

Hartree-Fock Theory

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1. N-electron problem
2. Independent electron approximation
 - ▶ Non-interacting electrons
 - ▶ Orbitals (*AOs* and *MOs*)
 - ▶ Electron-electron interactions
 - ▶ Self-Consistent Field Method
 - ▶ Slater determinant
 - ▶ Hartree-Fock equations
 - ▶ Roothan equations - atomic basis sets
 - ▶ A featuring system : H_2
3. General results : Brillouin, Koopmans' theorems
4. Beyond Hartree Fock : Configuration Interaction
5. Conclusions

N-electron Problem

N electrons $\rightarrow \{i\}$ light particles
M ions $\rightarrow \{A\}$ heavy particles

$$\hat{\mathcal{H}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \\ + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

$$m_i/M_A \approx 1/2000$$

frozen ions : Born-Oppenheimer approximation

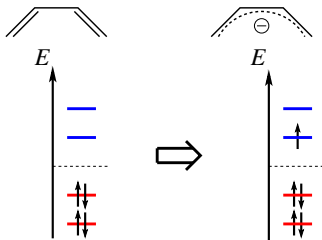
$\frac{1}{r_{ij}} \rightarrow$ NON-INDEPENDENT particles !

APPROXIMATED SOLUTION

Non-interacting electron Case

$$\text{"}\frac{1}{r_{ij}} = 0\text{"}$$

$$\hat{\mathcal{H}} = \sum_{i=1}^N \hat{h}(i) \rightarrow E_0 = \sum_{i=1}^N \epsilon_i$$



$$E(N+1) = E(N) + \epsilon_{N+1}$$

convenient and simple, though approximate !

Orbital Approximation

"electrons in boxes"

Atomic Orbitals $\rightarrow$ Molecular Orbitals

ORBITAL : eigenfunction of a *monoelectronic* problem

$$\hat{h}\varphi = \epsilon\varphi \quad \|\varphi\|^2 = \int \varphi^* \varphi d\mathbf{r} = \langle \varphi | \varphi \rangle = 1$$

Linear Combination of Atomic Orbitals (LCAO)

$$\psi_{MO} = \sum_{i=1}^N c_i \varphi_i$$

example 1 : Hückel for conjugated systems

$\{2p_z\}$ SIMPLE ZETA

example 2 : *extended* Hückel

$\{AO\}_i$ MULTIPLE ZETA

$$\varphi_i = a_1 \exp\{-\zeta_1 r\} + a_2 \exp\{-\zeta_2 r\}$$

how do the electrons see each other ?

Electron-Electron Interactions

$$\frac{1}{r_{ij}} \neq 0$$

Hartree's assumptions :

1. *instantaneous* interaction $\rightarrow$ *average* interaction
spherical for atoms

2. *self-consistency*

$$\{\varphi_i\} \rightarrow \text{Coulomb} \rightarrow \hat{h}\tilde{\varphi}_i = \epsilon_i\tilde{\varphi}_i \rightarrow \{\tilde{\varphi}_i\}$$
$$\|\tilde{\varphi}_i - \varphi_i\| \rightarrow 0$$

3. *Pauli exclusion* principle

"no two electrons with same spin in the same orbital"

$\rightarrow$ *spherical averaging* of the Coulomb potential

Self-Consistent Field Method

atomic calculations

- the electrons move *independently* one from the other :

$$\Psi(\{r_i\}, \{\theta_i\}, \{\phi_i\}) = \varphi_1(r_1, \theta_1, \phi_1) \cdots \varphi_N(r_N, \theta_N, \phi_N)$$

→ Hartree product

- let us write as for the hydrogen atom :

$$\varphi(r, \theta, \phi) = \frac{P(r)}{r} Y_l^m(\theta, \phi) \quad Y_l^m(\theta, \phi) : \text{spherical harmonics} \\ (\text{e.g. } Y_0^0(\theta, \phi) \triangleq 1s)$$

$$\hat{\mathcal{H}} = - \sum_i \frac{1}{2} \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{j>i} \frac{1}{r_{ij}} = \sum_i f_i + \sum_{j>i} g_{ij}$$

- electrostatic part $\sum_{j>i} g_{ij}$:

$$\int \varphi_i^*(r_1) \varphi_j^*(r_2) \left(\frac{1}{r_{12}} \right) \varphi_i(r_1) \varphi_j(r_2) d\mathbf{r}_1 d\mathbf{r}_2 = (ii, jj) : \text{Coulomb integral}$$

Spherical Averaging : Hartree's equations

$$\delta \langle \psi | \hat{\mathcal{H}} | \psi \rangle_{av} = 0$$

- averaging the charge distribution around r_1 :

$$\delta Q(r_1) = P_j^2(r_1) dr_1$$

- energy at r_2 : $\frac{\delta Q(r_2)}{r_1}$ if $r_1 > r_2$ and $\frac{\delta Q(r_2)}{r_2}$ if $r_1 < r_2$

$$Y_0(r_1, j) = \frac{1}{r_1} \left\{ \int_0^{r_1} \delta Q(r_2) dr_2 + \int_{r_1}^{\infty} \delta Q(r_2) \frac{r_1}{r_2} dr_2 \right\}$$

- spherically averaged i th and j th charge distributions :

$$F_0(i, j) = \int_0^{\infty} \delta Q(r_1) Y_0(r_1, j) dr_1 = \int_0^{\infty} \int_0^{\infty} \delta Q(r_1) \frac{1}{r_{\max}} \delta Q(r_2)$$

$$\left\{ -\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} - \frac{Z^*}{r} \right\} P_i(r) = \epsilon_i P_i(r)$$

$$Z^* = Z - \sum_{j \neq i} Y_0(r_i, j) : \text{screening effect}$$

Antisymmetry of the Wave Function

2-electron system

- experimental facts : $1s2s \rightarrow$ *antisymmetric* 1S
and *symmetric* 3S
- triplet/singlet spin parts : *symmetric*/*antisymmetric*
 $M_S = 0$ component : $\alpha(1)\beta(2) \pm \alpha(2)\beta(1)$

$$\text{triplet} : \uparrow\downarrow + \downarrow\uparrow$$

Slater determinant

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) \end{vmatrix} \quad \text{with} \quad x_i = (r_i, \omega_i)$$

Note : $\varphi_{i,j}$ = *spin-orbitals*

- *antisymmetry* : $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$
- Pauli's principle verified : $\Psi(x, x) = 0$ (identical lines !)

Properties-Generalization

$$\varphi(x_i) = \varphi(r_i)\alpha(\omega_i) \text{ or } \varphi(r_i)\beta(\omega_i)$$

- Space parts of the wave-functions :

$$|S = 1, M_S = 0\rangle = \varphi_i(r_1)\varphi_j(r_2) - \varphi_i(r_2)\varphi_j(r_1)$$

$$|S = 0, M_S = 0\rangle = \varphi_i(r_1)\varphi_j(r_2) + \varphi_i(r_2)\varphi_j(r_1)$$

$r_1 \neq r_2$ in the triplet

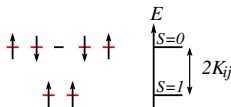
- Coulomb interactions larger in $S = 0$ than in $S = 1$

- Analytically, $E_0 - E_1 = 2K_{ij}$

$$\text{with } K_{ij} = \int \varphi_i^*(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\varphi_i(\mathbf{r}_2)\varphi_j(\mathbf{r}_1)\mathbf{d}\mathbf{r}_1\mathbf{d}\mathbf{r}_2$$

$$= \langle ij|1/r|ji\rangle = (ij,ji) : \text{exchange integral}$$

→ Hund's rule : $S_{\max}$ is favored



Generalization : Slater determinant

Starting from 2-electron functions :

$$\Psi_1(x_1, x_2) = \varphi_i(x_1)\varphi_j(x_2) \quad \Psi_2(x_1, x_2) = \varphi_j(x_1)\varphi_i(x_2)$$

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) \end{vmatrix} : \text{Slater determinant}$$

More generally :

$$\Psi(\{x_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) & \cdots & \varphi_k(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) & \cdots & \varphi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \varphi_i(x_N) & \varphi_j(x_N) & \cdots & \varphi_k(x_N) \end{vmatrix}$$

$$\text{notation} : \Psi = |\varphi_i \varphi_j \cdots \varphi_k|$$

$\{\varphi_j\} = $ <i>orthonormal</i> molecular <u>spin-orbital</u> basis set

Hartree-Fock Equations

$$E[\{\varphi_a\}] = \langle \psi | \hat{\mathcal{H}} | \psi \rangle \text{ and } \langle \psi | \psi \rangle = 1$$

(i) *single* Slater determinant : $\Psi = |\varphi_1 \varphi_2 \cdots \varphi_a \varphi_b \cdots \varphi_N|$

(ii) $\delta E = 0$ under the constraints $\langle \varphi_a | \varphi_b \rangle = \delta_{ab}$

$$\mathcal{L}[\{\varphi_a\}] = E[\{\varphi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \epsilon_{ba} (\langle \varphi_a | \varphi_b \rangle - \delta_{ab})$$

$$\implies \boxed{\hat{\mathcal{F}}(1)\varphi_i(1) = \epsilon_i \varphi_i(1)} : \text{Hartree-Fock equations } (\sim 1930)$$

$\hat{\mathcal{F}}$ = Fock operator $\rightarrow$ monoelectronic

$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_{\text{a, occupied}} \hat{J}_a(1) - \hat{K}_a(1)$$

$$\hat{J}_a(1) = \int dx_2 \varphi_a^*(2) r_{12}^{-1} \varphi_a(2)$$

$$\hat{K}_a(1)\varphi_i(1) = \left[\int dx_2 \varphi_a^*(2) r_{12}^{-1} \varphi_i(2) \right] \varphi_a(1)$$

$\hat{J}_a$ = Coulomb, LOCAL $\hat{K}_a$ = exchange, NON-LOCAL

Coulomb, Exchange Operators, Hartree-Fock Potential

Coulomb $\hat{J}_b$

$$\langle a | \hat{J}_b | a \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \varphi_a^*(1) \varphi_b^*(2) r_{12}^{-1} \varphi_b(2) \varphi_a(1) = (aa, bb) = J_{ab}$$

exchange $\hat{K}_b$

$$\langle a | \hat{K}_b | a \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \varphi_a^*(1) \varphi_b^*(2) r_{12}^{-1} \varphi_a(2) \varphi_b(1) = (ab, ba) = K_{ab}$$

$\langle \alpha | \beta \rangle = 0 \Rightarrow K_{ab} = 0$ for electrons of opposite spins

$$\text{HF potential } \hat{v}_{HF} = \sum_{occ} \hat{J}_b - \hat{K}_b$$

$$\langle a | \hat{v}_{HF} | a \rangle = \sum_{b, occ} (aa, bb) - (ab, ba)$$

$\rightarrow \alpha$ and β electrons are not *correlated*

Properties-Resolution

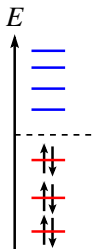
- α and β electrons form two discernable sets
($\hat{K}$ operator $\rightarrow$ *spin polarization*)

- closed-shell systems : *Restricted Hartree-Fock*

$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_{\text{MOs}}^{N/2} 2\hat{J}_a(1) - \hat{K}_a(1)$$

- $\langle a|\hat{J}_a|a\rangle = \langle a|\hat{K}_a|a\rangle$

cancellation in $\hat{V}_{HF}$: no *self-interaction*



- $\hat{\mathcal{F}} = f(\{\varphi_a, \text{occ}\}) \Rightarrow$ *iterative* resolution until
self-consistency : $\langle i|\hat{\mathcal{F}}|j\rangle = \delta_{ij}\epsilon_i$

- along the HF procedure $\frac{1}{r_{12}} \rightarrow \hat{V}_{HF}$: *mean field*

Roothaan Equations

introduction of a basis LCAO

$$\varphi_i = \sum_{\mu=1}^M c_{\mu i} \chi_{\mu} \quad M \sim 1000$$

two $M \times M$ matrices must be introduced :

$$S_{\mu\nu} = \int dr_1 \chi_{\mu}^*(1) \chi_{\nu}(1) \quad : \text{metric}$$

$$F_{\mu\nu} = \int dr_1 \chi_{\mu}^*(1) \mathcal{F}(1) \chi_{\nu}(1) \quad : \text{Fock matrix}$$

$$\sum_{\mu} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i}$$

$$\boxed{FC = SC\epsilon} \quad : \text{Roothaan equations}$$

Roothaan Equations in Practice

non-orthogonal atomic orbitals

- ▶ Slater type (*atomic-like*)
example : double dzéta, DZ

$$\varphi_i(r) = a_1 \exp\{-\zeta_1 r\} + a_2 \exp\{-\zeta_2 r\}$$

- ▶ Gaussian type and contractions
 - ▶ minimal basis sets Slater $\leftarrow$ linear combination of Gaussians

$$\varphi_i(r) = \sum_i c_i \exp\{-\alpha_i r^2\}$$

- ▶ *contraction* : some of the coefficients are frozen
example : 6-31G
6 for the core
3 + 1 for the valence $\rightarrow$ *split valence*

Unrestricted Hartree-Fock

different α and β spatial forms

$$\hat{\mathcal{F}}_{\alpha}(1) = \hat{h}(1) + \sum_{\mathbf{N}_{\alpha}} \left[\hat{J}_{a,\alpha}(1) - \hat{K}_{a,\alpha}(1) \right] + \sum_{\mathbf{N}_{\beta}} \hat{J}_{a,\beta}(1)$$

$J_{ij}^{\sigma\sigma}, K_{ij}^{\sigma\sigma}$ and $J_{ij}^{\alpha\beta}$: coupling between $\hat{\mathcal{F}}_{\alpha}$ and $\hat{\mathcal{F}}_{\beta}$!

How to practically solve $FC = SC\epsilon$?

Find X such as $X^{\dagger}SX$ diagonal $\rightarrow X = S^{-\frac{1}{2}}$

$$F'C' = C'\epsilon \text{ with } F' = X^{\dagger}FX$$

$\rightarrow$ "standard" *eigen-value problem*

Main drawback of UHF method : $\langle \hat{S}^2 \rangle \neq S(S+1)$

$\rightarrow$ *spin contamination* issue

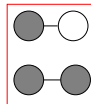
H₂ as an example

- *minimal* basis set : $\{1s_a, 1s_b\} = \{a, b\}$

$$\varphi_1 = \xi_1 a + \xi_2 b$$

$$\varphi_2 = \xi_2 a - \xi_1 b$$

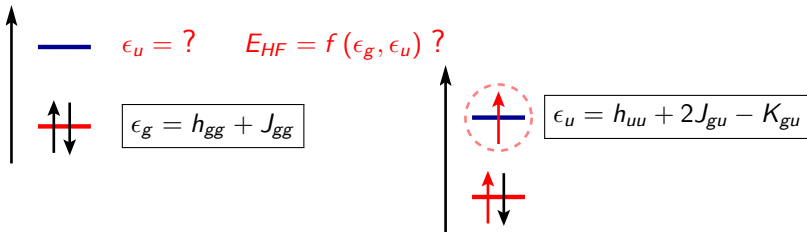
from *group theory*, $|\xi_1| = |\xi_2| = \frac{1}{\sqrt{2}}$



$\varphi_1 = g$ and $\varphi_2 = u$

- *self-consistency* is automatically achieved

$$F_{gu} = \langle u | \hat{\mathcal{F}} | g \rangle = 0 \quad F_{gg} = \langle g | \hat{\mathcal{F}} | g \rangle = \epsilon_g \quad F_{uu} = \langle u | \hat{\mathcal{F}} | u \rangle = \epsilon_u$$



Hartree-Fock Energy

$$E_{HF} = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle \quad \text{with } \Psi = |a\bar{a}\cdots\rangle$$

from a "natural" inspection : $E_{H_2} = 2h_{gg} + J_{gg}$

How does this compare to $2\epsilon_g$?

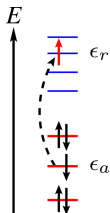
$$E_{H_2} = 2\epsilon_g - J_{gg} \Rightarrow E_{HF} \neq \sum_{a,occ} \epsilon_a !$$

$$\begin{aligned} E_{HF} &= \sum_{a,occ} h_{aa} + \frac{1}{2} \sum_{a,b} \left[(aa, bb) - (ab, ba) \right] \\ &= \sum_{a,occ} \epsilon_a - \frac{1}{2} \sum_{a,b} \left[(aa, bb) - (ab, ba) \right] \end{aligned}$$

$$- \frac{1}{2} \sum_{a,b} \left[(aa, bb) - (ab, ba) \right]$$

avoids *double counting* of e-e interactions

Brillouin and Koopmans Theorems

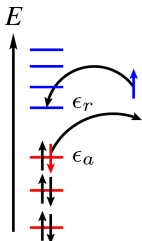


Single Excited Determinants

$$|\Psi_a^r\rangle = a_r^\dagger a_a |\Psi_{HF}\rangle$$

$$\langle \Psi_{HF} | \hat{\mathcal{H}} | \Psi_a^r \rangle = 0$$

What do we learn from the ϵ_i ?



$$eA = -\epsilon_r$$

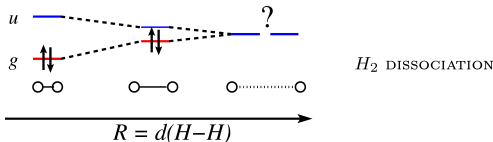
$$IP = -\epsilon_a$$

$$eA = {}^N E_{HF} - {}^{N+1} E_r$$

$$IP = {}^{N-1} E_a - {}^N E_{HF}$$

ϵ_i calculated for the *N-electron* system !

Pathology of the Hartree-Fock Solution



Does $\Psi_{HF} = |g\bar{g}|$ survive as $R \rightarrow \infty$?

Since $g = \frac{1}{\sqrt{2}}(a+b)$, $\Psi_{HF} = \frac{1}{2} [(|a\bar{a}| + |b\bar{b}|) + (|a\bar{b}| + |b\bar{a}|)]$

$$\Psi_{HF} = \frac{1}{\sqrt{2}} [\Psi_{ionic} + \Psi_{neutral}]$$

incompatible with $\Psi \approx \Psi_{neutral}$ as $R \rightarrow \infty$!

$\Rightarrow$ “suppress” the *ionic contributions* : $\Psi = \lambda |g\bar{g}| - \mu |u\bar{u}|$

Hartree-Fock invalidated : *beyond mean field* is necessary...

Configuration Interaction

Let us analyze $\Psi = \lambda|g\bar{g}| - \mu|u\bar{u}|$
 λ and μ are determined variationally

$$g = \frac{1}{\sqrt{2}}(a + b) \text{ and } u = \frac{1}{\sqrt{2}}(a - b)$$

$$\Psi = \frac{\lambda - \mu}{2}(|a\bar{a}| + |b\bar{b}|) + \frac{\lambda + \mu}{2}(|a\bar{b}| - |\bar{a}b|)$$

asymptotically, $\lambda - \mu \rightarrow 0$ as $R \rightarrow \infty$

$\{|g\bar{g}|, |u\bar{u}|\}$ define the basis set :

$$\langle g\bar{g} | \hat{\mathcal{H}} | u\bar{u} \rangle = (gu, ug) = K_{gu}$$

configuration interaction matrix :

$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{HF} + 2\Delta \end{pmatrix}$$

Correlation Energy and Wavefunction Expansion

definition : $E_{corr} = E - E_{HF}$

E_{corr} from the diagonalization of :

$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{HF} + 2\Delta \end{pmatrix}$$

The expansion of the lowest root leads to :

$$E_{corr} = -\frac{K_{gu}^2}{2\Delta} + O\left(\frac{K_{gu}^3}{\Delta^2}\right)$$

and

$$\Psi = |g\bar{g}\rangle - \frac{K_{gu}}{2\Delta} |u\bar{u}\rangle = \Psi_{HF} + c^{(1)} |u\bar{u}\rangle$$

$$\boxed{c^{(1)} = -\frac{K_{gu}}{2\Delta}} \text{ first order in } \textit{perturbation theory}$$

Generalization of CI Expansion

$$\text{From } \Psi = c_0 \Psi_0 + \sum_{ar} c_{ar} \Psi_a^r + \sum_{ab,rs} c_{ab}^{rs} \Psi_{ab}^{rs} + \dots$$

projection of Schrödinger equation onto $|\Psi_0\rangle$ leads to :

$$E = E_0 + \sum_{ab,rs} c_{ab}^{rs} \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle$$

$$\begin{pmatrix} \Psi_0 & \Psi_a^r & \Psi_{ab}^{rs} & \Psi_{abc}^{rst} & \dots \\ \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle & & & & \\ 0 & \langle \Psi_a^r | \hat{\mathcal{H}} | \Psi_a^r \rangle & & & \\ \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle & \langle \Psi_a^r | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle & \langle \Psi_{ab}^{rs} | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle & & \\ 0 & 0 & \langle \Psi_{ab}^{rs} | \hat{\mathcal{H}} | \Psi_{abc}^{rst} \rangle & \langle \Psi_{abc}^{rst} | \hat{\mathcal{H}} | \Psi_{abc}^{rst} \rangle & \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

- ▶ several millions of configurations !
- ▶ exponential growth
 → *truncation* : CI Singles Ψ_a^r and Doubles Ψ_{ab}^{rs}
- ▶ alternative methods : localization, entanglement

Conclusion and References

- ▶ Hartree-Fock as a starting point
- ▶ mean-field approximation : orbitals rotation
orthogonal MOs, Brillouin
- ▶ further expansion is necessary
→ CASSCF, MCSCF, CISD (Emmanuel Fromager's lecture)
- ▶ perturbation theory as an alternative
→ MP2, NEVPT2 (Celestino Angeli's lecture)

References :

A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*

J. C. Slater, *Quantum Theory*