

# Introduction to Quantum Chemistry and ab initio calculations of interatomic potentials

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## 1 - Modelling

- Ab initio interatomic potentials
- Hartree-Fock model
- Density Functional Theory (DFT)
- Kohn-Sham model

## 2 - Numerical issues

- Discretization in atomic orbital basis sets
- Algorithms (prelude to Yousef Saad's lectures)
- Analytical derivatives

## 3 - A few words about spin

# 1 - Modelling

**Atomic units:**  $\hbar = 1$ ,  $m_e = 1$ ,  $e = 1$ ,  $\frac{1}{4\pi\epsilon_0} = 1$

**Length unit:**  $a_0 \simeq 0.529 \times 10^{-10}$  m (Bohr radius)

**Energy unit:** 1 Ha (Hartree)  $\simeq 27.2$  eV  $\simeq 627$  kcal/mol

## Functional spaces

$$L^2(\mathbb{R}^d) = \left\{ \phi : \mathbb{R}^d \longrightarrow \mathbb{R} \quad | \quad \|\phi\|_{L^2}^2 = \int_{\mathbb{R}^d} |\phi|^2 < \infty \right\}$$

$$H^1(\mathbb{R}^d) = \{ \phi \in L^2(\mathbb{R}^d) \quad | \quad \nabla\phi \in (L^2(\mathbb{R}^d))^d \}$$

$$\bigwedge_{i=1}^N L^2(\mathbb{R}^3) = \{ \psi \in L^2(\mathbb{R}^{3N}) \quad | \quad \psi(x_{p(1)}, \dots, x_{p(N)}) = \varepsilon(p) \psi(x_1, \dots, x_N) \}$$

$$\bigwedge_{i=1}^N H^1(\mathbb{R}^3) = H^1(\mathbb{R}^{3N}) \cap \left( \bigwedge_{i=1}^N L^2(\mathbb{R}^3) \right)$$

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In the absence of nuclear reactions, matter can be described as an assembly of quantum nuclei and electrons interacting through the Coulomb potential: **No empirical parameters!**

Electrons: mass  $m_e = 1$ , charge  $-1$ ,

Nucleus  $k$  : mass  $1836 \leq m_k \leq 400\,000$ , charge  $z_k \in \mathbb{N}^*$

$$m_k \gg m_e = 1$$



$\left\{ \begin{array}{l} \text{nuclei} \stackrel{\text{most often}}{\simeq} \text{classical point-like particles} \\ \text{electrons} = \text{quantum delocalized particles} \end{array} \right.$

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Born-Oppenheimer approximation ( $M$  nuclei and  $N$  electrons)

$M + N$ -body time-dependent Schrödinger equation (nuclei + electrons)

Extremely accurate model - No empirical parameters - Intractable

$$\text{Adiabatic limit} \quad \Downarrow \quad \varepsilon = \left( \frac{m_e}{m_{\text{nuc}}} \right)^{1/2} \rightarrow 0$$

$M$ -body time-dependent Schrödinger equation (nuclei only)

Effective potential  $W(\bar{x}_1, \dots, \bar{x}_M)$

$$\text{Semiclassical limit} \quad \Downarrow \quad \hbar \rightarrow 0$$

Classical Hamiltonian dynamics (point-like nuclei)

Same effective potential  $W(\bar{x}_1, \dots, \bar{x}_M)$

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## Ab initio molecular dynamics

Nuclear positions and momenta:  $(\{\bar{x}_k(t)\}, \{\bar{p}_k(t)\}) \in \mathbb{R}^{3M} \times \mathbb{R}^{3M}$

$$\begin{cases} \frac{d\bar{x}_k}{dt}(t) = \frac{\partial H_{\text{nuc}}}{\partial \bar{p}_k} = \frac{\bar{p}_k(t)}{m_k} \\ \frac{d\bar{p}_k}{dt}(t) = -\frac{\partial H_{\text{nuc}}}{\partial \bar{x}_k} = -\nabla_{\bar{x}_k} W(\{\bar{x}_l(t)\}, \{\bar{p}_l(t)\}) \end{cases}$$

$$H_{\text{nuc}}(\{\bar{x}_k\}, \{\bar{p}_k\}) = \sum_{k=1}^M \frac{|\bar{p}_k|^2}{2 m_k} + W(\bar{x}_1, \dots, \bar{x}_M)$$

$W(\bar{x}_1, \dots, \bar{x}_M)$  effective potential (free of empirical parameters)

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 Effective interatomic potential (singlet spin state)

$$W(\bar{x}_1, \dots, \bar{x}_M) = E_0(H_N^{\{\bar{x}_k\}}) + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\bar{x}_k - \bar{x}_l|}$$

$$H_N^{\{\bar{x}_k\}} = - \sum_{i=1}^N \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \bar{x}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \quad \text{on} \quad \bigwedge_{i=1}^N L^2(\mathbb{R}^3)$$

Spectrum of the electronic Hamiltonian  $H_N^{\{\bar{x}_k\}}$  for neutral molecules and positive ions (Zhislin theorem)

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

$$H_N^{\{\bar{x}_k\}} \psi = E \psi$$

$$\psi(x_{p(1)}, \dots, x_{p(N)}) = \varepsilon(p) \psi(x_1, \dots, x_N)$$



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### Strengths of the model:

- allows to simulate a wide variety of phenomena
- does not contain any parameter specific to the system
- is extremely accurate

Ionization energy of Helium (Korobov & Yelkhovsky PRL 2001)

- calculations: 5 945 262 288 MHz, 5 945 204 223 MHz with RC
- exp.: 5 945 204 238 MHz (1997), 5 945 204 356 MHz (1998)

### Weaknesses of the model:

- PDE (spectral problem) set in  $\mathbb{R}^{3N}$
- Chemical accuracy is required

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### Chemical accuracy:

energy of a C atom :  $\sim 100$  Ha

energy of a H atom : 0.5 Ha

energy of a covalent bond :  $\sim 0.15$  Ha (100 kcal/mol)

electronic excitation energy :  $\sim 0.03$  Ha (1 eV)

$k_B T$  at room temperature :  $\sim 0.001$  Ha (1/40 eV)

van der Waals characteristic energy :  $\sim 0.0003$  Ha (0.2 kcal/mol)

spectroscopic accuracy :  $\sim 0.000005$  Ha ( $1 \text{ cm}^{-1}$ )

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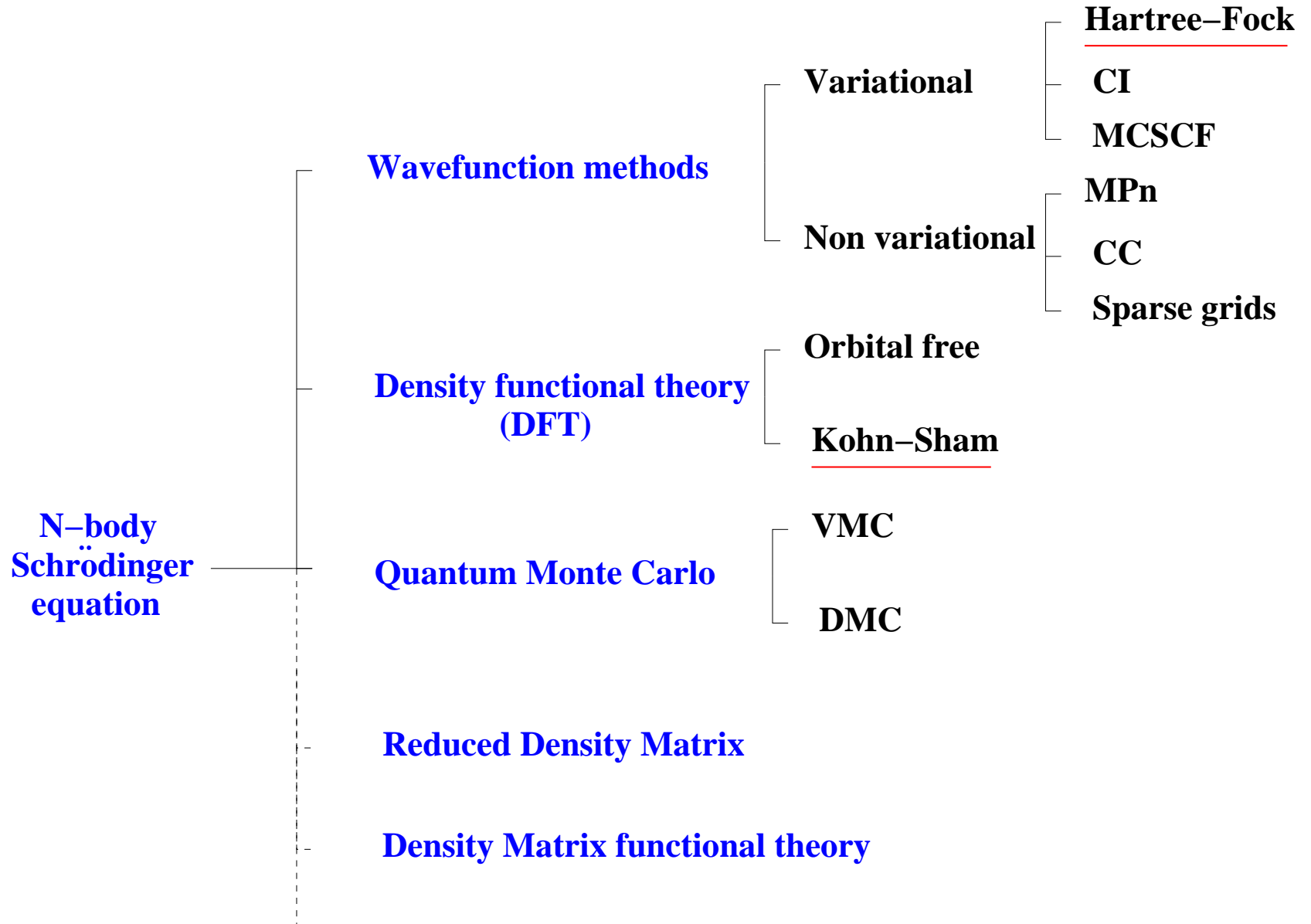
### Ab initio simulations in 2007

A few atoms (small organic molecules): spectroscopic accuracy

A few dozens of first- or second-row atoms: chemical accuracy

Several hundreds / a few thousands of atoms: qualitative results

W.R.(?): 1.4 million-atom DFT simulation on  $1.2 \times 10^{11}$  grid points  
(A. Nakano et al. 2006)



From now on, the positions  $\{\bar{x}_k\}$  of the nuclei are considered as fixed.

In order to simplify the notation, we set

$$V_{\text{nuc}}(\boldsymbol{x}) = - \sum_{k=1}^M \frac{z_k}{|\boldsymbol{x} - \bar{\boldsymbol{x}}_k|}$$

and

$$H_N = - \sum_{i=1}^N \frac{1}{2} \Delta_{x_i} + \sum_{i=1}^N V_{\text{nuc}}(x_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$$

The problem is now to compute the lowest eigenvalue  $E_0$  of  $H_N$  operating on  $\bigwedge_{i=1}^N L^2(\mathbb{R}^3)$ . The variational characterization of  $E_0$  reads

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

## Hartree-Fock approximation

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

The HF method is variational: the **exact** energy  $\langle \psi | H_N | \psi \rangle$  is minimized on the **subset of  $\mathcal{W}_N$**  consisting of **Slater determinants**

$$\left\{ \psi = \phi_1 \wedge \cdots \wedge \phi_N, \quad \phi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$(\phi_1 \wedge \cdots \wedge \phi_N)(x_1, \cdots, x_N) \stackrel{\text{def}}{=} \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix}$$

Rewriting the minimization problem in terms of  $\Phi = \{\phi_i\}$ , one obtains

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

$$\begin{aligned} E^{\text{HF}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V_{\text{nuc}} \\ &\quad + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(x) \rho_{\Phi}(y)}{|x-y|} dx dy - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(x, y)|^2}{|x-y|} dx dy \end{aligned}$$

$$V_{\text{nuc}}(x) = - \sum_{k=1}^M \frac{z_k}{|x - \bar{x}_k|}, \quad \gamma_{\Phi}(x, y) = \sum_{i=1}^N \phi_i(x) \phi_i(y), \quad \rho_{\Phi}(x) = \sum_{i=1}^N |\phi_i(x)|^2$$

Existence of a minimizer of the HF problem for neutral systems and positive ions: Lieb-Simon (1977), see also P.-L. Lions (1987)

kinetic energy



nuclear-electron interaction



$$E^{\text{HF}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V_{\text{nuc}}$$

$$+ \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(x) \rho_{\Phi}(y)}{|x-y|} dx dy - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(x, y)|^2}{|x-y|} dx dy$$



Coulomb electronic energy



(exact) exchange

$$\sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 = \sum_{i=1}^N \int_{\mathbb{R}^3} (-\Delta \phi_i) \phi_i = - \int_{\mathbb{R}^3} \Delta_x \gamma_{\Phi}(x, y) |_{y=x} dx = \mathbf{Tr}(-\Delta \gamma_{\Phi})$$

$$E^{\text{HF}}(\Phi) = \mathcal{E}^{\text{HF}}(\gamma_{\Phi})$$



Hartree-Fock equations (Euler-Lagrange + invariance + loc. min.)

$$\left\{ \begin{array}{l} -\frac{1}{2}\Delta\phi_i + \mathcal{W}_\Phi\phi_i = \varepsilon_i\phi_i \quad 1 \leq i \leq N \\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \quad 1 \leq i, j \leq N \\ \varepsilon_1 \leq \varepsilon_2 \leq \cdots \leq \varepsilon_N \quad \text{are the lowest } N \text{ eigenvalues of } -\frac{1}{2}\Delta + \mathcal{W}_\Phi \end{array} \right.$$

**Nonlinear eigenvalue problem**

$$\mathcal{W}_\Phi\phi = \left( V_{\text{nuc}} + \rho_\Phi \star \frac{1}{|x|} \right) \phi - \int_{\mathbb{R}^3} \frac{\gamma_\Phi(\cdot, y)}{|\cdot - y|} \phi(y) dy$$

No unfilled shell property (Bach, Lieb, Loss, Solovej):  $\varepsilon_N < \varepsilon_{N+1}$

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### Limitations of the Hartree-Fock method

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

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  $\Rightarrow$  DFT or Quantum Monte Carlo**

## Hohenberg-Kohn splitting of the electronic Hamiltonian

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

$$H_N = H_N^0 + \sum_{i=1}^N V_{\text{nuc}}(\mathbf{x}_i)$$

$$H_N^0 = - \sum_{i=1}^N \frac{1}{2} \Delta_{x_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}, \quad V_{\text{nuc}}(\mathbf{x}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{x} - \bar{\mathbf{x}}_k|}$$

### Electronic density

$$\psi \in \mathcal{W}_N \quad \mapsto \quad \rho_\psi(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(\mathbf{x}, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N$$

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**Levy-Lieb constrained search approach**

$$\begin{aligned} E_0 &= \inf_{\psi} \langle \psi | H_N | \psi \rangle \\ &= \inf_{\psi} \left( \langle \psi | H_N^0 | \psi \rangle + \langle \psi | \left( \sum_{i=1}^N V_{\text{nuc}}(x_i) \right) | \psi \rangle \right) \\ &= \inf_{\psi} \left( \langle \psi | H_N^0 | \psi \rangle + \int_{\mathbb{R}^3} \rho_{\psi} V_{\text{nuc}} \right) \\ &= \inf_{\rho} \inf_{\psi | \rho_{\psi} = \rho} \left( \langle \psi | H_N^0 | \psi \rangle + \int_{\mathbb{R}^3} \rho V_{\text{nuc}} \right) \\ &= \inf_{\rho} \left( F_{\text{LL}}^N(\rho) + \int_{\mathbb{R}^3} \rho V_{\text{nuc}} \right) \end{aligned}$$

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## Levy-Lieb functional

$$E_0 = \inf \left\{ F_{\text{LL}}^N(\rho) + \int_{\mathbb{R}^3} \rho V_{\text{nuc}}, \quad \rho \in \mathcal{R}_{\text{LL}}^N \right\}$$

$$F_{\text{LL}}^N(\rho) = \inf \left\{ \langle \psi | H_N^0 | \psi \rangle, \quad \psi \in \mathcal{W}_N \text{ s.t. } \rho_\psi = \rho \right\}$$

$$\mathcal{R}_{\text{LL}}^N = \left\{ \rho, \quad \exists \psi \in \mathcal{W}_N \text{ s.t. } \rho_\psi = \rho \right\} = \left\{ \rho \geq 0, \quad \sqrt{\rho} \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \rho = N \right\}$$

$F_{\text{LL}}^N(\rho)$  is a “universal” functional of the density

**Problem:** no easy-to-compute expression of  $F_{\text{LL}}^N(\rho)$  is known.

1. For  $N$  *non interacting* electrons, the density functional is (approximately) given by

$$T_{\text{KS}}^N(\rho) = \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \quad \phi_i \in H^1(\mathbb{R}^3) \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \quad \sum_{i=1}^N |\phi_i|^2 = \rho \right\}$$

2. For a classical charge distribution of density  $\rho$ , the Coulomb interaction reads

$$J(\rho) \stackrel{\text{def}}{=} \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(y)}{|x - y|} dx dy$$

3. Kohn and Sham proposed the following decomposition of  $F_{\text{LL}}^N$

$$F_{\text{LL}}^N(\rho) = T_{\text{KS}}^N(\rho) + J(\rho) + E_{xc}(\rho) \quad \text{where} \quad E_{xc}(\rho) \stackrel{\text{def}}{=} F_{\text{LL}}^N(\rho) - T_{\text{KS}}^N(\rho) - J(\rho)$$

$E_{xc}$  is called the **exchange-correlation functional**

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## Exchange-correlation functional

$$|E_{\text{xc}}(\rho)| \ll J(\rho) \text{ and } T_{\text{KS}}^N(\rho)$$

A possible approximation of  $E_{\text{xc}}(\rho)$  is

$$E_{\text{xc}}^{\text{LDA}}(\rho) = \int_{\mathbb{R}^3} e_{\text{xc}}(\rho(x)) dx$$

where  $e_{\text{xc}}(\bar{\rho})$  is the exchange-correlation energy density in a homogeneous electron gas of density  $\bar{\rho}$

→ **Local Density Approximation (LDA)**

The function  $e_{\text{xc}} : \mathbb{R}_+ \rightarrow \mathbb{R}$  is obtained by interpolation of benchmark Quantum Monte Carlo calculations on the homogeneous electron gas

Rewriting the minimization problem in terms of  $\Phi = \{\phi_i\}$ , one obtains

$$E_0 \simeq \inf \left\{ E^{\text{KS}}(\Phi), \quad \Phi = \{\phi_i\} \in (H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\begin{aligned} E^{\text{KS}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V_{\text{nuc}} \\ &\quad + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(x) \rho_{\Phi}(y)}{|x-y|} dx dy + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(x)) dx \end{aligned}$$

with

$$V_{\text{nuc}} = - \sum_{k=1}^M \frac{z_k}{|\cdot - \bar{x}_k|} \quad \rho_{\Phi}(x) = \sum_{i=1}^N |\phi_i(x)|^2$$



Although obtained by totally different approaches, **Hartree-Fock** and **Kohn-Sham LDA** models have **similar mathematical structures**

Hartree-Fock

Kohn-Sham LDA

$$E_0 \underset{\simeq}{\lesssim} \inf \{ E^{\text{HF}}(\Phi), \quad \Phi \in \mathcal{S} \}$$

$$E_0 \simeq \inf \{ E^{\text{KS}}(\Phi), \quad \Phi \in \mathcal{S} \}$$

$$E^{\text{HF}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V_{\text{nuc}} + J(\rho_{\Phi}) - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(x, y)|^2}{|x - y|} dx dy$$

$$E^{\text{KS}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V_{\text{nuc}} + J(\rho_{\Phi}) + \int_{\mathbb{R}^3} \varepsilon_{\text{xc}}(\rho_{\Phi}(x)) dx$$

$$\mathcal{S} = \left\{ \Phi = \{ \phi_i \} \in (H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

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LDA can be improved (on average) by taking into account

- the local inhomogeneities of  $\rho$  through the gradient of  $\rho$

$$E_{\text{xc}}^{\text{GGA}}(\Phi) = \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(x), \nabla \rho_{\Phi}(x)) dx$$

→ **Generalized Gradient Approximation (GGA)**

- the nonlocality of the exact functional through the kinetic energy density of the Kohn-Sham orbitals

$$E_{\text{xc}}^{\text{meta-GGA}}(\Phi) = \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(x), \nabla \rho_{\Phi}(x), \tau_{\Phi}(x)) dx, \quad \tau_{\Phi}(x) = \frac{1}{2} \sum_{i=1}^N |\nabla \phi_i(x)|^2$$

→ **meta-GGA**

- some exact-exchange contribution

$$E_{\text{xc}}^{\text{hybrid}}(\Phi) = \int_{\mathbb{R}^3} e_{\text{xc}}^{\text{local}}(\rho_{\Phi}(x), \nabla \rho_{\Phi}(x), \tau_{\Phi}(x)) dx - \frac{\lambda}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(x, y)|^2}{|x - y|} dx dy$$

→ **Hybrid functionals**

## Self interaction in DFT

For one electron systems ( $\rho_{\phi}(x) = |\phi(x)|^2$ )

$$E^{\text{HF}}(\phi) = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2 + \int_{\mathbb{R}^3} \rho_{\phi} V_{\text{nuc}}$$

$$E^{\text{KS}}(\phi) = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2 + \int_{\mathbb{R}^3} \rho_{\phi} V_{\text{nuc}} + J(\rho_{\phi}) + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\phi}(x), \nabla \rho_{\Phi}(x), \tau_{\Phi}(x)) dx$$

For one-electron systems, the Hartree-Fock energy coincide with the exact (Schrödinger) energy, while the Kohn-Sham energy does not

## Jacob's ladder (Perdew)

Heaven	Exact exchange–correlation functional
Rung 5	explicit functionals of the Kohn-Sham occupied and unoccupied orbitals SAOP, ...
Rung 4	explicit functionals of the density matrix (ex: hybrid functionals) 1/2 & 1/2, B3P, B3LYP, PBE0, O3LYP, X3LYP, mPW1PW91, BMK, PWB6K, B1B95, PW6B95, TPSSh, M05,
Rung 3	meta-GGA (explicit in $\rho(x)$ , $\nabla\rho(x)$ and $\tau(x) = \sum_{i=1}^N  \nabla\phi_i(x) ^2$ ) BR89, tauPBE, VSXC, BB95, TPSS, PBS00, LAP, ...
Rung 2	GGA (explicit in $\rho(x)$ and $\nabla\rho(x)$ ) SIC, PW91, BLYP, mPWPW91, PBE, revPBE, G96LYP, HCTH, OPTX, EDF1, ...
Rung 1	LDA (explicit in $\rho(x)$ )
Earth	

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Exchange-correlation functionals are usually split as follows

$$E_{xc} = E_x + E_c$$

$E_x$ : exchange functional, local approximation of the Hartree-Fock exchange energy

$$E_x^{\text{LDA}}(\Phi) = -C_x \int_{\mathbb{R}^3} \rho_\Phi(x)^{4/3} dx$$

$$E_x^{\text{GGA,PBE}}(\Phi) = -C_x \int_{\mathbb{R}^3} \rho_\Phi(x)^{4/3} \left( 1 + \frac{b s_\Phi(x)^2}{1 + a s_\Phi(x)^2} \right) dx, \quad s_\Phi(x) = \frac{|\nabla \rho_\Phi(x)|}{\rho_\Phi(x)^{4/3}}$$

$E_c$ : correlation functional

ugly multiline analytical formulas ...

## 2 - Numerical issues

## Discretization of the Hartree-Fock and Kohn-Sham models

	Molecules, clusters Implicit solvent	Crystalline materials Periodic systems
Atomic orbitals (variational)	Gaussian, Gamess, Molpro, Dalton, QChem, Jaguar, ADF (Slater AO), ...	Crystal, Gaussian, Siesta (numerical AO)
Planewaves (variational)	<i>irrelevant</i>	PWSCF (Quantum espresso), Abinit, Castep, CPMD, Onetep, Vasp, ...
Grid methods (non variational)	Parsec (Talk by Y. Saad), Talk by J.-L Fattebert	Parsec
Wavelets (variational)	Bigdft (Talk by S. Goedecker)	Bigdft

## Galerkin variational approximation

$\chi = \{\chi_\mu\}_{1 \leq \mu \leq N_b}$  basis of a finite dimensional subset of  $H^1(\mathbb{R}^3)$ .

$$E_0^{\text{HF}} \underset{\approx}{\leq} E_0^{\text{HF},\chi} = \inf \{ E^{\text{HF}}(\Phi), \quad \Phi \in \mathcal{S}_\chi \}$$

$$\mathcal{S}_\chi = \left\{ \Phi = \{\phi_i\} \in (H^1(\mathbb{R}^3))^N, \quad \phi_i(x) = \sum_{\mu=1}^{N_b} C_{\mu i} \chi_\mu(x), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\gamma_\Phi(x, y) = \sum_{i=1}^N \phi_i(x) \phi_i(y) = \sum_{i,j=1}^N [CC^T]_{\mu\nu} \chi_\mu(x) \chi_\nu(y)$$



## Discretized formulation of the HF problem

$$E_0^{\text{HF},\chi} = \inf \{ E^{\text{HF}}(CC^T), \quad C \in \mathcal{M}(N_b, N), \quad C^T SC = I_N \}$$

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

## Electronic integrals

- Overlap integrals:  $S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu$
- Monoelectronic integrals :  $h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu + \int_{\mathbb{R}^3} V_{\text{nuc}} \chi_\mu \chi_\nu$
- Bielectronic integrals:  $(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(x) \chi_\nu(x) \chi_\kappa(x') \chi_\lambda(x')}{|x - x'|} dx dx'$

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**Fundamental remark (Boys 1950):** if the  $\chi_\mu$  are **gaussian-polynomials**

$$\chi_\mu(x) = p_\mu(x) \exp(-\alpha_\mu |x - x_\mu|^2) \quad p_\mu \text{ polynomial}$$

then the *monoelectronic integrals*

$$S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu, \quad h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu - \sum_{k=1}^M z_k \int_{\mathbb{R}^3} \frac{\chi_\mu(x) \chi_\nu(x)}{|x - \bar{x}_k|}$$

and the *bielectronic integrals*

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

can be computed analytically

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## Gaussian atomic orbital basis sets

1. A collection  $\{\xi_\mu^A\}_{1 \leq \mu \leq n_A}$  of  $n_A$  linearly independent contracted 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 $\text{H}_2\text{O}$

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

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

$$\begin{aligned}
E_0^{HF} \leq E_0^{\text{HF disc}} &= \inf \{ E^{HF}(CC^T), \quad C \in \mathcal{C}_N \} \\
&= \inf \{ E^{HF}(D), \quad D \in \mathcal{P}_N \} \\
&\stackrel{(\text{Lieb})}{=} \inf \{ E^{HF}(D), \quad D \in \tilde{\mathcal{P}}_N \}
\end{aligned}$$

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

↑
↑  
**linear**
**quadratic**

$$\begin{aligned}
\mathcal{C}_N &= \{ C \in \mathbb{R}^{N_b \times N}, \quad C^T S C = I_N \} \\
\mathcal{P}_N &= \{ D \in \mathbb{R}^{N_b \times N_b}, \quad D^T = D, \quad D S D = D, \quad \text{Tr}(S D) = N \} \\
\tilde{\mathcal{P}}_N &= \{ D \in \mathbb{R}^{N_b \times N_b}, \quad D^T = D, \quad D S D \leq D, \quad \text{Tr}(S D) = N \}
\end{aligned}$$

We denote by  $F(D) = h + G(D)$  the **Fock matrix**, i.e. the gradient of  $E^{HF}(D) = \text{Tr}(hD) + \frac{1}{2}\text{Tr}(G(D)D)$  for the Frobenius inner product.

Necessary conditions for  $D$  being a local minimum of the HF problem

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

**Nonlinear generalized eigenvalue problem**

Discrete no unfilled shell property:  $\varepsilon_N < \varepsilon_{N+1}$

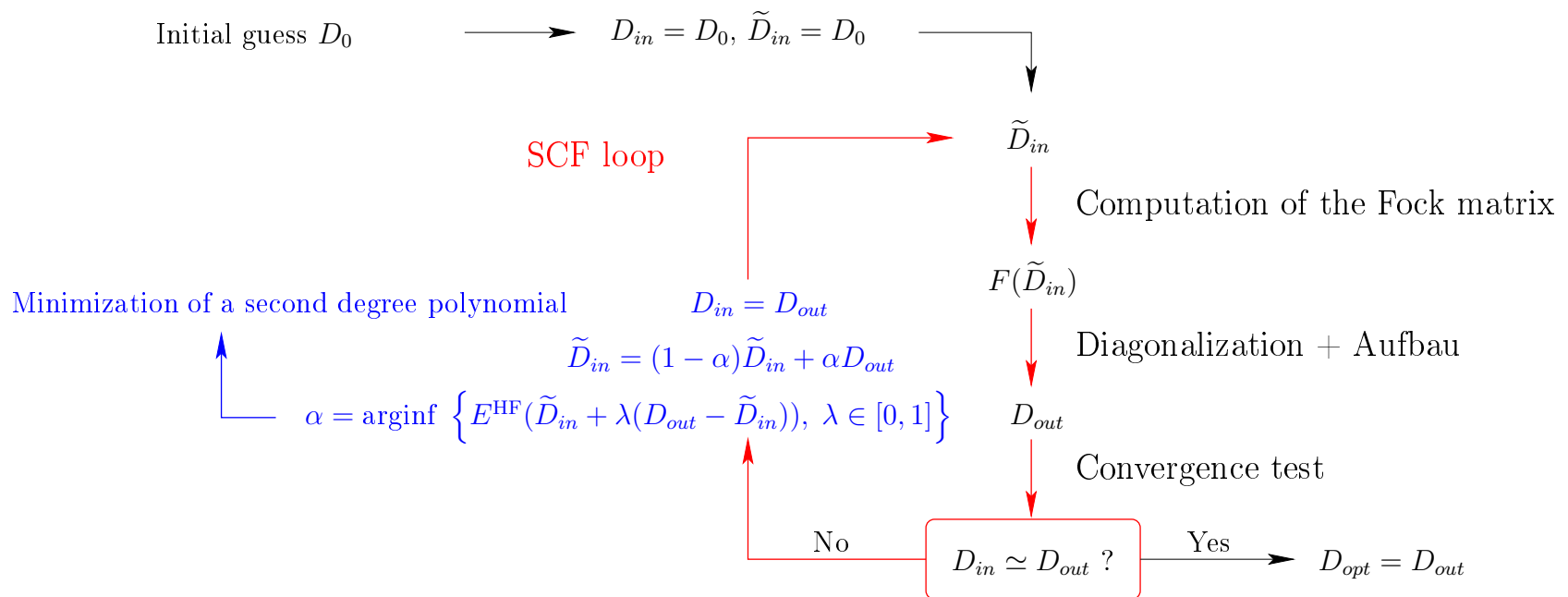
## Roothaan algorithm

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

**Theorem.** (E. C. and C. Le Bris, M2AN 2000) *The sequence  $(D_k^{Rth})$  generated by the Roothaan algorithm satisfies one of the following two properties*

- *either  $(D_k^{Rth})$  converges toward a solution to the HF equations*
- *or  $(D_k^{Rth})$  oscillates between two states, none of them being solution to the HF equations*

Optimal damping algorithm (E.C. and C. Le Bris, IJQC 2000)



**Theorem.** The sequence  $(E^{\text{HF}}(\tilde{D}_k))$  generated by the ODA algorithm monotonically decreases to a critical value  $I$  of the HF problem. Both  $(D_k)$  and  $(\tilde{D}_k)$  “numerically” converge to a critical point of the HF problem with energy  $I$

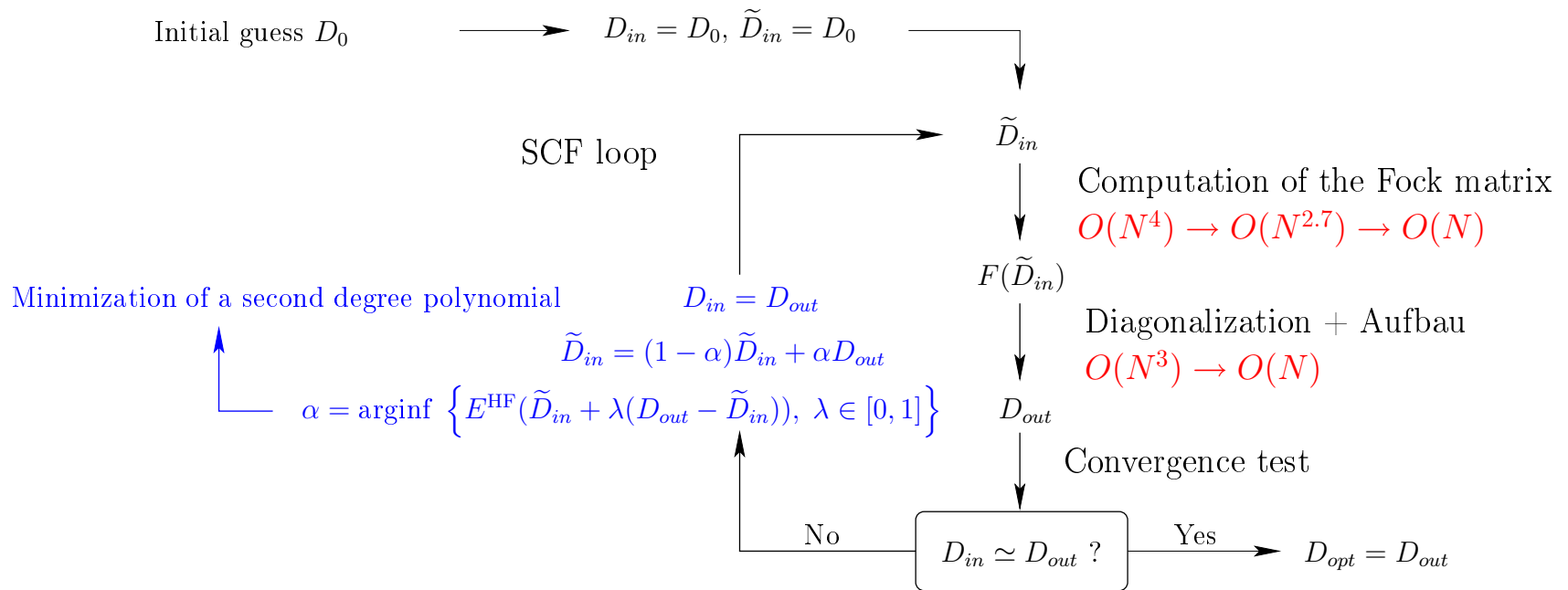
Extension to KS and improvements of ODA (joint work with K. Kudin, G. Scuseria and G. Turinici, JCP 2001-2002-2003)

Comparison between DIIS (Gaussian 98) and EDIIS (Gaussian 03)

System	$E^{\text{HF}}(D_0)$	DIIS (Ha)	EDIIS (Ha)	$\Delta E$ (kcal/mol)
CH <sub>3</sub> -NH-CH=CH-NO <sub>2</sub> 6-31G	-374.0038 -322.2373	<b>-375.3869</b> <b>Do not CV</b>	<b>-375.3869</b> <b>-375.3869</b>	0 -
Cr <sub>2</sub> 6-31G	-2069.5400 -2051.4339	<b>-2085.5449</b> <b>-2085.4042</b>	<b>-2085.8060</b> <b>-2085.8060</b>	163.71 251.93
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> 178 AO	-1700.7596 -1538.7283	<b>-1717.8928</b> <b>-1717.7355</b>	<b>-1718.0151</b> <b>-1718.0151</b>	76.68 175.31



### Computational bottlenecks



- 
- For quantum nuclear dynamics, the quantity of interest is the potential  $W$
  - For classical nuclear dynamics, the quantities of interest are the forces  $-\nabla_{\bar{x}_k} W$
  - For semi-classical nuclear dynamics and for computing some properties as well, higher derivatives of  $W$  are also needed

Often, and in particular for HF et KS models,  $W$  is defined by an equality constrained minimization problem and **analytical derivatives** are available

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Functions defined by equality constrained optimization problems

$$W(\bar{x}) = \inf \{E(\bar{x}, \phi), \quad \phi \in \mathcal{H}, \quad c(\bar{x}, \phi) = 0\} \quad (1)$$

Assume (1) has a unique minimizer  $\phi(\bar{x})$  and  $\bar{x} \mapsto \phi(\bar{x})$  is regular

$$\frac{dW}{d\bar{x}}(\bar{x}_0) = \frac{d}{d\bar{x}} (E(\bar{x}, \phi(\bar{x}))) \Big|_{\bar{x}=\bar{x}_0} = \frac{\partial E}{\partial \bar{x}}(\bar{x}_0, \phi(\bar{x}_0)) + \langle \nabla_{\phi} E(\bar{x}_0, \phi(\bar{x}_0)), \frac{d\phi}{d\bar{x}}(\bar{x}_0) \rangle$$

**Euler-Lagrange:**  $\nabla_{\phi} E(\bar{x}_0, \phi(\bar{x}_0)) + \nabla_{\phi} c(\bar{x}_0, \phi(\bar{x}_0))^T \cdot \lambda(\bar{x}_0) = 0,$

$$c(\bar{x}, \phi(\bar{x})) = 0 \quad \Rightarrow \quad \frac{\partial c}{\partial \bar{x}}(\bar{x}_0, \phi(\bar{x}_0)) + \nabla_{\phi} c(\bar{x}_0, \phi(\bar{x}_0)) \cdot \frac{d\phi}{d\bar{x}}(\bar{x}_0) = 0.$$

**Therefore**  $\frac{dW}{d\bar{x}}(\bar{x}_0) = \frac{\partial E}{\partial \bar{x}}(\bar{x}_0, \phi(\bar{x}_0)) + \langle \lambda(\bar{x}_0), \frac{\partial c}{\partial \bar{x}}(\bar{x}_0, \phi(\bar{x}_0)) \rangle$

### 3 - *A few words about spin*

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## One-electron systems

The wavefunction of a one-electron system is not a function of  $\psi(x) \in L^2(\mathbb{R}^3)$  but a function

$$\Psi(x, \sigma) \in L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{C})$$

$$\sigma \in \{|\uparrow\rangle, |\downarrow\rangle\} \quad \sigma: \text{spin variable}$$

As

$$H_1 = -\frac{1}{2}\Delta + V_{\text{nuc}}$$

is real and spin-independent, the eigenvalues of  $H_1$  on  $L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{C})$  and on  $L^2(\mathbb{R}^3)$  are the same

---

## Two-electron systems

Two-electron systems are described by wavefunctions

$$\Psi(x_1, \sigma_1; x_2, \sigma_2) \in \bigwedge_{i=1}^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{C})$$

i.e. satisfying the Pauli principle

$$\Psi(x_2, \sigma_2; x_1, \sigma_1) = -\Psi(x_1, \sigma_1; x_2, \sigma_2)$$

As

$$H_2 = -\frac{1}{2}\Delta_{x_1} - \frac{1}{2}\Delta_{x_2} + V_{\text{nuc}}(x_1) + V_{\text{nuc}}(x_2) + \frac{1}{|x_1 - x_2|}$$

is real, the eigenvalues of  $H_2$  on  $\bigwedge_{i=1}^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{C})$  and on  $\bigwedge_{i=1}^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{R})$  are the same

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Electronic Hamiltonians commute with the spin operators  $S_z$  and  $S^2$

It is possible to search eigenfunctions of  $H_2$  that also are eigenfunctions of  $S_z$  and  $S^2$

The eigenfunctions of both  $S_z$  and  $S^2$  are known:

- singlet states

$$\Psi(x_1, \sigma_1; x_2, \sigma_2) = \Psi_s(x_1, x_2) f_a(\sigma_1, \sigma_2), \quad \Psi_s \text{ symmetric, } f_a \text{ antisymmetric}$$

- triplet states

$$\Psi(x_1, \sigma_1; x_2, \sigma_2) = \Psi_a(x_1, x_2) f_s(\sigma_1, \sigma_2), \quad \Psi_a \text{ antisymmetric, } f_s \text{ symmetric}$$

To get the eigenvalues of  $H_2$  on  $\bigwedge_{i=1}^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{R})$ , it suffices to compute the eigenvalues of  $H_2$

- first on  $L^2(\mathbb{R}^3) \otimes_{\text{symm}} L^2(\mathbb{R}^3)$  (singlet states)
- then on  $L^2(\mathbb{R}^3) \wedge L^2(\mathbb{R}^3)$  (triplet states)

## *N*-electron systems

*N*-electron wavefunctions are of the form

$$\psi(x_1, \sigma_1; \dots; x_N, \sigma_N) \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{C})$$

As  $H_N$  is real, the eigenvalues of  $H_N$  on  $\bigwedge_{i=1}^N L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbf{C})$  and on  $\bigwedge_{i=1}^N L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{R})$  are the same.

Hartree-Fock and Kohn-Sham one-electron functions are spinorbitals

$$\phi_i(x, \sigma) \in H^1(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{R})$$

Let  $\alpha$  and  $\beta$  defined by

$$\alpha(|\uparrow\rangle) = 1 \quad \alpha(|\downarrow\rangle) = 0 \quad \beta(|\uparrow\rangle) = 0 \quad \beta(|\downarrow\rangle) = 1$$

One can associate with any orbital  $\phi_i \in H^1(\mathbb{R}^3)$  the  $\alpha$  and  $\beta$ -spinorbitals

$$(\phi_i \otimes \alpha)(x, \sigma) = \phi_i(x) \alpha(\sigma) \quad \text{and} \quad (\phi_i \otimes \beta)(x, \sigma) = \phi_i(x) \beta(\sigma)$$



Restricted HF and KS models (for closed shell systems,  $N = 2N_p$ )

RHF and RKS states are points of the manifold

$$\left\{ \Phi = (\phi_i)_{1 \leq i \leq N_p} \mid \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

The related spinorbitals are

$$\phi_1 \otimes \alpha, \phi_1 \otimes \beta, \dots, \phi_{N_p} \otimes \alpha, \phi_{N_p} \otimes \beta$$

Denoting by  $\gamma_\Phi(x, y) = 2 \sum_{i=1}^{N_p} \phi_i(x) \phi_i(y)$ ,  $\rho_\Phi(x) = 2 \sum_{i=1}^{N_p} |\phi_i(x)|^2$ , one has

$$E^{\text{RHF}}(\Phi) = \sum_{i=1}^{N_p} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_\Phi V_{\text{nuc}} + J(\rho_\Phi) - \frac{1}{4} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_\Phi(x, y)|^2}{|x - y|} dx dy$$

$$E^{\text{RKS}}(\Phi) = \sum_{i=1}^{N_p} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_\Phi V_{\text{nuc}} + J(\rho_\Phi) + \int_{\mathbb{R}^3} \varepsilon_{\text{xc}}(\rho_\Phi(x)) dx$$

## Unrestricted HF and KS models

UHF and UKS states are of the form

$$\left\{ (\Phi^\alpha, \Phi^\beta) = ((\phi_i^\alpha)_{1 \leq i \leq N_\alpha}, (\phi_i^\beta)_{1 \leq i \leq N_\beta}) \mid \phi_i^\sigma \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i^\sigma \phi_j^\sigma = \delta_{ij} \right\}$$

The related spinorbitals are

$$\phi_1^\alpha \otimes \alpha, \dots, \phi_{N_\alpha}^\alpha \otimes \alpha, \phi_1^\beta \otimes \beta, \dots, \phi_{N_\beta}^\beta \otimes \beta$$

Denoting by  $\gamma_{\Phi^\sigma}(x, y) = \sum_{i=1}^{N_\sigma} \phi_i^\sigma(x) \phi_i^\sigma(y)$ ,  $\rho_{\Phi^\sigma} = \sum_{i=1}^{N_\sigma} |\phi_i^\sigma|^2$ ,  $\rho_\Phi = \rho_{\Phi^\alpha} + \rho_{\Phi^\beta}$ ,

$$E^{\text{UHF}}(\Phi^\alpha, \Phi^\beta) = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} \int_{\mathbb{R}^3} |\nabla \phi_i^\sigma|^2 + \int_{\mathbb{R}^3} \rho_\Phi V_{\text{nuc}} + J(\rho_\Phi) - \frac{1}{2} \sum_{\sigma} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^\sigma}(x, y)|^2}{|x - y|} dx dy$$

$$E^{\text{UKS}}(\Phi^\alpha, \Phi^\beta) = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} \int_{\mathbb{R}^3} |\nabla \phi_i^\sigma|^2 + \int_{\mathbb{R}^3} \rho_\Phi V_{\text{nuc}} + J(\rho_\Phi) + \int_{\mathbb{R}^3} \varepsilon_{\text{xc}}(\rho_{\Phi^\alpha}(x), \rho_{\Phi^\beta}(x)) dx$$