = \langle \varphi_{HF} | \hat{h} | \varphi_{HF} \rangle \dots \textcircled{2}$$

compare ① and ②

$$\rightarrow E_{IP} = -\Sigma_{HF} = \langle \varphi_{HF} | \hat{h} | \varphi_{HF} \rangle - \langle \Psi_{HF} | \hat{A} | \Psi_{HF} \rangle$$

#

Koopman's theorem (KT)

"the negative orbital energy from Hartree-Fock method can be approximated as the ionization potential"

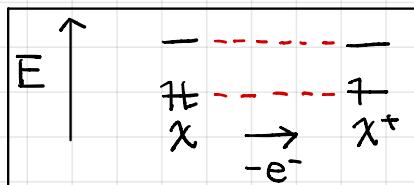
- pros. \rightarrow a convenient way to make prediction, and it is a good approximation for certain cases.

e.g. in He atom, the error of E_{IP} is only 2%.

- cons. \rightarrow ① Static approach

(c.f. pg 432)

the orbital are "frozen" after ionization

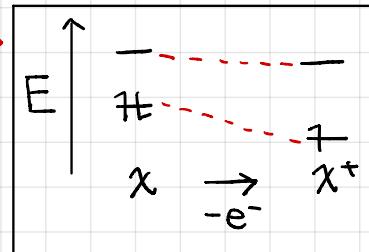


\therefore no orbital relaxation

$\therefore E_{IP}^{KT} = \max E_{IP}$

\uparrow the upper bound for $E_{IP}^{\text{expt.}}$

adding orbital relaxation to get a more realistic pic.



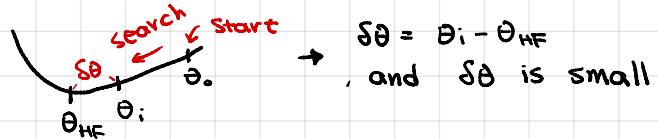
② Neglect electronic correlation

• Convergence problem

In this paper, they use non-degenerate perturbation theory (i.e. RSPT) to calculate the convergence criteria for theta, θ . However, in the standard EST simulation, convergence problem in SCF cycle is always a big problem, which is not only affected by the initial condition but also the numerical algorithm.

- In the current set-up: the SCF loop is $F^{(i+1)} \cdot C^{(i+1)} = \varepsilon^{(i+1)} \cdot C^{(i+1)}$, and $F^{(i+1)} = F(\theta_i)$

For a successful event, the last step is



$$S\theta = \theta_i - \theta_{HF}$$

, and $S\theta$ is small

$$\rightarrow F^{(i+1)} = F(\theta_i) = F(\theta_{HF}) + \underbrace{F'(\theta_{HF}) \cdot (\theta_i - \theta_{HF})}_{\text{known}} + \underbrace{\theta_i}_{\text{Unknown}} \xrightarrow{\text{treat as perturbation}}$$

$$C^{(i+1)} = \underbrace{C_{HF}}_{\text{Unknown}} + \underbrace{C_{\perp}}_{\text{Known}} = \begin{pmatrix} \text{known} \\ \text{Unknown} \end{pmatrix} \xrightarrow{\text{known}} C_{HF}$$

$$= \underbrace{C_{HF}}_{\text{known}} + \frac{C_{HF}^T \cdot F'(\theta_{HF}) \cdot (\theta_i - \theta_{HF}) \cdot C_{\perp}}{\varepsilon_{\perp} - \varepsilon_{HF}} \cdot C_{\perp} \dots \textcircled{1}$$

, and we also know

$$C^{(i+1)} = \begin{pmatrix} \cos(\theta_{i+1}) \\ \sin(\theta_{i+1}) \end{pmatrix}$$

$$= \underbrace{\cos(\theta_{i+1})}_{1 - \frac{\theta^2}{2} + \dots} \cdot C_{HF} + \underbrace{\sin(\theta_{i+1})}_{\theta - \frac{\theta^3}{3} + \dots} \cdot C_{\perp}$$

$$\approx C_{HF} + (\theta_{i+1} - \theta_{HF}) \cdot C_{\perp} \dots \textcircled{2}$$

compare \textcircled{1} and \textcircled{2}

$$\rightarrow \theta_{i+1} - \theta_{HF}$$

$$= \frac{C_{HF}^T \cdot F'(\theta_{HF}) \cdot C_{\perp}}{\varepsilon_{\perp} - \varepsilon_{HF}} (\theta_i - \theta_{HF})$$

0.2403 for Z=2.

c.f.

$$|\vartheta_i - \vartheta_{HF}| \approx 0.293^i |\vartheta_0 - \vartheta_{HF}| \approx 0.293^i \times 0.195. \quad (49)$$

Based on this, we would expect that it requires at least ten iterations for $|\vartheta_i - \vartheta_{HF}|$ to become smaller than 10^{-5} . This is consistent with what we observed in Sec. III A.

* RSPT

Known: $\hat{H}^0 |n^0\rangle = E_n^0 |n^0\rangle, \{ |n^0\rangle \}$
 Unknown: $\hat{H} = \hat{H}^0 + \lambda \hat{V}$
 Let $|n\rangle = |n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle \dots$
 $E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 \dots$
 $\rightarrow \hat{H}|n\rangle = E_n|n\rangle$
 $(\hat{H}^0 + \lambda \hat{V})(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle \dots)$
 $= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 \dots)(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle \dots)$
 $\rightarrow \lambda^0: \hat{H}^0 |n^0\rangle = E_n^0 |n^0\rangle$
 $\lambda^1: \hat{H}^0 |n^0\rangle + \hat{V} |n^0\rangle = E_n^0 |n^0\rangle + E_n^1 |n^0\rangle$
 $|n^0\rangle = \sum_m C_{nm}^0 |m^0\rangle$
 $\rightarrow \langle n^0 | \hat{H} | \sum_m C_{nm}^0 |m^0\rangle \rangle + \langle n^0 | \hat{V} | n^0 \rangle = E_n^0 \langle n^0 | \sum_m C_{nm}^0 |m^0\rangle \rangle + E_n^1 \langle n^0 | n^0 \rangle$
 $C_{nm}^0 E_n^0 + \langle n^0 | \hat{V} | n^0 \rangle = C_{nm}^0 E_n^0 + E_n^1$
 $\langle n^0 | \hat{V} | n^0 \rangle = E_n^1 \#$
 $\rightarrow C_{nm}^1 E_n^0 + \langle m^0 | \hat{V} | n^0 \rangle = E_n^0 C_{nm}^1 + \#$
 $C_{nm}^1 = \frac{\langle m^0 | \hat{V} | n^0 \rangle}{E_n^0 - E_n^1} \#$

• Brief summary

- Hartree-Fock uses one-electron orbital as the basis, and then uses iteration method (SCF) to solve Schrödinger equation.
- For ground states of molecules, Hartree-Fock method provides an upper bound energy (i.e. variational principle).