

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

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

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

frozen ions : Born-Oppenheimer approximation

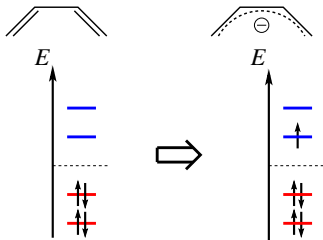
$\frac{1}{r_{ij}}$ \rightarrow NON-INDEPENDENT particles !

APPROXIMATED SOLUTION

Non-interacting electron Case

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

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



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

convenient and simple, though approximate !

Digression : Hückel Theory

semi *empirical* method for π -conjugated hydrocarbons

$$\hat{\mathcal{H}} = \sum_{i=1}^N \hat{h}(i) \quad \rightarrow \quad \Psi(r_1, r_2, \dots, r_N) = \prod_{i=1}^N \varphi(r_i)$$

$$\langle \varphi_i | \hat{h} | \varphi_i \rangle = \alpha \sim -10\text{eV} \quad \leftarrow \quad \text{Coulomb}$$

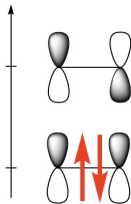
$$\langle \varphi_i | \hat{h} | \varphi_j \rangle = \beta \text{ or } t \sim -1\text{eV} \quad \leftarrow \quad \text{resonance}$$

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

example : ethylene, 2AOs \rightarrow 2MOs

$$\epsilon_b = \alpha + \beta \quad \epsilon_a = \alpha - \beta$$

$$\Delta E = 2|\beta| = h\nu \rightarrow \text{parametrization}$$



Digression : Hückel Theory
comments (see Nathalie Guihéry's lecture)

- ▶ effective electron-electron repulsion
- ▶ qualitative MOs : nodal structure
- ▶ energetics : one-electron picture !

BUT

- ▶ *transferability* of parameters ?
- ▶ *steric hindrance* ?

$$\Delta E(4e) = 2(\alpha + \beta) + 2(\alpha - \beta) - 4\alpha = 0 !$$

Orbital Approximation

"electrons in boxes"

Atomic Orbitals \rightarrow Molecular Orbitals

ORBITAL : eigenfunction of a *monoelectronic* problem

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

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

$$\left\langle \frac{1}{r_{ij}} \right\rangle \neq 0$$

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 :

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

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

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

$$\int \varphi_a^*(r_1) \varphi_b^*(r_2) \frac{1}{r_{12}} \varphi_a(r_1) \varphi_b(r_2) \mathbf{d}r_1 \mathbf{d}r_2 = (aa, bb) : \text{Coulomb integral}$$

Spherical Averaging : Hartree's equations

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

- averaging the charge distribution between r_2 and $r_2 + dr_2$:

$$\delta Q(r_2) = P_j^2(r_2) dr_2$$

- potential energy at r_1 in the presence of $\delta Q(r_2)$:

$$\frac{\delta Q(r_2)}{r_1} \text{ if } r_1 > r_2 \text{ and } \frac{\delta Q(r_2)}{r_2} \text{ if } r_1 < r_2$$

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

- *spherically averaged* i th and j th charge distributions :

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

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

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

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 : $\alpha(1)\beta(2) \pm \alpha(2)\beta(1)$
triplet : $\uparrow\downarrow + \downarrow\uparrow$

Slater determinant

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

Note : $\varphi_{a,b}$ = 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 :

$$|S = 1, M_S = 0\rangle = \varphi_a(r_1)\varphi_b(r_2) - \varphi_a(r_2)\varphi_b(r_1)$$

$$|S = 0, M_S = 0\rangle = \varphi_a(r_1)\varphi_b(r_2) + \varphi_a(r_2)\varphi_b(r_1)$$

$r_1 \neq r_2 \text{ in the triplet}$

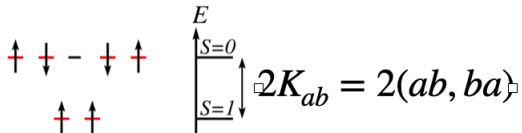
- Coulomb interactions larger in $S = 0$ than in $S = 1$

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

$$\text{with } K_{ab} = \int \varphi_a^*(\mathbf{r}_1)\varphi_b^*(\mathbf{r}_2)\frac{1}{r_{12}}\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2$$

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

→ Hund's rule : S_{max} is favored



Generalization : Slater determinant

Starting from 2-electron functions :

$$\Psi_1(x_1, x_2) = \varphi_a(x_1)\varphi_b(x_2) \quad \Psi_2(x_1, x_2) = \varphi_b(x_1)\varphi_a(x_2)$$

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

More generally :

$$\Psi(\{x_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_a(x_1) & \varphi_b(x_1) & \cdots & \varphi_c(x_1) \\ \varphi_a(x_2) & \varphi_b(x_2) & \cdots & \varphi_c(x_2) \\ \vdots & \vdots & & \vdots \\ \varphi_a(x_N) & \varphi_b(x_N) & \cdots & \varphi_c(x_N) \end{vmatrix}$$

notation : $\Psi = |\varphi_a\varphi_b \cdots \varphi_c|$

$\{\varphi_j\} =$ *orthonormal* molecular spin-orbital 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

$$\langle a | \hat{J}_b | a \rangle = \int dx_1 dx_2 \varphi_a^*(1) \varphi_b^*(2) r_{12}^{-1} \varphi_b(2) \varphi_a(1) = (aa, bb) = J_{ab}$$

exchange \hat{K}_b

$$\langle a | \hat{K}_b | a \rangle = \int dx_1 dx_2 \varphi_a^*(1) \varphi_b^*(2) r_{12}^{-1} \varphi_a(2) \varphi_b(1) = (ab, ba) = K_{ab}$$

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

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*

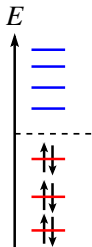
$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_{\text{MOs}}^{N/2} 2\hat{J}_a(1) - \hat{K}_a(1)$$

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

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 :

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

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

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

$$\boxed{FC = SC\epsilon}$$

: 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 $\rightarrow X = S^{-\frac{1}{2}}$

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

\rightarrow "standard" *eigen-value problem*

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

\rightarrow *spin contamination* issue

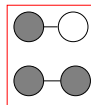
H₂ as an example

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

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

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

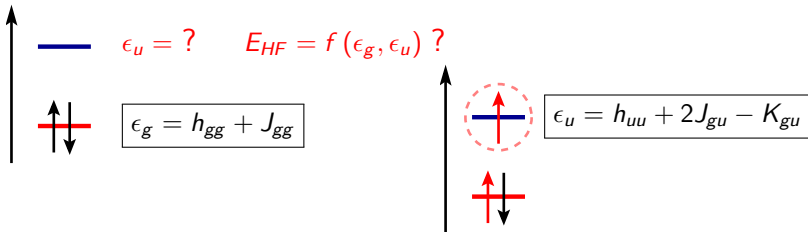
from *group theory*, $|\xi_1| = |\xi_2| = \frac{1}{\sqrt{2}}$



$$\varphi_1 = g \text{ and } \varphi_2 = u$$

- *self-consistency* is automatically achieved

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



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 $2\epsilon_g$?

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

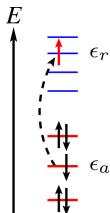
$$E_{HF} = \sum_{a,occ} h_{aa} + \frac{1}{2} \sum_{a,b} [(aa, bb) - (ab, ba)] \quad \leftarrow \text{Slater's rules}$$

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

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

avoids *double counting* of e-e interactions

Brillouin and Koopmans' Theorems

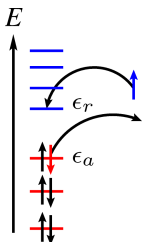


Single Excited Determinants

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

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

What do we learn from the ϵ_i ?



$$eA = -\epsilon_r$$

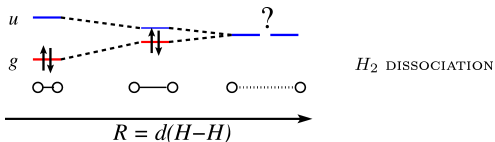
$$IP = -\epsilon_a$$

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

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

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

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

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

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

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

$$\langle g\bar{g} | \hat{H} | u\bar{u} \rangle = (gu, ug) = K_{gu} \text{ and } E_{u\bar{u}} - E_{g\bar{g}} = 2\Delta$$

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

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

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

$$E = E_0 + \sum_{a<b, r<s} c_{ab}^{rs} \langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle$$

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

- ▶ 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)
- ▶ perturbation theory as an alternative
→ **MP2, MRPT** (Pierre François Loos, Celestino Angeli)

References :

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

J. C. Slater, *Quantum Theory*