Introduction to Quantum Chemistry and ab initio calculations of interatomic potentials

Eric CANCES

CERMICS - ENPC and INRIA

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Outline of the talk

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: $\hbar = 1$, $m_e = 1$, $e = 1$, $\frac{1}{4\pi \varepsilon_0} = 1$

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

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

$$H^1(\mathbb{R}^d) = \left\{ \phi \in L^2(\mathbb{R}^d) \mid \nabla \phi \in (L^2(\mathbb{R}^d))^d \right\}$$

$$\bigwedge_{i=1}^N L^2(\mathbb{R}^3) = \left\{ \psi \in L^2(\mathbb{R}^{3N}) \mid \psi(x_{p(1)}, \cdots, x_{p(N)}) = \varepsilon(p) \psi(x_1, \cdots, x_N) \right\}$$

$$\bigwedge_{i=1}^N H^1(\mathbb{R}^3) = H^1(\mathbb{R}^{3N}) \cap \left( \bigwedge_{i=1}^N L^2(\mathbb{R}^3) \right)$$
1.1 - Ab initio interatomic potentials

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 paramaters!

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

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

$$m_k \gg m_e = 1$$

\[\downarrow\]

\begin{align*}
\left\{ \begin{array}{l}
\text{nuclei most often} \\ 
\text{classical point-like particles} \\ 
\text{electrons} = \text{quantum delocalized particles}
\end{array} \right. 
\end{align*}
1.1 - Ab initio interatomic potentials

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 $W(\bar{x}_1, \cdots, \bar{x}_M)$

\[
\text{Semiclassical limit} \quad \downarrow \quad \hbar \rightarrow 0
\]

Classical Hamiltonian dynamics (point-like nuclei)

Same effective potential $W(\bar{x}_1, \cdots, \bar{x}_M)$
1.1 - Ab initio interatomic potentials

Ab initio molecular dynamics

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

\[
\begin{align*}
\frac{d\bar{x}_k}{dt}(t) &= \frac{\partial H_{\text{nuc}}}{\partial \bar{p}_k} = \frac{\bar{p}_k(t)}{m_k} \\
\frac{d\bar{p}_k}{dt}(t) &= -\frac{\partial H_{\text{nuc}}}{\partial \bar{x}_k} = -\nabla_{\bar{x}_k} W(\{\bar{x}_l(t)\} , \{\bar{p}_l(t)\})
\end{align*}
\]

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

\(W(\bar{x}_1, \cdots, \bar{x}_M)\) effective potential (free of empirical parameters)
1.1 - Ab initio interatomic potentials

Effective interatomic potential (singlet spin state)

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

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

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

\[ \sigma(H_N^{\{\bar{x}_k\}}) = \left\{ E_0(H_N^{\{\bar{x}_k\}}) \leq E_1(H_N^{\{\bar{x}_k\}}) \leq E_2(H_N^{\{\bar{x}_k\}}) \cdots \right\} \cup \left[ \sum(\{H_N^{\{\bar{x}_k\}}\}), +\infty \right) \]

\[ H_N^{\{\bar{x}_k\}} \psi = E \psi \quad \psi(x_{p(1)}, \cdots, x_{p(N)}) = \varepsilon(p) \psi(x_1, \cdots, x_N) \]
1.1 - Ab initio interatomic potentials

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
1.1 - Ab initio interatomic potentials

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 cm$^{-1}$)
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)
1.1 - Ab initio interatomic potentials

Wavefunction methods

Variational
- CI
- MCSCF
- MPn
- CC
- Sparse grids

Non variational
- Orbital free
- Kohn–Sham

Density functional theory (DFT)

Quantum Monte Carlo
- VMC
- DMC

N-body Schrödinger equation

Reduced Density Matrix

Density Matrix functional theory
1.1 - Ab initio interatomic potentials

From now on, the positions \( \{ \bar{x}_k \} \) of the nuclei are considered as fixed. In order to simplify the notation, we set

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

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

\[
E_0 = \inf \left\{ \langle \psi | H_N | \psi \rangle, \psi \in \mathcal{W}_N \right\}
\]

\[
\mathcal{W}_N = \left\{ \psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3), \| \psi \|_{L^2} = 1 \right\}
\]
Hartree-Fock approximation

\[ E_0 = \inf \{ \langle \psi | H_N | \psi \rangle, \; \psi \in \mathcal{W}_N \} \]

\[ \mathcal{W}_N = \left\{ \psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3), \; \| \psi \|_{L^2} = 1 \right\} \]

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

\[ \begin{cases} 
\psi = \phi_1 \wedge \cdots \wedge \phi_N, & \phi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} 
\end{cases} \]

\[ (\phi_1 \wedge \cdots \wedge \phi_N)(x_1, \cdots, x_N) \overset{\text{def}}{=} \frac{1}{\sqrt{N!}} \begin{vmatrix} 
\phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\
\phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) 
\end{vmatrix} \]
Rewriting the minimization problem in terms of $\Phi = \{\phi_i\}$, one obtains

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

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

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

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

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

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

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

\[
E^{\text{HF}}(\Phi) = \mathcal{E}^{\text{HF}}(\gamma_{\Phi})
\]
1.2 - Hartree-Fock approximation

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

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

Nonlinear eigenvalue problem

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

No unfilled shell property (Bach, Lieb, Loss, Solovej): \( \varepsilon_N < \varepsilon_{N+1} \)
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
1.3 - Density Functional Theory

Hohenberg-Kohn splitting of the electronic Hamiltonian

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

\[ H_N = H_N^0 + \sum_{i=1}^N V_{\text{nuc}}(x_i) \]

\[ H_N^0 = -\sum_{i=1}^N \frac{1}{2} \Delta x_i + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}, \quad V_{\text{nuc}}(x) = -\sum_{k=1}^M \frac{z_k}{|x - \bar{x}_k|} \]

Electronic density

\[ \psi \in \mathcal{W}_N \ \rightarrow \ \rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \cdots, x_N)|^2 \, dx_2 \cdots dx_N \]
1.3 - Density Functional Theory

Levy-Lieb constrained search approach

\[ E_0 = \inf_{\psi} \langle \psi | H_N | \psi \rangle \]

\[ = \inf_{\psi} \left( \langle \psi | H^0_N | \psi \rangle + \langle \psi | \sum_{i=1}^{N} V_{\text{nuc}}(x_i) | \psi \rangle \right) \]

\[ = \inf_{\psi} \left( \langle \psi | H^0_N | \psi \rangle + \int_{\mathbb{R}^3} \rho_{\psi} V_{\text{nuc}} \right) \]

\[ = \inf_{\rho} \inf_{\psi | \rho_{\psi} = \rho} \left( \langle \psi | H^0_N | \psi \rangle + \int_{\mathbb{R}^3} \rho V_{\text{nuc}} \right) \]

\[ = \inf_{\rho} \left( F^{N}_{\text{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V_{\text{nuc}} \right) \]
1.3 - Density Functional Theory

Levy-Lieb functional

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

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

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

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

Problem: no easy-to-compute expression of \( F_{\text{LL}}^N(\rho) \) is known.
1.4 - Kohn-Sham model

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

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

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

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

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

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

$E_{xc}$ is called the exchange-correlation functional
1.4 - Kohn-Sham model

Exchange-correlation functional

\[ |E_{xc}(\rho)| << J(\rho) \text{ and } T_{KS}^N(\rho) \]

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

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

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

\[ \rightarrow \quad \text{Local Density Approximation (LDA)} \]

The function \( e_{xc} : \mathbb{R}_+ \rightarrow \mathbb{R} \) is obtained by interpolation of benchmark Quantum Monte Carlo calculations on the homogeneous electron gas
1.4 - Kohn-Sham model

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

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

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

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

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.

\[
E_0 \leq \inf \{ E^{\text{HF}}(\Phi), \quad \Phi \in \mathcal{S} \} \quad \text{Hartree-Fock} \\
E_0 \simeq \inf \{ E^{\text{KS}}(\Phi), \quad \Phi \in \mathcal{S} \} \quad \text{Kohn-Sham LDA}
\]

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

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

\[
\mathcal{S} = \left\{ \Phi = \{\phi_i\} \in (H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}
\]
LDA can be improved (on average) by taking into account

- the local inhomogeneities of \( \rho \) through the gradient of \( \rho \)

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

\[\rightarrow\] Generalized Gradient Approximation (GGA)

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

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

\[\rightarrow\] meta-GGA
1.4 - Kohn-Sham model

- some exact-exchange contribution

\[ E_{xc}^{\text{hybrid}}(\Phi) = \int_{\mathbb{R}^3} e_{xc}^{\text{local}}(\rho\Phi(x), \nabla\rho\Phi(x), \tau\Phi(x)) \, dx - \frac{\lambda}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma\Phi(x, y)|^2}{|x - y|} \, dx \, dy \]

\[ \longrightarrow \quad \text{Hybrid functionals} \]

Self interaction in DFT

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

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

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

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

## Jacob's ladder (Perdew)

<table>
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<th>Heaven</th>
<th>Exact exchange–correlation functional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rung 5</td>
<td>explicit functionals of the Kohn-Sham occupied and unoccupied orbitals SAOP, ...</td>
</tr>
<tr>
<td>Rung 4</td>
<td>explicit functionals of the density matrix (ex: hybrid functionals) $1/2 &amp; 1/2$, B3P, B3LYP, PBE0, O3LYP, X3LYP, mPW1PW91, BMK, PWB6K, B1B95, PW6B95, TPSSH, M05, ...</td>
</tr>
<tr>
<td>Rung 3</td>
<td>meta-GGA (explicit in $\rho(x)$, $\nabla \rho(x)$ and $\tau(x) = \sum_{i=1}^{N}</td>
</tr>
<tr>
<td>Rung 2</td>
<td>GGA (explicit in $\rho(x)$ and $\nabla \rho(x)$) SIC, PW91, BLYP, mPW1PW91, PBE, revPBE, G96LYP, HCTH, OPTX, EDF1, ...</td>
</tr>
<tr>
<td>Rung 1</td>
<td>LDA (explicit in $\rho(x)$)</td>
</tr>
<tr>
<td>Earth</td>
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</tbody>
</table>

$\rho(x)$ and $\nabla \rho(x)$.
1.4 - Kohn-Sham model

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

\[ E_{x}^{\text{LDA}}(\Phi) = -C_x \int_{\mathbb{R}^3} \rho_{\Phi}(x)^{4/3} \, dx \]

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

\( E_c \): correlation functional

... ugly multilime analytical formulas ...
2 - Numerical issues
## 2.1 - Discretization in atomic orbital basis sets

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

<table>
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<th>Method</th>
<th>Molecules, clusters</th>
<th>Crystalline materials</th>
</tr>
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<tr>
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<tr>
<td><strong>Atomic orbitals</strong> (variational)</td>
<td>Gaussian, Gamess, Molpro, Dalton, QChem, Jaguar, ADF (Slater AO), ...</td>
<td>Crystal, Gaussian, Siesta (numerical AO)</td>
</tr>
<tr>
<td><strong>Planewaves</strong> (variational)</td>
<td><em>irrelevent</em></td>
<td>PWSCF (Quantum espresso), Abinit, Castep, CPMD, Onetep, Vasp, ...</td>
</tr>
<tr>
<td><strong>Grid methods</strong> (non variational)</td>
<td>Parsec (Talk by Y. Saad), Talk by J.-L Fattebert</td>
<td>Parsec</td>
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<tr>
<td><strong>Wavelets</strong> (variational)</td>
<td>Bigdft (Talk by S. Goedecker)</td>
<td>Bigdft</td>
</tr>
</tbody>
</table>
2.1 - Discretization in atomic orbital basis sets

Galerkin variational approximation

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

\[ E_0^{\text{HF}} \leq E_0^{\text{HF},\chi} = \inf \{ E^{\text{HF}}(\Phi), \quad \Phi \in S_\chi \} \]

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

\[ \gamma_\Phi(x, y) = \sum_{i=1}^{N} \phi_i(x) \phi_i(y) = \sum_{i,j=1}^{N} [CC^T]_{\mu \nu} \chi_\mu(x) \chi_\nu(y) \]
2.1 - Discretization in atomic orbital basis sets

Discretized formulation of the HF problem

\[ E_{0}^{\text{HF}, \chi} = \inf \left\{ E^{\text{HF}}(CC^T), \quad C \in \mathcal{M}(N_b, N), \quad C^T S C = I_{N} \right\} \]

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

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: \( (\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_{\mu}(x) \chi_{\nu}(x) \chi_{\kappa}(x') \chi_{\lambda}(x')}{|x - x'|} \ dx \ dx' \)
2.1 - Discretization in atomic orbital basis sets

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
2.1 - Discretization in atomic orbital basis sets

Gaussian atomic orbital basis sets

1. A collection \( \{ \xi^A_\mu \}_{1 \leq \mu \leq n_A} \) 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 \( \text{H}_2\text{O} \)

\[
\{ \chi_\mu \} = \left\{ \xi^H_1(x - \bar{x}_H_1), \ldots, \xi^H_{n_H}(x - \bar{x}_H_1); \xi^H_1(x - \bar{x}_H_2), \ldots, \xi^H_{n_H}(x - \bar{x}_H_2); \xi^O_1(x - \bar{x}_O), \ldots, \xi^O_{n_O}(x - \bar{x}_O) \right\},
\]

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.
2.1 - Discretization in atomic orbital basis sets

\[ E_0^{HF} \leq E_0^{HF\,\text{disc}} = \inf \left\{ E^{HF}(CC^T), \ C \in \mathcal{C}_N \right\} \]
\[ = \inf \left\{ E^{HF}(D), \ D \in \mathcal{P}_N \right\} \]
\[ \overset{\text{(Lieb)}}{=} \inf \left\{ E^{HF}(D), \ D \in \tilde{\mathcal{P}}_N \right\} \]

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

\[ \uparrow \quad \uparrow \]

linear \quad \text{quadratic}

\[ \mathcal{C}_N = \left\{ C \in \mathbb{R}^{N_b \times N}, \quad C^T SC = I_N \right\} \]
\[ \mathcal{P}_N = \left\{ D \in \mathbb{R}^{N_b \times N_b}, \quad D^T = D, \quad DSD = D, \quad \text{Tr}(SD) = N \right\} \]
\[ \tilde{\mathcal{P}}_N = \left\{ D \in \mathbb{R}^{N_b \times N_b}, \quad D^T = D, \quad DSD \leq D, \quad \text{Tr}(SD) = N \right\} \]
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**

\[
\begin{align*}
F(D)\Phi_i &= \varepsilon_i S \Phi_i \\
\Phi_i^T S \Phi_j &= \delta_{ij} \\
\varepsilon_1 &\leq \varepsilon_2 \leq \cdots \leq \varepsilon_N \text{ are the lowest } N \text{ eigenvalues of } F(D)\phi = \varepsilon S\phi \\
D &= \sum_{i=1}^{N} \Phi_i \Phi_i^T
\end{align*}
\]

Nonlinear generalized eigenvalue problem

Discrete no unfilled shell property: $\varepsilon_N < \varepsilon_{N+1}$
2.2 - Algorithms (prelude to Yousef Saad’s lectures)

Roothaan algorithm

\[
\begin{aligned}
F(D^k)\Phi^{k+1}_i &= \varepsilon^{k+1}_i S\Phi^{k+1}_i \\
\Phi^{k+1}_i S\Phi^{k+1}_j &= \delta_{ij} \\
\varepsilon^{k+1}_1 &\leq \varepsilon^{k+1}_2 \leq \cdots \leq \varepsilon^{k+1}_N \text{ are the lowest } N \text{ eigenvalues of } F(D^k)\phi = \varepsilon S\phi \\
D^{k+1} &= \sum_{i=1}^N \Phi^{k+1}_i \Phi^{k+1}_i T
\end{aligned}
\]

Theorem. (E. C. and C. Le Bris, M2AN 2000) The sequence \((D^R_{th})_k\) generated by the Roothaan algorithm satisfies one of the following two properties

- either \((D^R_{th})_k\) converges toward a solution to the HF equations
- or \((D^R_{th})_k\) oscillates between two states, none of them being solution to the HF equations
Optimal damping algorithm (E.C. and C. Le Bris, IJQC 2000)

Initial guess $D_0 \rightarrow D_{in} = D_0, \tilde{D}_{in} = D_0 \rightarrow$ SCF loop

Minimization of a second degree polynomial

$\tilde{D}_{in} = (1 - \alpha)\tilde{D}_{in} + \alpha D_{out}$

$\alpha = \text{arginf} \{ E^{HF}(\tilde{D}_{in} + \lambda(D_{out} - \tilde{D}_{in})), \lambda \in [0, 1] \}$

Computation of the Fock matrix

$F(\tilde{D}_{in}) \rightarrow$ Diagonalization + Aufbau

$D_{out} \rightarrow$ Convergence test

$D_{in} \simeq D_{out} ?$ Yes $D_{opt} = D_{out}$ No

**Theorem.** The sequence $(E^{HF}(\tilde{D}_k))$ 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 $I$. 

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

<table>
<thead>
<tr>
<th>System</th>
<th>(E^{\text{HF}}(D_0))</th>
<th>DIIS (Ha)</th>
<th>EDIIS (Ha)</th>
<th>(\Delta E) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)-NH-CH=CH-NO(_2) 6-31G</td>
<td>-374.0038, -322.2373</td>
<td>-375.3869 (Do not CV)</td>
<td>-375.3869</td>
<td>0</td>
</tr>
<tr>
<td>Cr(_2) 6-31G</td>
<td>-2069.5400, -2051.4339</td>
<td>-2085.5449</td>
<td>-2085.8060</td>
<td>163.71</td>
</tr>
<tr>
<td>[Fe(H(_2)O)(_6)](^{2+}) 178 AO</td>
<td>-1700.7596, -1538.7283</td>
<td>-1717.8928</td>
<td>-1718.0151</td>
<td>76.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175.31</td>
</tr>
</tbody>
</table>
2.2 - Algorithms (prelude to Yousef Saad’s lectures)

Computational bottlenecks

Initial guess $D_0$ ➔ $D_{in} = D_0, \tilde{D}_{in} = D_0$

SCF loop

Minimization of a second degree polynomial

$\tilde{D}_{in} = (1 - \alpha)\tilde{D}_{in} + \alpha D_{out}$

$\alpha = \text{arginf} \left\{ E_{HF}(\tilde{D}_{in} + \lambda(D_{out} - \tilde{D}_{in})), \; \lambda \in [0, 1] \right\}$

Computation of the Fock matrix

$O(N^4) \rightarrow O(N^{2.7}) \rightarrow O(N)$

Diagonalization + Aufbau

$O(N^3) \rightarrow O(N)$

Convergence test

$D_{in} \simeq D_{out}$?

No ➔ $D_{in} \simeq D_{out}$?

Yes ➔ $D_{opt} = D_{out}$
• 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
Functions defined by equality constrained optimization problems

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

(1)

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

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

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
3 - A few words about spin

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

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

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

As

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

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

Two-electron systems are described by wavefunctions

$$\Psi(x_1, \sigma_1; x_2, \sigma_2) \in \bigwedge_1^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{C})$$

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 $\bigwedge_1^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{C})$ and on $\bigwedge_1^2 L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{R})$ are the same
3 - A few words about spin

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)
3 - A few words about spin

\(N\)-electron systems

\(N\)-electron wavefunctions are of the form

\[\psi(x_1, \sigma_1; \cdots; x_N, \sigma_N) \in \bigwedge_i L^2(\mathbb{R}^3 \times \{ | \uparrow \rangle, | \downarrow \rangle \}, \mathbb{C})\]

As \(H_N\) is real, the eigenvalues of \(H_N\) on \(\bigwedge_i L^2(\mathbb{R}^3 \times \{ | \uparrow \rangle, | \downarrow \rangle \}, \mathbb{C})\) and on \(\bigwedge_i L^2(\mathbb{R}^3 \times \{ | \uparrow \rangle, | \downarrow \rangle \}, \mathbb{R})\) 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

\[(\phi_i \otimes \alpha)(x, \sigma) = \phi_i(x) \alpha(\sigma) \quad \text{and} \quad (\phi_i \otimes \beta)(x, \sigma) = \phi_i(x) \beta(\sigma)\]
3 - A few words about spin

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

RHF and RKS states are points of the manifold

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

The related spinorbitals are

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

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
\[
\left\{ \left( \Phi^\alpha, \Phi^\beta \right) = \left( (\phi^\alpha_i)_{1 \leq i \leq N_\alpha}, (\phi^\beta_i)_{1 \leq i \leq N_\beta} \right) \mid \phi^\sigma_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi^\sigma_i \phi^\sigma_j = \delta_{ij} \right\}
\]

The related spinorbitals are
\[
\phi_1^\alpha \otimes \alpha, \cdots, \phi_{N_\alpha}^\alpha \otimes \alpha, \phi_1^\beta \otimes \beta, \cdots, \phi_{N_\beta}^\beta \otimes \beta
\]

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

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

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