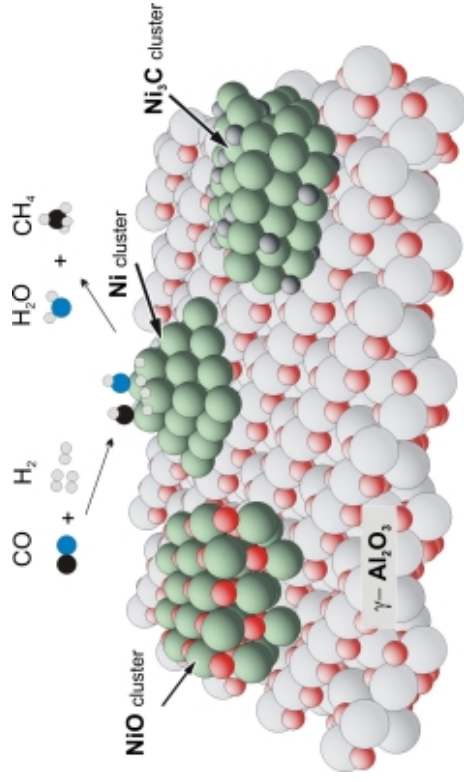


Introduction à la simulation moléculaire et au modèle de Hartree-Fock

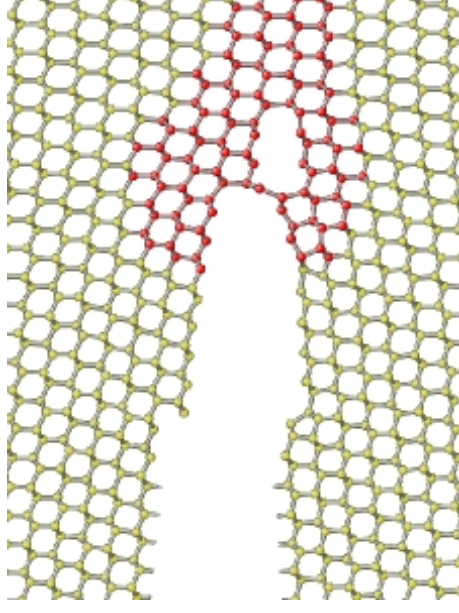
Eric CANCES

Ecole Polytechnique - MAP 583

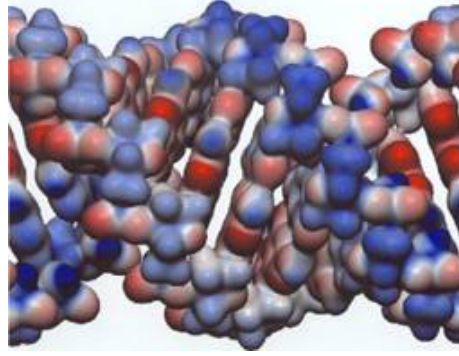
1 - Overview of electronic structure models



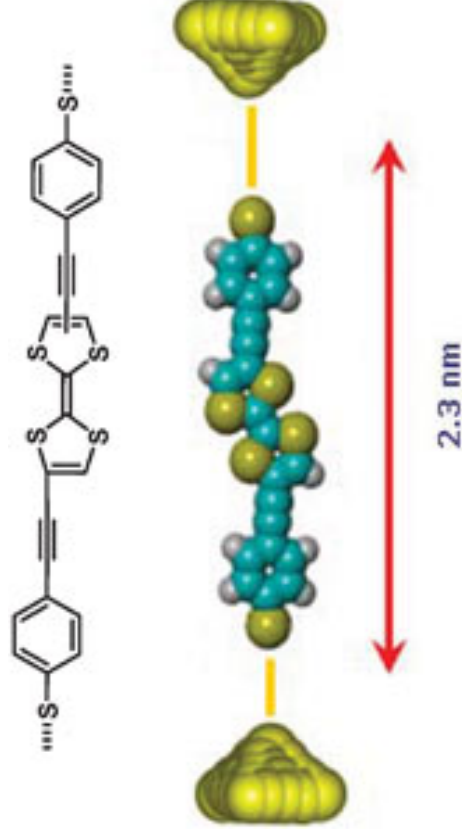
Chemistry



Materials science



Molecular biology



Nanotechnology

First-principle molecular simulation

- A molecular system is a set of M nuclei and N electrons.
- The state space $\mathcal{H} \subset L^2(\mathbb{R}^{3(M+N)}, \mathbb{C}^s)$, the Hamiltonian and the other observables of the molecule can be deduced from its chemical formula :

$$H^{\text{mol}} = - \sum_{k=1}^M \frac{1}{2m_k} \Delta_{\mathbf{R}_k} - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{k=1}^M \sum_{i=1}^N \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$

Atomic units : $\hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\epsilon_0 = 1.$

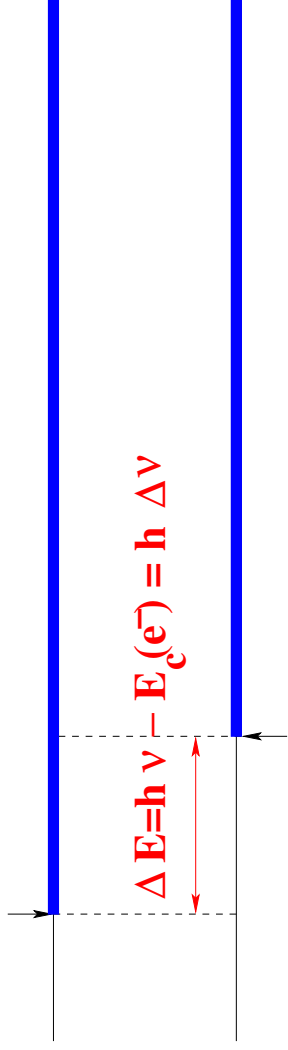
- This model is free of empirical parameters specific to the system.

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solved. (Dirac, 1929)

Ionization energy of Helium (Nakatsuji et al., '01) :



Ground state energy of He



exp. : **5 945 204 238** MHz ('97)

5 945 204 356 MHz ('98)

calc. : **5 945 262 288** MHz

5 945 204 223 MHz (R.C.)

Ground state energy of He^+

$$H_{\text{He}} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \text{Breit terms}$$

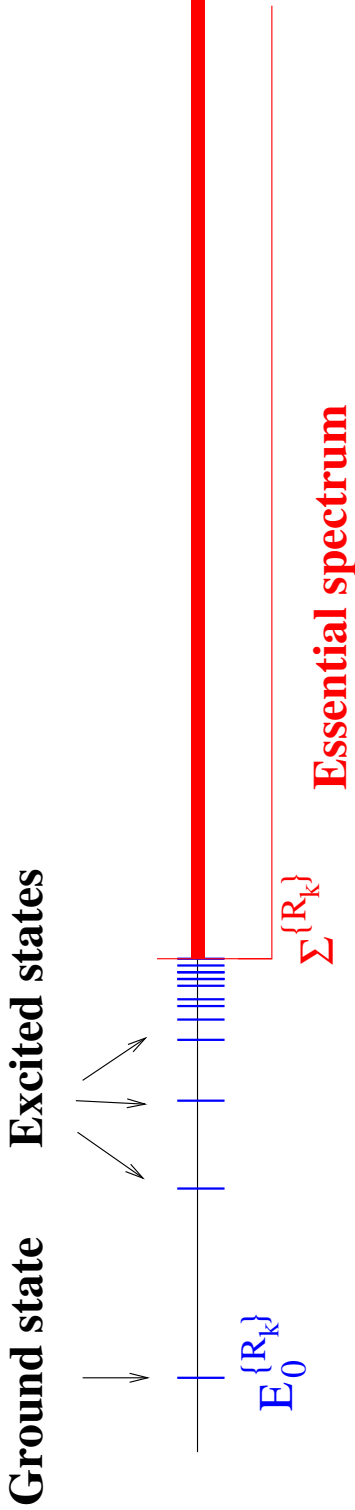
$$H_{\text{He}^+} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} + \text{Breit terms}, \quad m = 7294.2984 \dots \text{ a.u.}$$

The electronic problem for a fixed nuclear configuration $\{\mathbf{R}_k\}_{1 \leq k \leq M}$

$$H_N^{\{\mathbf{R}_k\}} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{on} \quad \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2) \quad \text{(Pauli principle)}$$

Zhislin's theorem : if $N \leq \sum_{k=1}^M z_k$ (neutral or positively charged system), then

$$\sigma(H_N^{\{\mathbf{R}_k\}}) = \left\{ E_0^{\{\mathbf{R}_k\}} \leq E_1^{\{\mathbf{R}_k\}} \leq E_2^{\{\mathbf{R}_k\}} \dots \right\} \cup [\Sigma^{\{\mathbf{R}_k\}}, +\infty).$$



The electronic problem for a fixed nuclear configuration $\{\mathbf{R}_k\}_{1 \leq k \leq M}$

$$H_N^{\{\mathbf{R}_k\}} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{on} \quad \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2) \quad \text{(Pauli principle)}$$

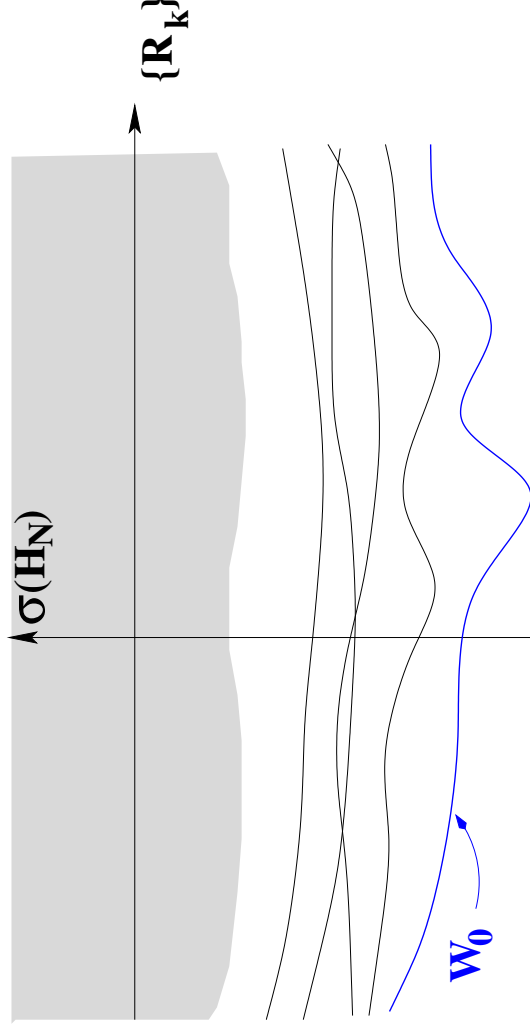
The bound states are obtained by solving the Schrödinger equation

$$\left(-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$$

$$\forall p \in \mathfrak{S}_N, \quad \Psi(\mathbf{x}_{p(1)}, \dots, \mathbf{x}_{p(N)}) = \varepsilon(p) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$$

$$\mathbf{x}_i = (\mathbf{r}_i, \sigma_i) \in \mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\} \quad \text{position and spin,} \quad V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

Potential energy surfaces :
$$W_n(\mathbf{R}_1, \dots, \mathbf{R}_M) = E_n^{\{\mathbf{R}_k\}} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$



Born-Oppenheimer approximation of the full Schrödinger equation :

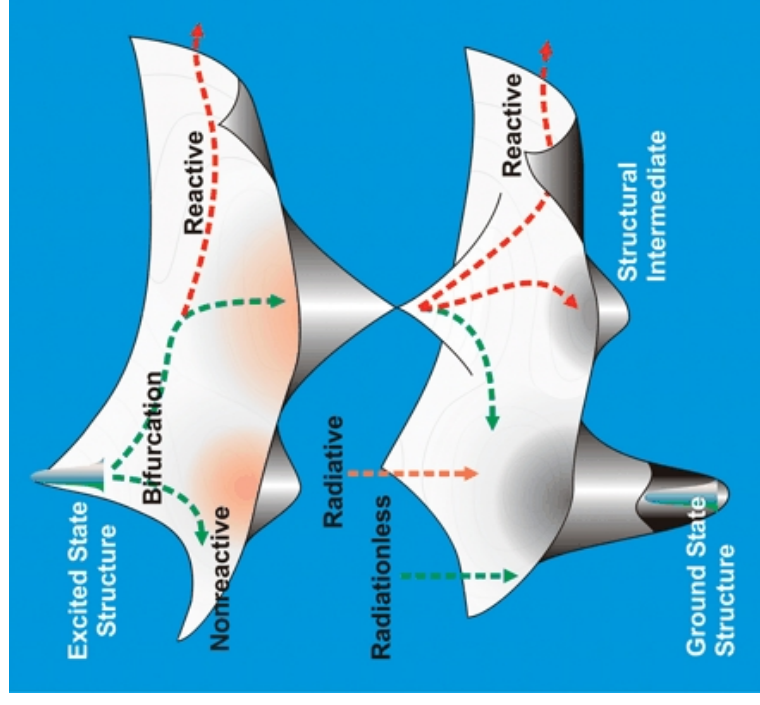
- adiabatic approximation : electron mass \ll masses of the nuclei
 - semiclassical approximation on the nuclear dynamics : $\hbar \rightarrow 0$.
- **Classical molecular dynamics on the ground state PES.**

Beyond the Born-Oppenheimer approximation

Quantum nuclear dynamics
Electronic excited states
Non-adiabatic electronic dynamics

**Applications in molecular biology,
photochemistry, femtochemistry,
laser control of molecular processes, ...**

**Mathematical contributions by
Hagedorn, Joye, Panati, Spohn,
Teufel, Fermanian, Lasser,
Lubich, ...**



Zewail's group (Caltech)

Main challenge in first principle molecular simulation :

- solve numerically the electronic Schrödinger equation (3N dim. PDE)
- up to chemical accuracy

energy of a C atom : ~ 100 ha

energy of a H atom : 0.5 ha

energy of a covalent bond : ~ 0.15 ha (100 kcal/mol)

electronic excitation energy : ~ 0.03 ha (1 eV)

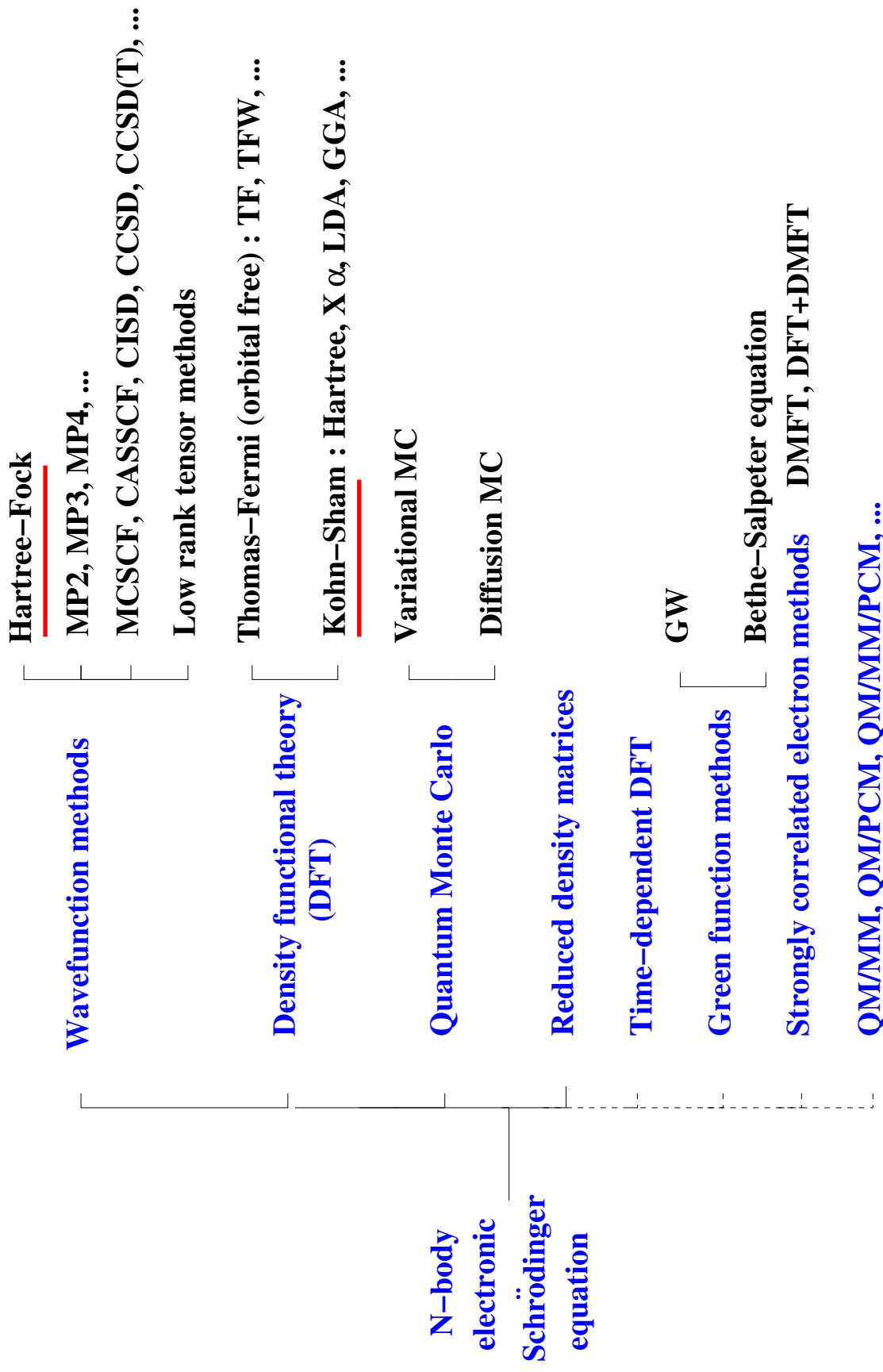
energy of a hydrogen bond : ~ 0.003 ha (2 kcal/mol)

$k_B T$ at room temperature : ~ 0.001 ha (1/40 eV)

van der Waals characteristic energy : ~ 0.0003 ha (0.2 kcal/mol)

spectroscopic accuracy : ~ 0.000005 ha ($1 \text{ cm}^{-1} = 29,470 \text{ MHz}$)

Methods for electronic structure calculations



2 - Mathematical formulation of the Hartree-Fock model

From now on,

- the positions of the nuclei are fixed : we drop the superscript $\{\mathbf{R}_k\}$;
- we omit the spin variable.

Variational expression of the ground state energy

$$E_0 = \inf \{ \langle \psi | H_N | \psi \rangle, \psi \in \mathcal{W}_N \} \quad \mathcal{W}_N = \left\{ \psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3), \|\psi\|_{L^2} = 1 \right\}.$$

Hartree-Fock approximation : minimize the **exact energy $\langle \psi | H_N | \psi \rangle$ on the subset of \mathcal{W}_N defined as**

$$\left\{ \psi_\Phi = \phi_1 \wedge \dots \wedge \phi_N, \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\psi_\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \stackrel{\text{def}}{=} \frac{1}{\sqrt{N!}}$$

$$\begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

(Slater determinant)

Molecular orbital formulation of the Hartree-Fock model

$$E_0 \leq E_0^{\text{HF}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$E^{\text{HF}}(\Phi) = \underbrace{\frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V^{\text{ne}} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{\text{Coulomb term}} \underbrace{- \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{\text{exchange term}}$$

$$V^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}, \quad \gamma_{\Phi}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r}) \phi_i(\mathbf{r}'), \quad \rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2.$$

Invariance property : if $\Phi \in (H^1(\mathbb{R}^3))^N$ satisfies the L^2 -orthonormality constraints, then so does ΦU for all $U \in O(N)$ and $E(\Phi U) = E(\Phi)$.

Theorem. Assume that $N \leq Z := \sum_{k=1}^M z_k$ (neutral or positively charged molecular system). Then

1. the HF model has a ground state $\Phi^0 = (\phi_1^0, \dots, \phi_N^0)$ (Lieb & Simon '77);
2. Euler-Lagrange equations : there exists $\lambda \in \mathbb{R}^{N \times N}$ symmetric such that

$$\left\{ \begin{array}{l} \Phi^0 = (\phi_1^0, \dots, \phi_N^0) \in (H^1(\mathbb{R}^3))^N \\ -\frac{1}{2}\Delta\phi_i^0 + V^{\text{ne}}\phi_i^0 + (\rho_{\Phi^0} \star |\cdot|^{-1})\phi_i^0 - \int_{\mathbb{R}^3} \frac{\gamma_{\Phi^0}(\cdot, \mathbf{r}')}{|\cdot - \mathbf{r}'|} \phi_i^0(\mathbf{r}') d\mathbf{r}' = \sum_{j=1}^N \lambda_{ij} \phi_j^0 \\ \int_{\mathbb{R}^3} \phi_i^0 \phi_j^0 = \delta_{ij}; \end{array} \right.$$

3. Elliptic regularity : $\phi_i^0 \in H^2(\mathbb{R}^3) \cap C^{0,1}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{\mathbf{R}_k\})$;

Theorem (continued).

4. Fock operator :

$$\mathcal{F}_{\Phi^0} := -\frac{1}{2}\Delta + V^{\text{ne}} + \rho_{\Phi^0} \star |\cdot|^{-1} + \mathcal{K}_{\Phi^0} \quad \text{where} \quad (\mathcal{K}_{\Phi^0} \phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{\gamma_{\Phi^0}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}'$$

is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$. It is bounded below and $\sigma_{\text{ess}}(H_0) = [0, +\infty)$;

5. Hartree-Fock equations : up to replacing Φ^0 by $\Phi^0 U$ for some $U \in O(N)$, it holds

$$\mathcal{F}_{\Phi^0} \phi_i^0 = \varepsilon_i \phi_i^0, \quad \int_{\mathbb{R}^3} \phi_i^0 \phi_j^0 = \delta_{ij}, \quad \varepsilon_1 \leq \dots \leq \varepsilon_N < 0;$$

6. *Aufbau* principle : $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$ are the lowest N eigenvalues of \mathcal{F}_{Φ^0} ;

7. No unfilled-shell property (Bach, Lieb, Loss, Solovej '94) : $\varepsilon_N < \varepsilon_{N+1}$ where ε_{N+1} is the $(N+1)^{\text{st}}$ eigenvalue of \mathcal{F}_{Φ^0} (counting multiplicities) if \mathcal{F}_{Φ^0} has at least $(N+1)$ negative eigenvalues and 0 otherwise.

3 - Discretization of the Hartree-Fock model

Galerkin Approximation

$\mathcal{X} = \text{Span}(\chi_1, \dots, \chi_{N_b})$ **subspace of** $H^1(\mathbb{R}^3)$ **of finite dimension** N_b .

$$E_0 \leq E_0^{\text{HF}} \leq E_{0,\mathcal{X}}^{\text{HF}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in \mathcal{X}^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\Phi = (\phi_1, \dots, \phi_N) \in \mathcal{X}^N \quad \Rightarrow \quad \phi_i(\mathbf{r}) = \sum_{\mu=1}^{N_b} C_{\mu i} \chi_{\mu}(\mathbf{r})$$

Discretized formulation of the Hartree-Fock model

$$E_{0,\mathcal{X}}^{\text{HF}} = \inf \{ E^{\text{HF}}(CC^T), \ C \in \mathbb{R}^{N_b \times N}, \ C^T SC = I_N \}$$

$$E^{\text{HF}}(D) = \text{Tr}(hD) + \frac{1}{2} \text{Tr}(G(D)D), \quad [G(D)]_{\mu\nu} = \sum_{\kappa\lambda} [(\mu\nu|\kappa\lambda) - (\mu\lambda|\kappa\nu)] D_{\kappa\lambda}$$

Electronic integrals

- **Overlap matrix :** $S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu$
- **Core Hamiltonian matrix :** $h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu - \sum_{k=1}^M z_k \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r}$
- **Two-electron integrals :** $(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\kappa(\mathbf{r}') \chi_\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$

Fundamental remark (Boys 1950) : if the χ_μ are gaussian-polynomials

$$\chi_\mu(\mathbf{r}) = p(\mathbf{r}) \exp(-\alpha|\mathbf{r}|^2)$$

then the one-electron integrals

$$S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu, \quad h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu + \int_{\mathbb{R}^3} V^{\text{ne}} \chi_\mu \chi_\nu$$

and the two-electron integrals

$$(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\kappa(\mathbf{r}') \chi_\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

can be computed analytically.

Atomic orbital basis sets

1. A collection $\{\xi_\mu^A\}_{1 \leq \mu \leq n_A}$ of n_A linearly independent linear combination of gaussian polynomials are associated with each chemical element A of the periodic table : these are the atomic orbitals of A .
2. To perform a calculation on a given chemical system, one builds a basis $\{\chi_\mu\}$ by putting together all the atomic orbitals related to all the atoms of the system.

Example of the water molecule H_2O

$$\{\chi_\mu\} = \left\{ \xi_1^H(\mathbf{r} - \mathbf{R}_{H_1}), \dots, \xi_{n_H}^H(\mathbf{r} - \mathbf{R}_{H_1}); \xi_1^H(\mathbf{r} - \mathbf{R}_{H_2}), \dots, \xi_{n_H}^H(\mathbf{r} - \mathbf{R}_{H_2}); \right. \\ \left. \xi_1^O(\mathbf{r} - \mathbf{R}_O), \dots, \xi_{n_O}^O(\mathbf{r} - \mathbf{R}_O) \right\},$$

where \mathbf{R}_{H_1} , \mathbf{R}_{H_2} and \mathbf{R}_O denote the positions in \mathbb{R}^3 of the Hydrogen nuclei and of the Oxygen nucleus respectively.

Molecular orbital formulation

For simplicity, the basis $\{\chi_\mu\}_{1 \leq \mu \leq N_b}$ is assumed to be orthonormal.

$$E_{0,\mathcal{C}}^{\text{HF}} = \inf \{ E^{\text{HF}}(CC^T), C \in \mathcal{C} \}$$

$$\mathcal{C} = \{ C \in \mathbb{R}^{N_b \times N}, C^T C = I_N \} \quad (\text{Stiefel manifold})$$

$$E^{\text{HF}}(D) = \text{Tr}(hD) + \frac{1}{2} \text{Tr}(G(D)D)$$

\uparrow
linear

\uparrow
quadratic

When C varies in the set

$$\mathcal{C} = \{C \in \mathbb{R}^{N_b \times N}, C^T C = I_N\},$$

$D = CC^T$ varies in the set

$$\mathcal{P} = \{D \in \mathbb{R}^{N_b \times N_b}, D = D^T, \text{Tr}(D) = N, D^2 = D\}$$

$= \{ \text{set of rank-}N \text{ orthogonal projectors} \}$ (Grassmann manifold)

Density matrix formulation

$$E_{0,\chi}^{\text{HF}} = \inf \{ E^{\text{HF}}(D), D \in P \}$$

$$E^{\text{HF}}(D) = \mathbf{Tr}(hD) + \frac{1}{2}\mathbf{Tr}(G(D)D)$$

\uparrow \uparrow
linear **quadratic**

$$\begin{aligned} \mathcal{P} &= \{ D \in \mathbb{R}^{N_b \times N_b}, D = D^T, \mathbf{Tr}(D) = N, D^2 = D \} \\ &= \{ \text{rank-}N \text{ orthogonal projectors} \} \end{aligned}$$

4 - SCF algorithms

Numerical simulations show that the (discretized) Hartree-Fock problem has **many local minima**.

Local optimization methods usually lead to local, non global, minima.

Most numerical methods aim at solving the associated Euler-Lagrange equation by a fixed point method.

Let us denote by $F(D) = h + G(D)$ the **Fock matrix**, i.e. the gradient of

$$E^{\text{HF}}(D) = \text{Tr}(hD) + \frac{1}{2}\text{Tr}(G(D)D).$$

Necessary conditions for D being a minimizer of the HF energy

$$\left\{ \begin{array}{l} F(D)\Phi_i = \varepsilon_i \Phi_i \\ \Phi_i^T \Phi_j = \delta_{ij} \\ \varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N \text{ are the lowest } N \text{ eigenvalues of } F(D) \\ D = \sum_{i=1}^N \Phi_i \Phi_i^T \end{array} \right.$$

Roothaan algorithm

$$\left\{ \begin{array}{l} F(D^{\textcolor{red}{k}}) \Phi_i^{\textcolor{red}{k}+1} = \varepsilon_i^{\textcolor{red}{k}+1} \Phi_i^{\textcolor{red}{k}+1} \\ \Phi_i^{\textcolor{red}{k}+1}{}^T \Phi_j^{\textcolor{red}{k}+1} = \delta_{ij} \\ \varepsilon_1^{\textcolor{red}{k}+1} \leq \varepsilon_2^{\textcolor{red}{k}+1} \leq \dots \leq \varepsilon_N^{\textcolor{red}{k}+1} \text{ are the lowest } N \text{ eigenvalues of } F(D^{\textcolor{red}{k}}) \\ D^{\textcolor{red}{k}+1} = \sum_{i=1}^N \Phi_i^{\textcolor{red}{k}+1} \Phi_i^{\textcolor{red}{k}+1}{}^T \end{array} \right.$$

Theorem. The sequence (D_k) generated by the Roothaan algorithm satisfies one of the following two properties :

- either (D_k) converges towards an *Aufbau* solution to the HF equations ;
- or (D_k) oscillates between two states, none of them being an *Aufbau* solution to the HF equations.

Calculations performed with the DIIS algorithm (Pulay 1982, default algorithm in several codes)

System	Energy of D^0 (Ha)	Energy at convergence (Ha)
$\text{CH}_3\text{-NH-CH=CH-NO}_2$ 6-31G	-374.0038 -322.2373	-375.3869 Does not CV
Cr_2 6-31G	-2069.5400 -2051.4339	-2085.5449 -2085.4042
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ 178 AO	-1700.7596 -1538.7283	-1717.8928 -1717.7355

Relaxed Constrained Algorithm

Replace the Hartree-Fock problem

$$\inf \{ E^{\text{HF}}(D), D \in \mathcal{P} \} \quad (1)$$

$$\mathcal{P} = \{ D \in \mathbb{R}^{N_b \times N_b}, D^T = D, \text{Tr}(D) = N, D^2 = D \}$$

by

$$\inf \{ E^{\text{HF}}(D), D \in \tilde{\mathcal{P}} \} \quad (2)$$

$$\tilde{\mathcal{P}} = \{ D \in \mathbb{R}^{N_b \times N_b}, D^T = D, \text{Tr}(D) = N, D^2 \leq D \}$$

Fundamental property : (1) and (2) have the same local minima
(discrete counterpart of Lieb's variational principle, Lieb '81).

What is gained : the set $\tilde{\mathcal{P}}$ is convex

Proof. Assume that $\tilde{\tilde{D}}$ is a minimizer of E^{HF} on $\tilde{\mathcal{P}}$ that does not verify the constraint $\tilde{\tilde{D}}^2 = \tilde{D}$.

The optimality conditions lead to

$$\tilde{\tilde{D}} = \sum_{\varepsilon_i < \varepsilon_F} \Phi_i \Phi_i^T + \sum_{\varepsilon_j = \varepsilon_F} n_j \Phi_j \Phi_j^T \quad \text{with } 0 \leq n_j \leq 1.$$

Let Φ and Φ' two partially occupied orbitals ($0 < n, n' < 1$). By transferring $0 < \delta n \ll 1$ electron from Φ to Φ' , one obtains

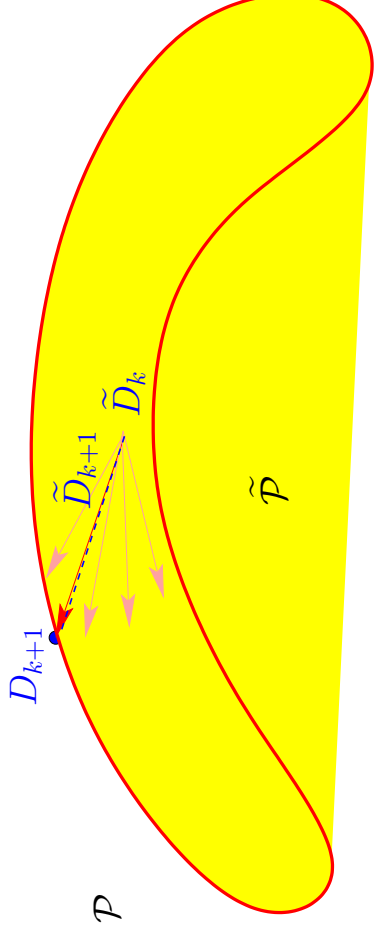
$$\tilde{\tilde{D}}' = \tilde{\tilde{D}} + \delta n \left(\Phi' \Phi'^T - \Phi \Phi^T \right) \in \tilde{\mathcal{P}}$$

and

$$\Delta E = E^{\text{HF}}(\tilde{\tilde{D}}') - E^{\text{HF}}(\tilde{\tilde{D}}) = -\frac{\delta n^2}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\phi(\mathbf{r}) \phi'(\mathbf{r}') - \phi(\mathbf{r}') \phi'(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' < 0,$$

$$\text{where } \phi(\mathbf{r}) = \sum_{\mu=1}^{N_b} \Phi_{\mu} \chi_{\mu}(\mathbf{r}) \text{ and } \phi'(\mathbf{r}) = \sum_{\mu=1}^{N_b} \Phi'_{\mu} \chi_{\mu}(\mathbf{r}).$$

Optimal Damping Algorithm (ODA)



“Optimal step gradient” :

1. Calculation of a descent direction $d = D^{k+1} - \tilde{D}^k$ **where**

$$D^{k+1} = \mathbf{arginf} \left\{ \frac{d}{d\lambda} E \left(\tilde{D}^k + \lambda(\tilde{D} - \tilde{D}^k) \right) \Big|_{\lambda=0}, \tilde{D} \in \tilde{\mathcal{P}} \right\} ;$$

2. Line search : **set** $\tilde{D}^{k+1} = \mathbf{arginf} \left\{ E(\tilde{D}), \tilde{D} \in \mathbf{Seg}[\tilde{D}^k, D^{k+1}] \right\}$ **where**

$$\mathbf{Seg}[\tilde{D}^k, D^{k+1}] = \left\{ (1 - \lambda)\tilde{D}^k + \lambda D^{k+1}, \lambda \in [0, 1] \right\}.$$

ODA steepest descent calculation

$$\begin{aligned}
 D^{k+1} &= \mathbf{arginf} \left\{ \frac{d}{d\lambda} E^{\text{HF}} \left(\tilde{D}^k + \lambda(\tilde{D} - \tilde{D}^k) \right) \right\}_{\lambda=0}, \quad \tilde{D} \in \tilde{\mathcal{P}} \} \\
 &= \mathbf{arginf} \left\{ \mathbf{Tr}(F(\tilde{D}^k)D), \quad D \in \mathcal{P} \right\}
 \end{aligned}$$

$$\left\{ \begin{array}{l}
 D^{k+1} = \sum_{i=1}^N \Phi_i^{k+1} \Phi_i^{k+1} T \\
 F(\tilde{D}^k) \Phi_i^{k+1} = \varepsilon_i^{k+1} \Phi_i^{k+1} \\
 \Phi_i^{k+1} T \Phi_j^{k+1} = \delta_{ij} \\
 \varepsilon_1^{k+1} \leq \varepsilon_2^{k+1} \leq \dots \leq \varepsilon_N^{k+1} \text{ are the lowest } N \text{ eigenvalues of } F(\tilde{D}^k)
 \end{array} \right.$$

Comparison between DIIS (default algorithm in Gaussian 98) and ODA (default algorithm in Gaussian 03).

System	$E^{RHF}(D_0)$	DIIS (Ha)	ODA (Ha)	ΔE (kcal/mol)
CH ₃ -NH-CH=CH-NO ₂ 6-31G	-374.0038	-375.3869	-375.3869	0
	-322.2373	Does not CV	-375.3869	-
Cr ₂ 6-31G	-2069.5400	-2085.5449	-2085.8060	163.71
	-2051.4339	-2085.4042	-2085.8060	251.93
[Fe(H ₂ O) ₆] ²⁺ 178 AO	-1700.7596	-1717.8928	-1718.0151	76.68
	-1538.7283	-1717.7355	-1718.0151	175.31

5 - Limitations of the Hartree-Fock method

Correlation energy

$$E_{\text{correlation}} := E_0^{\text{HF}} - E_0 \geq 0.$$

Three situations may occur :

1. Hartree-Fock is accurate enough for the purpose of the study
2. Hartree-Fock is not accurate enough but the N -body ground state can be correctly approximated by a “small” number of Slater determinants

Non dynamical correlation \Rightarrow **Multiconfigurations or DFT**

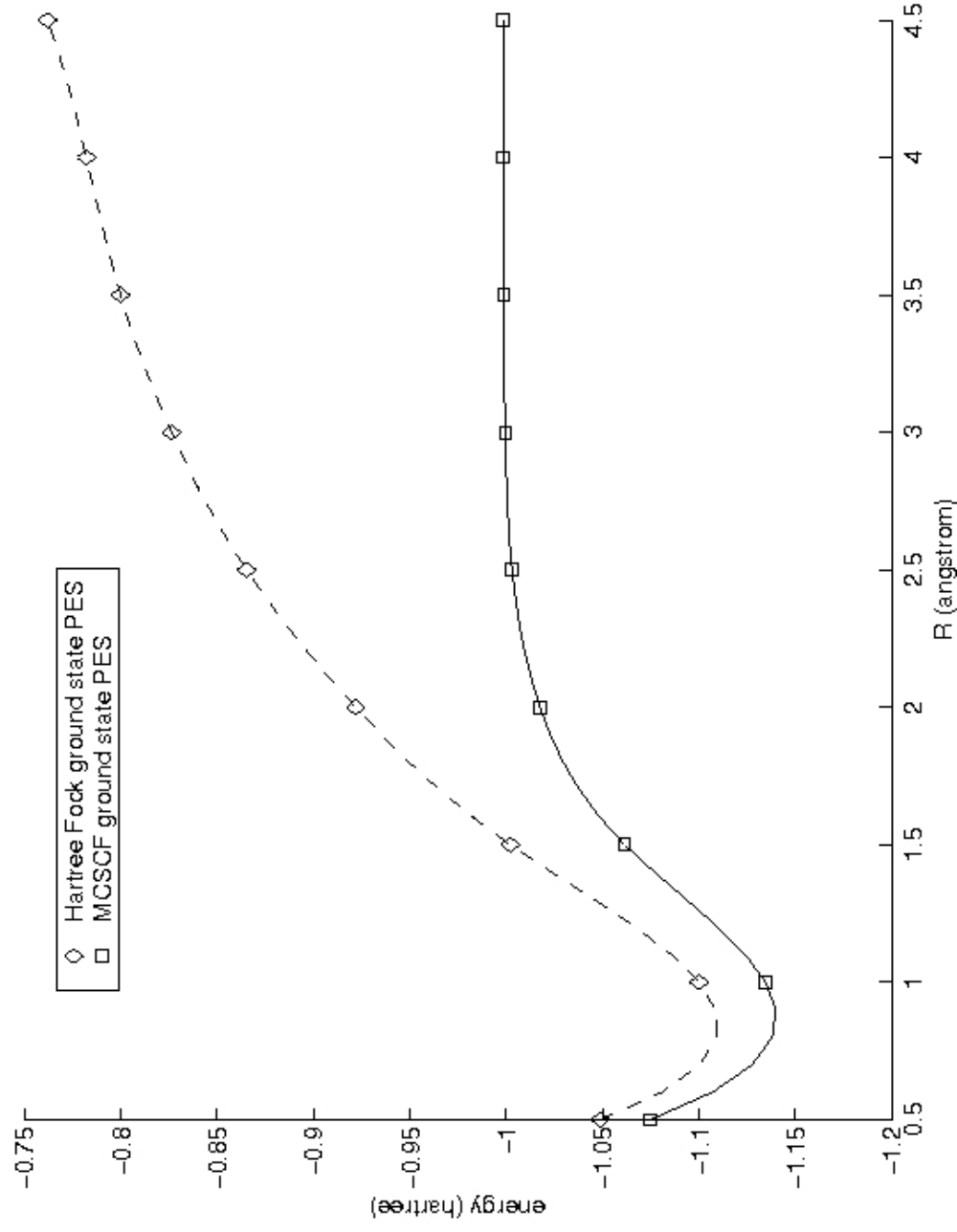
3. The ground state cannot be correctly approximated by a “small” number of Slater determinants

Dynamical correlation \Rightarrow **Quantum Monte Carlo or DFT**

Example when the Hartree-Fock approximation works well :

System	Bulk modulus HF	Bulk modulus exp.	Relative error
Al_2O_3	287	261	+10 %
BeO	253	224	+12 %
MgAl_2O_4	227	206	+10 %
MgO	186	167	+11.4 %
CaO	128	120	+6.7 %
MgCO_3	125	117	+6.8 %
CaCO_3	75.3	79.9	-5.8 %

Example of non-dynamical correlation : dissociation of H_2



Example of dynamical correlation : CuCl₂ (Daudéy et al., 2005)

Transition between two electronic states : $X^2\Pi_g - ^2\Delta_g$

Method	Number of config.	Wavenumber in cm ⁻¹
Hartree-Fock	1	5273
CASSCF(21,14)	22 920	5984
CASSCF(21,14) + ACPF	39 337 683	6910
Exp.		7130/7753/7780/7893

The Hartree-Fock problem is now well understood from both theoretical and numerical viewpoints.

- **Theoretical foundations (1977-1994) : V. Bach, E.H. Lieb, P.-L. Lions, M. Loss, B. Simon, J.-P. Solovej, ...**
- **Numerical analysis (1999-2013) : E.C., C. Le Bris, A. Levitt, Y. Maday, G. Turinici, ...**

The simulation of very large molecular systems still is an active field of research.