PDEs and electronic structure calculations

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First-principle molecular simulation is becoming an essential tool in Chemistry, Materials Science, Molecular Biology and Nanosciences

Some objective facts :

– The most cited four articles in Physics are

1. Kohn & Sham, PR 1965 - Density Functional Theory (LDA)
2. Hohenberg & Kohn, PR 1964 - Density Functional Theory
3. Perdew & Zunger, PRB 1981 - Density Functional Theory (GGA)
4. Ceperley & Alder, PRL 1980 - Quantum Monte Carlo

– W. Kohn and J. Pople shared the 1998 Nobel Price in Chemistry

– First-principle molecular simulation utilizes more than 20% of the resources available in scientific computing centers

– Only a handful of Mathematicians are working in this field

First-principle (or *ab initio*) molecular simulation

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 !

Atomic units : $\hbar = 1,\ m_e = 1,\ e = 1,\ \dfrac{1}{4\pi\varepsilon_0} = 1$

Electrons and nuclei

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

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

Born-Oppenheimer approximation (classical nuclei, quantum electrons)

Atomic positions and momenta : $(\{\mathbf{R}_k(t)\}, \{\mathbf{P}_k(t)\}) \in \mathbb{R}^{3M} \times \mathbb{R}^{3M}$

$$\left\{ \begin{array}{l} \dfrac{d\mathbf{R}_k}{dt}(t) = \dfrac{\partial H_{\rm nuc}}{\partial \mathbf{P}_k} = \dfrac{\mathbf{P}_k(t)}{m_k} \\[1em] \dfrac{d\mathbf{P}_k}{dt}(t) = -\dfrac{\partial H_{\rm nuc}}{\partial \mathbf{R}_k} = -\nabla_{\mathbf{R}_k} W(\mathbf{R}_1(t), \cdots, \mathbf{R}_M(t)) \end{array} \right.$$

$$H_{\rm nuc}(\{\mathbf{R}_k\}, \{\mathbf{P}_k\}) = \sum_{k=1}^{M} \frac{|\mathbf{P}_k|^2}{2\, m_k} + W(\mathbf{R}_1, \cdots, \mathbf{R}_M)$$

$W(\mathbf{R}_1, \cdots, \mathbf{R}_M)$ effective potential (free of empirical parameters)

Ab initio interatomic potentials and forces

$$\begin{aligned} W(\mathbf{R}_1, \cdots, \mathbf{R}_M) &= E^0_{\{\mathbf{R}_k\}} + V^{\mathrm{nn}}_{\{\mathbf{R}_k\}} \\ \nabla_{\mathbf{R}_k} W(\mathbf{R}_1, \cdots, \mathbf{R}_M) &= \int_{\mathbb{R}^3} \rho^0_{\{\mathbf{R}_k\}}(\mathbf{r}) \nabla_{\mathbf{R}_k} V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(\mathbf{r})\, d\mathbf{r} + \nabla_{\mathbf{R}_k} V^{nn}_{\{\mathbf{R}_k\}} \end{aligned}$$

$$V^{\mathrm{nn}}_{\{\mathbf{R}_k\}} = \sum_{1 \le k < l \le M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$ **nuclear Coulomb repulsion energy**

$$V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$ **nuclear Coulomb potential**

$E^0_{\{\mathbf{R}_k\}}$ **and** $\rho^0_{\{\mathbf{R}_k\}}(\mathbf{r})$ **electronic ground state energy and density**

From now on, the positions $\{\mathbf{R}_k\}$ of the nuclei are considered as fixed

In order to simplify the notation, we set

$$E^0 = E^0_{\{\mathbf{R}_k\}}$$

$$\rho^0(\mathbf{r}) = \rho^0_{\{\mathbf{R}_k\}}(\mathbf{r})$$

$$V^{\rm ne}(\mathbf{r}) = V^{\rm ne}_{\{\mathbf{R}_k\}}(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

E^0 is the lowest eigenvalue of the electronic Schrödinger equation

$$H_N \Psi^0 = E^0 \Psi^0$$

where the electronic Hamiltonian is given by

$$H_N = -\sum_{i=1}^{N} \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

and where the electronic ground state wavefunction Ψ^0 satisfies

– the Pauli principle

$$\forall i < j, \qquad \Psi^0(\cdots, \mathbf{r}_j, \cdots, \mathbf{r}_i, \cdots) = -\Psi^0(\cdots, \mathbf{r}_i, \cdots, \mathbf{r}_j, \cdots)$$

– the normalization condition

$$\int_{\mathbb{R}^{3N}} |\Psi^0(\mathbf{r}_1, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_1 \cdots d\mathbf{r}_N = 1$$

$\rho^0(\mathbf{r})$ is the density associated with Ψ^0

The density associated with a function $\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ satisfying

– the Pauli principle

$$\forall i < j, \qquad \Psi(\cdots, \mathbf{r}_j, \cdots, \mathbf{r}_i, \cdots) = -\Psi(\cdots, \mathbf{r}_i, \cdots, \mathbf{r}_j, \cdots)$$

– the normalization condition

$$\int_{\mathbb{R}^{3N}} |\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_1 \cdots d\mathbf{r}_N = 1$$

is the function $\rho_\Psi(\mathbf{r})$ defined by

$$\rho_\Psi(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

It holds

$$\rho_\Psi(\mathbf{r}) \geq 0 \qquad \text{and} \qquad \int_{\mathbb{R}^3} \rho_\Psi(\mathbf{r}) \, d\mathbf{r} = N$$

Strengths of the model :

- It allows to simulate a wide variety of phenomena
- It does not contain any parameter specific to the system
- It 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)

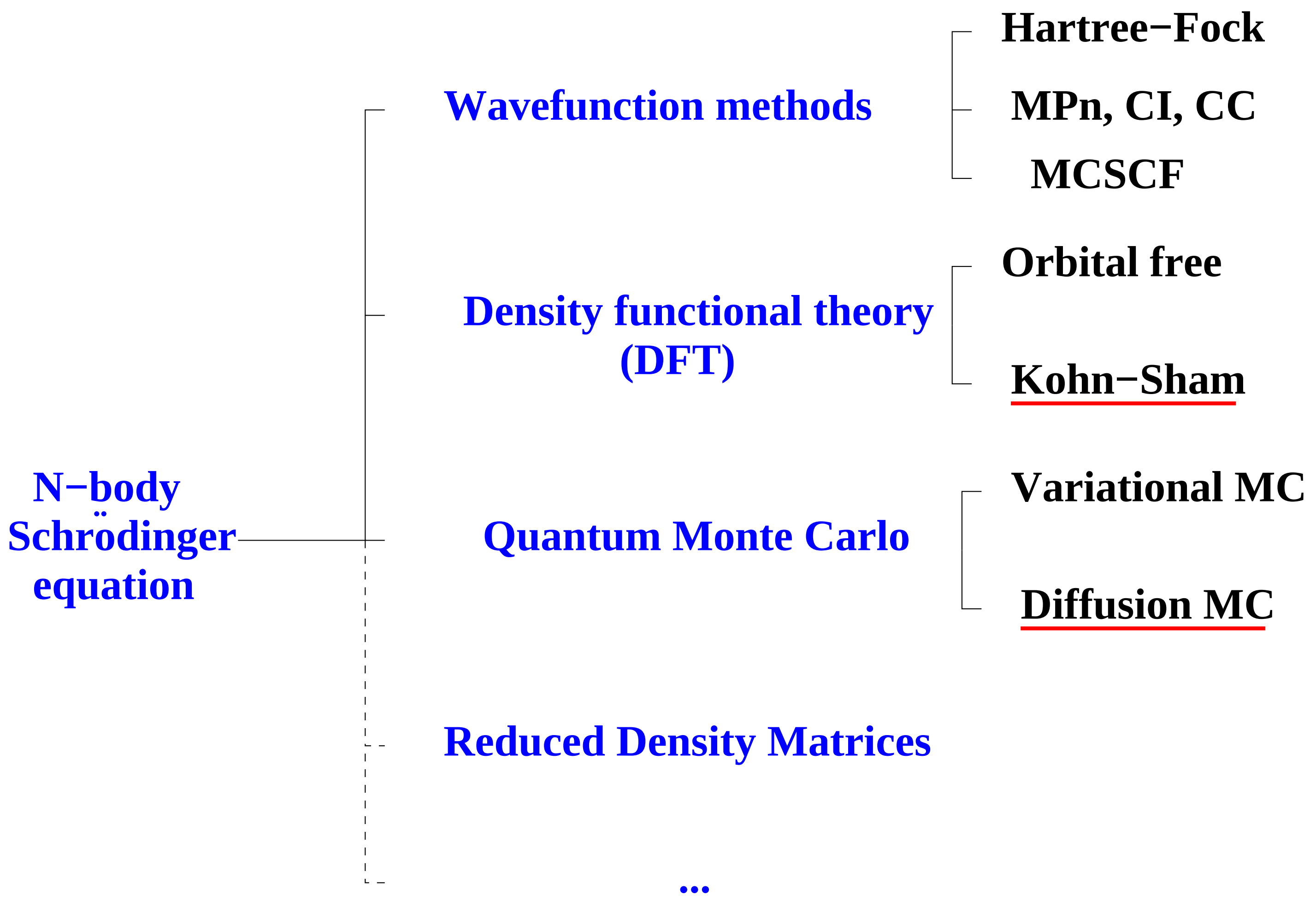
Weaknesses of the model :

- The Schrödinger equation $H_N\Psi = E\Psi$ is a $3N$-dimensional PDE
- Chemical accuracy is required

  example : atomization energy of water

$$\begin{aligned}\Delta E_{\mathrm{H_2O}} &= E_{\mathrm{H_2O}} - 2E_{\mathrm{H}} - E_{\mathrm{O}} \\ &= -76.4389 - 2\times(-0.5) - (-75.0840) = -0.3549 \textbf{ a.u.}\end{aligned}$$

Methods for electronic structure calculations



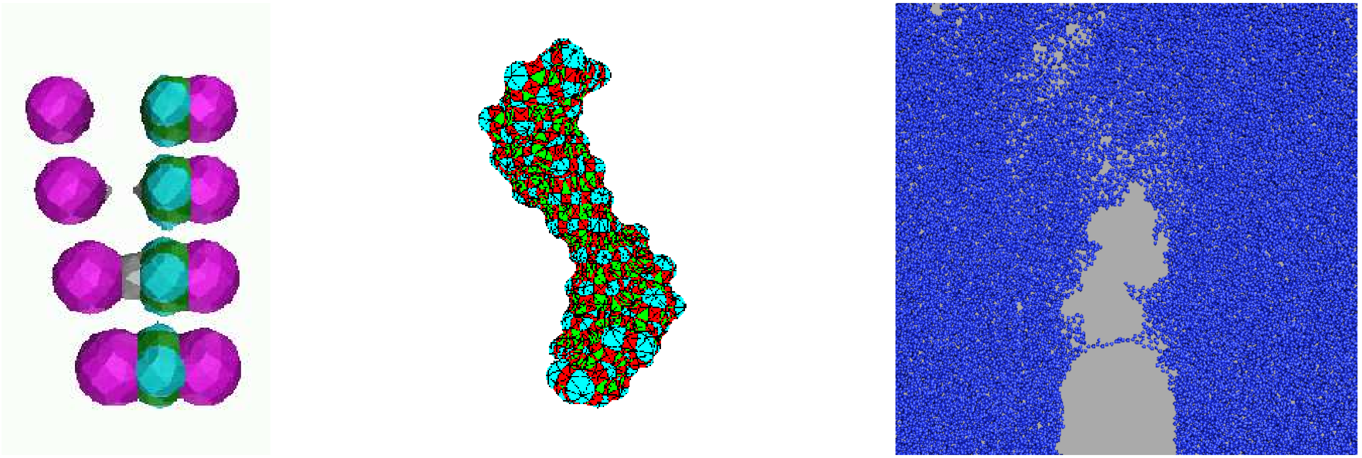
Ab initio simulations today

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

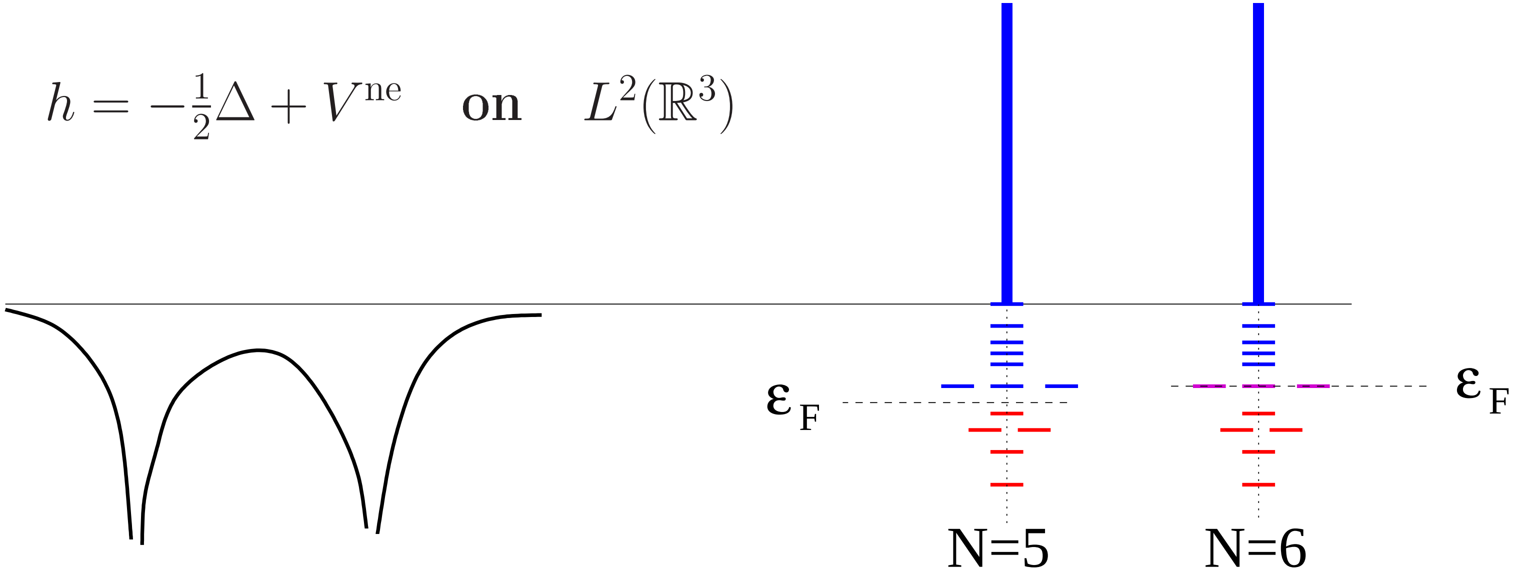
W.R.(?) : 11.8 million-atom (1.04×10^{12} grid points) DFT simulation (A. Nakano et al., Int. J. High Perform. C. Appl. 2008)



1 - Linear scaling algorithms

For a system of N non-interacting electrons : $H_N = \sum_{i=1}^{N} h_{\mathbf{r}_i}$

$$h = -\tfrac{1}{2}\Delta + V^{\rm ne} \quad \textbf{on} \quad L^2(\mathbb{R}^3)$$



$$h\phi_i = \varepsilon_i \phi_i, \qquad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \qquad \varepsilon_1 < \varepsilon_2 \le \varepsilon_3 \le \ldots \ \textbf{negative eigenvalues of } h$$

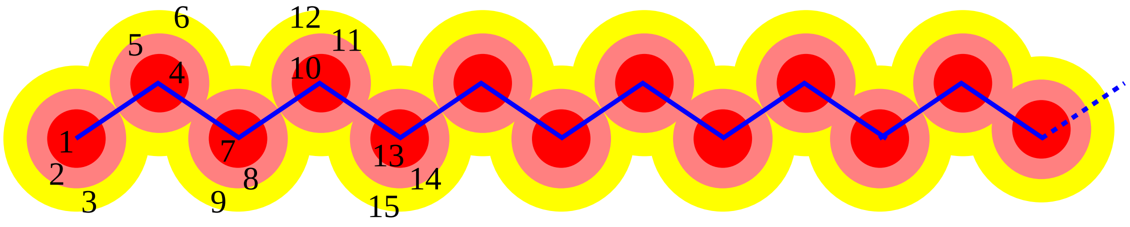
$$E^0 = \sum_{i=1}^{N} \varepsilon_i, \qquad \Psi^0(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \mathbf{det}(\phi_i(\mathbf{r}_j)), \qquad \rho^0(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

For non-interacting electrons, $E^0 = \sum_{i=1}^{N} \varepsilon_i$ and $\rho^0(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$ with

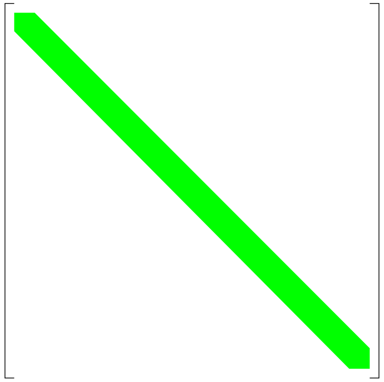
$$\left\{ \begin{array}{l} -\dfrac{1}{2}\Delta\phi_i + V^{\mathrm{ne}}\phi_i = \varepsilon_i\phi_i \\ \\ \displaystyle\int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \\ \\ \varepsilon_1 < \varepsilon_2 \leq \cdots \leq \varepsilon_N \quad \textbf{lowest } N \textbf{ eigenvalues of } h = -\frac{1}{2}\Delta + V^{\mathrm{ne}} \end{array} \right.$$

⟶ **Linear eigenvalue problem**

Galerkin approximation in atomic orbital basis sets $(\chi_\mu)_{1\le\mu\le N_b}$



S,H =



dimension of the approximation space : N_b $\qquad 2\times N \le N_b \le 5\times N$

$$\left\{\begin{array}{l} H\Phi_i = \varepsilon_i S \Phi_i \qquad\qquad H = [\langle\chi_\mu|h|\chi_\nu\rangle] \in \mathbb{R}^{N_b\times N_b}, \quad S = [\langle\chi_\mu|\chi_\nu\rangle] \in \mathbb{R}^{N_b\times N_b} \\ \\ \Phi_i^{\rm T} S \Phi_j = \delta_{ij} \\ \\ \varepsilon_1 < \varepsilon_2 \le \cdots \le \varepsilon_N \quad \textbf{lowest } N \textbf{ eigenvalues of } H\Phi = \varepsilon S\Phi \end{array}\right.$$

Assume for simplicity that $S = I_{N_b}$ (orthonormal basis)

$H = [\langle \chi_\mu | h | \chi_\nu \rangle]$ symmetric $N_b \times N_b$ matrix with $N_b \sim 5N$

$$\begin{cases} E^0 = \sum_{i=1}^{N} \varepsilon_i = \qquad (HD), \quad \rho^0(\mathbf{r}) = \sum_{i=1}^{N} \left| \sum_{\mu=1}^{N_b} \Phi_{i,\mu}\chi_\mu(\mathbf{r}) \right| = \sum_{\mu,\nu} D_{\mu,\nu}\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \\ D = \sum_{i=1}^{N} \Phi_i \, \Phi_i^{\mathrm{T}} \qquad\qquad\qquad\qquad (\Phi_1, \cdots, \Phi_N) \\ H\Phi_i = \varepsilon_i \, \Phi_i \\ \Phi_i^{\mathrm{T}}\Phi_j = \delta_{ij} \\ \varepsilon_1 \le \varepsilon_2 \le \cdots \le \varepsilon_N \qquad\qquad N \qquad\qquad H \end{cases}$$

- for a generic matrix H : algorithmic complexity in N^3
- for a sparse matrix : algorithmic complexity in N^2
- for some hamiltonian matrices : algorithmic complexity in N

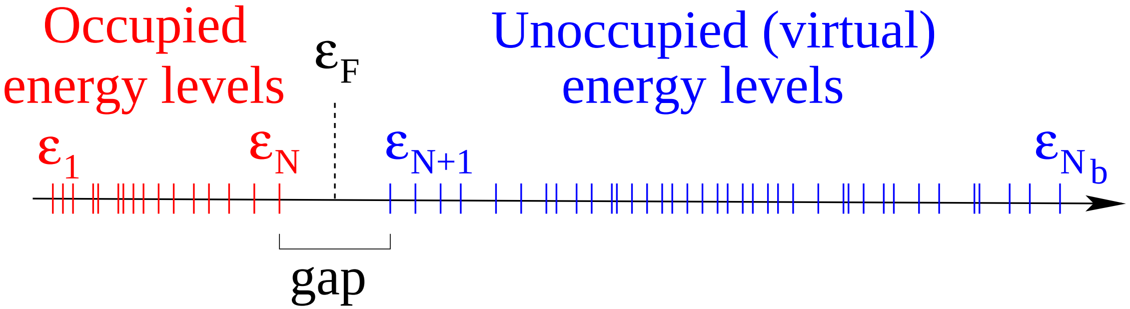
Fundamental remarks :

1. We do not need to compute the individual eigenvectors but only the orthogonal projector D
2. For insulators and semiconductors, the matrix D is sparse

Formulation in D

$$D_{\rm opt} = \mathcal{H}(\varepsilon_F - H), \qquad \mathcal{H} \text{ Heaviside function}$$

$$D_{\rm opt} = \operatorname{arginf}\left\{ \mathrm{Tr}(HD), \quad D \in \mathcal{M}_S(N_b), \quad D^2 = D, \quad \mathrm{Tr}(D) = N \right\}$$



Some alternatives to brute force diagonalization

- Polynomial or rational fraction approximation of $\mathcal{H}(\varepsilon_F - H)$: FOE, FOP (Goedecker 1999)

- Exact penalization methods : DMM (Li, Numes, Vanderbilt 1993)

- Domain decomposition methods :
  - Divide and Conquer (Yang, Lee 1992)
  - Multilevel Domain Decomposition (Barrault, Bencteux, E.C., Le Bris, Hager, 2007)
  - Fragment method (Zhao, Meza, Wang 2008)

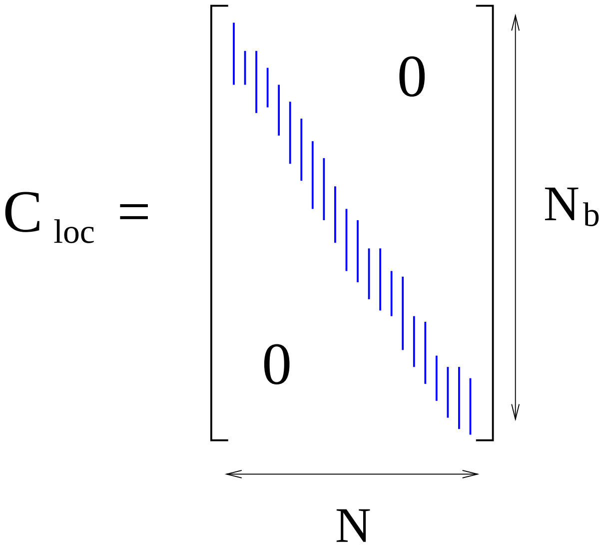
Linear scaling on grids : García-Cervera, Lu, Xuan, E (2008)

Formulation in C : $D_{\rm opt} = C_{\rm opt} C_{\rm opt}^{\rm T}$, where $C_{\rm opt}$ is solution to

$$\inf \left\{ \mathbf{Tr}(HCC^{\rm T}), \quad C \in \mathcal{M}(N_b, N), \quad C^{\rm T} C = I_N \right\} \qquad (1)$$

Rotational invariance : if $C_{\rm opt}$ is solution, so is $C_{\rm opt} U$, for any orthogonal matrix $U \in U(N)$

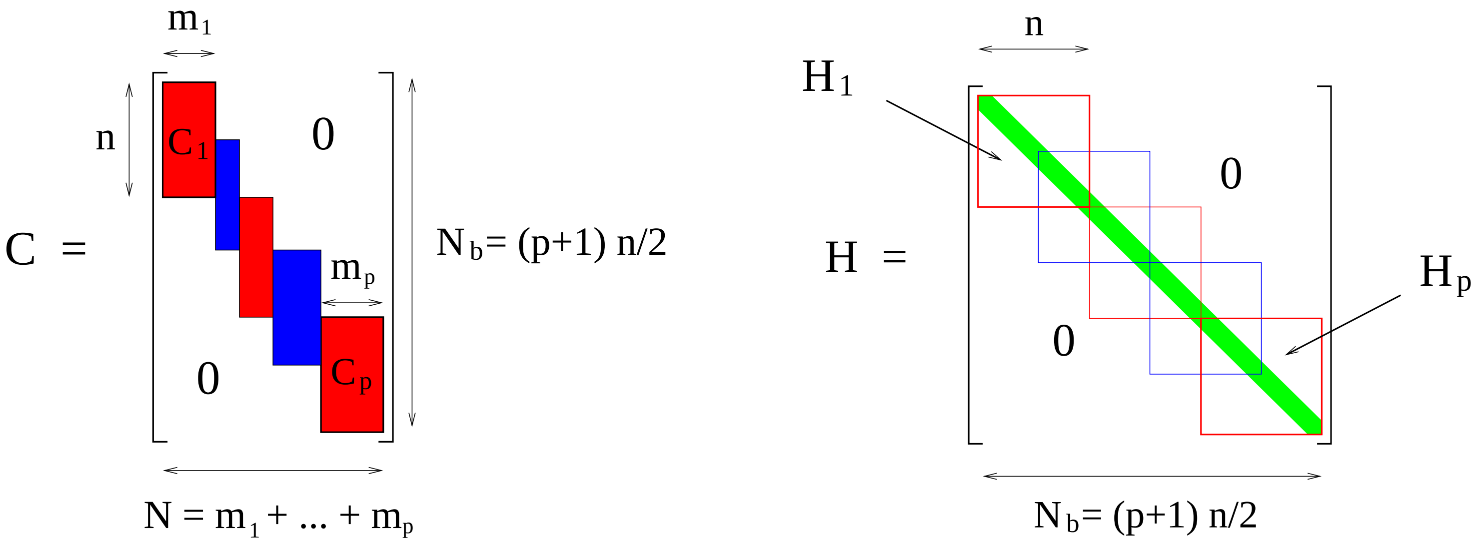
Localized orbitals. For an insulator ($\varepsilon_{N+1} - \varepsilon_N > 0$ not too small), there exists a matrix $C_{\rm loc}$ such that $D_{\rm opt} = C_{\rm loc} C_{\rm loc}^{\rm T}$ where the matrix $C_{\rm loc}$ is made of almost locally supported vectors



For insulators, it suffices to solve

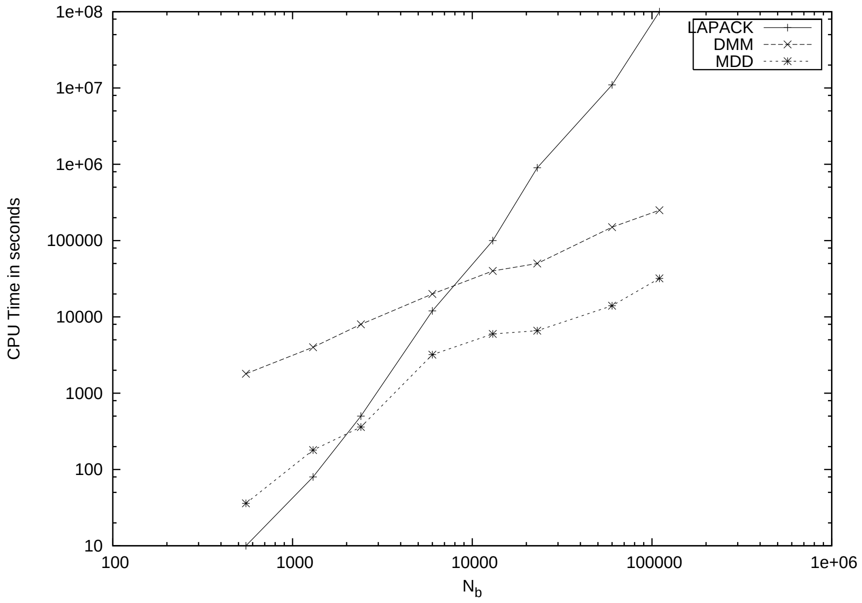
$$\inf\left\{\mathbf{Tr}(HCC^{\mathrm{T}}),\quad C\in\mathcal{M}(N_b,N),\quad C^{\mathrm{T}}C=I_N\right\} \tag{2}$$

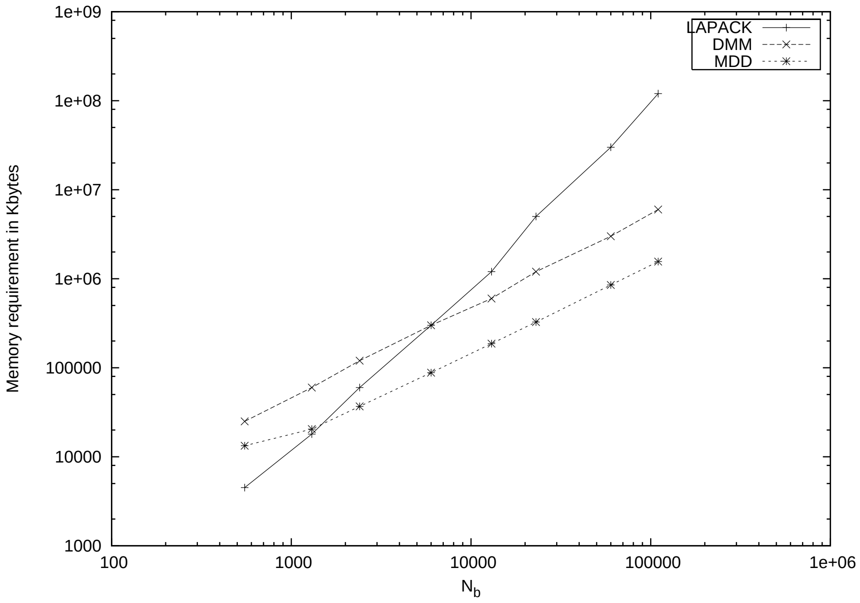
for matrices C of the form



$$\inf\left\{\begin{aligned}&\sum_{i=1}^{p}\mathbf{Tr}\left(H_iC_iC_i^{\mathrm{T}}\right),\quad C_i\in\mathcal{M}(n,m_i),\quad m_i\in\mathbb{N},\\ &\qquad C_i^{\mathrm{T}}C_i=I_{m_i},\quad C_i^{\mathrm{T}}TC_{i+1}=0,\quad \sum_{i=1}^{p}m_i=N\end{aligned}\right\}. \tag{3}$$

Comparison with LAPACK and DMM (sequential codes)





Parallel MDD code (G. Bencteux, EDF) :

5 million atom polyethylen chain , STO-3G (17.5×10^6 AO)
solution of the linear subproblem in 60 minutes on 1024 processors

1. Our approach (exact decomposition of the energy, localization of the constraints) provides a general framework for constructing efficient, variational, linear scaling, domain decomposition algorithms

2. We have demonstrated the efficiency of this general strategy by proposing a multilevel domain decomposition algorithm (MDD) performing very well on a benchmark of linear molecules

3. The convergence properties of the MDD algorithm have been established in a simplified setting (G. Bencteux, E.C., W.W. Hager and C. Le Bris, submitted)

4. Relaxing the orthonormality constraints on the localized orbitals would further increase the performance of the MDD algorithm

5. The implementation of a 3D version of the MDD algorithm is a work in progress (G. Bencteux, EDF and Cermics, ANR Parmat)

2 - Density Functional Theory

Constrained optimization formulation of the non-interacting model

For non-interacting electrons, the ground state energy and density can be obtained by solving

$$\inf\left\{E^{\mathrm{NI}}(\Phi), \quad \Phi=(\phi_1,\cdots,\phi_N)\in(H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij}\right\}$$

$$E^{\mathrm{NI}}(\Phi)=\sum_{i=1}^N\langle\phi_i|h|\phi_i\rangle=\sum_{i=1}^N\frac{1}{2}\int_{\mathbb{R}^3}|\nabla\phi_i|^2+\int_{\mathbb{R}^3}\rho_\Phi V^{\mathrm{ne}}$$

$$V^{\mathrm{ne}}(\mathbf{r})=-\sum_{k=1}^M\frac{z_k}{|\mathbf{r}-\mathbf{R}_k|} \qquad \rho_\Phi(\mathbf{r})=\sum_{i=1}^N|\phi_i(\mathbf{r})|^2$$

The case of interacting electrons

In the Kohn-Sham model, the ground state energy and density are obtained by solving

$$\inf \left\{ E^{\mathrm{KS}}(\Phi), \quad \Phi = (\phi_1, \cdots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$E^{\mathrm{KS}}(\Phi) = \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_\Phi V^{\mathrm{ne}} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\Phi(\mathbf{r}) \rho_\Phi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + E_{\mathrm{xc}}[\rho_\Phi]$$

$$V^{\mathrm{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \qquad \rho_\Phi(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

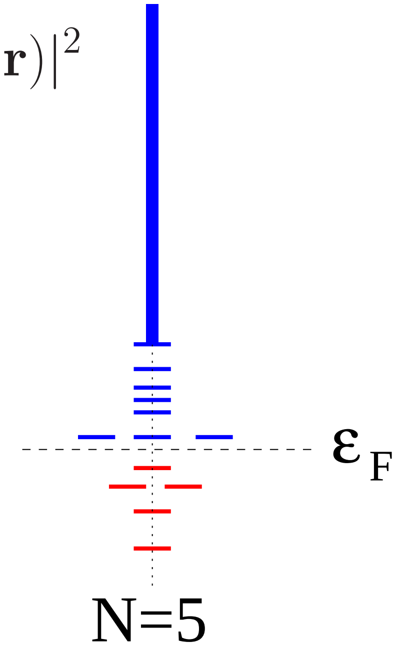
E_{xc} : exchange-correlation functional

Hohenberg-Kohn theorem : existence of an exact XC functional

Prototypical approximate XC functional : $E_{\mathrm{xc}}^{\mathrm{X}\alpha}[\rho] = -C_{\mathrm{X}} \int_{\mathbb{R}^3} \rho^{4/3}(\mathbf{r}) \, d\mathbf{r}$

Kohn-Sham equations ('insulating' case)

$$\left\{\begin{array}{l}
\gamma^0 = \displaystyle\sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| = 1_{(-\infty,\varepsilon_{\rm F}]}(H_{\rho^0}), \qquad \rho^0(\mathbf{r}) = \gamma^0(\mathbf{r},\mathbf{r}) = \displaystyle\sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \\[2ex]
H_{\rho^0}\phi_i = \varepsilon_i \phi_i \\[2ex]
\displaystyle\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \\[2ex]
\varepsilon_1 < \varepsilon_2 \leq \cdots \leq \varepsilon_N \quad \textbf{lowest } N \textbf{ eigenvalues of } H_{\rho^0} \\[2ex]
H_{\rho^0} = -\dfrac{1}{2}\Delta + V^{\rm KS}_{\rho^0}, \qquad V^{\rm KS}_{\rho^0} = V^{\rm ne} + \rho^0 \star |\cdot|^{-1} - \dfrac{4}{3} C_{\rm X} {\rho^0}^{1/3}
\end{array}\right.$$



$\longrightarrow$ Nonlinear eigenvalue problem

Mathematical and numerical analysis of the models arising in DFT

1. Proof of existence of a solution for neutral and positively charged systems
   (a) for LDA : $E_{\rm xc}^{\rm LDA}(\rho) = \int_{\mathbb{R}^3} e_{\rm xc}(\rho(\mathbf{r}))\, d\mathbf{r}$ (Le Bris 1993)
   (b) for GGA : $E_{\rm xc}^{\rm GGA}(\rho) = \int_{\mathbb{R}^3} e_{\rm xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))\, d\mathbf{r}$ but only for two electron systems (Anantharaman, E.C., submitted)

2. Construction and proof of convergence of some simple SCF algorithms (E.C., Le Bris, 2000-2003). A priori error estimates for Kohn-Sham LDA (E.C., Chakir, Maday, ongoing work)

3. Thermodynamical limits with $E_{\rm xc}(\rho) = 0$: perfect crystal (Catto, Le Bris, Lions 1998), crystals with local defects (E.C., Deleurence, Lewin, 2008)

4. A lot of work remains to be done !

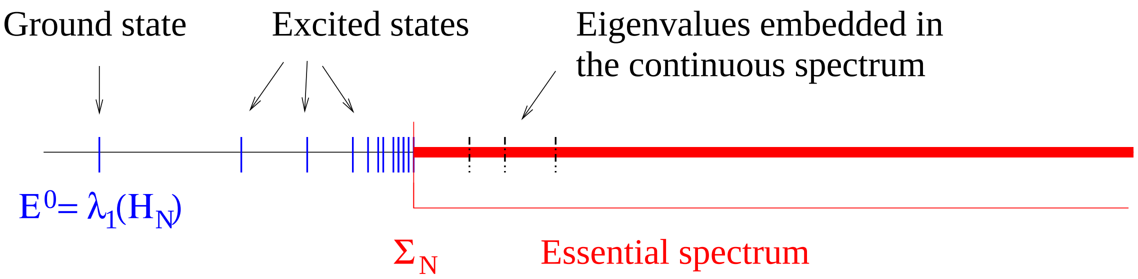
3 - Quantum Monte Carlo

Spectrum of the N-body Hamiltonian (operating on $\mathcal{H}_e = \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3)$)

$$H_N = -\sum_{i=1}^{N} \frac{1}{2}\Delta_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1\le i<j\le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad = \quad -\frac{1}{2}\Delta + V$$

If $Z = \sum_{k=1}^{M} z_k \geq N$ **(neutral or positively charged system),**

- $\sigma_{\mathrm{ess}}(H_N) = [\Sigma_N, +\infty)$ **with** $\Sigma_N < 0$ **if** $N \geq 2$ **and** $\Sigma_1 = 0$ **;**
- H_N **has an infinite sequence of finite multiplicity eigenvalues** $E^0 = \lambda_1(H_N) \leq \lambda_2(H_N) \leq \lambda_3(H_N) \leq \cdots$ **converging to** Σ_N



Notations :

- Electronic ground state (supposed to be non-degenerate)

$$H_N \Psi^0 = E^0 \psi^0 \qquad\qquad E^0 = \lambda_1(H_N)$$

- Let $\gamma = \lambda_2(H_N) - \lambda_1(H_N) > 0$
- Let Ψ_I be a trial wavefunction, relatively close to Ψ_0 for which the local fields

$$b(x) = \frac{\nabla \Psi_I(x)}{\Psi_I(x)} \qquad \text{and} \qquad E_L(x) = \frac{(H_N \Psi_I)(x)}{\Psi_I(x)} = -\frac{1}{2}\frac{\Delta \Psi_I(x)}{\Psi_I(x)} + V(x)$$

are not too difficult to compute (finite sum of Slater determinants)

Let us consider the **parabolic** (imaginary time Schrödinger) equation

$$\begin{cases} \frac{\partial \phi}{\partial t} = -H_N \phi = \frac{1}{2}\Delta\phi - V\phi \\ \phi(0,x) = \Psi_I(x) \end{cases} \tag{4}$$

and

$$E(t) = \frac{(H_N \Psi_I, \phi(t))_{L^2}}{(\Psi_I, \phi(t))_{L^2}}. \tag{5}$$

One has

$$0 \ \leq \ E(t) - E^0 \ \leq \ \frac{\left((H_N\Psi_I, \Psi_I)_{L^2} - E^0\right)}{(\Psi^0, \Psi_I)_{L^2}^2} \exp(-\gamma t)$$

Diffusion Monte Carlo : simulation of (4)-(5) with probabilistic methods using variance reduction techniques (importance sampling).

Set $f_1(t,x) = \Psi_I(x)\phi(t,x)$. A simple calculation shows that

$$E(t) = \frac{(H_N\Psi_I, \phi(t))_{L^2}}{(\Psi_I, \phi(t))_{L^2}} = \frac{\displaystyle\int_{\mathbb{R}^3} (H_N\Psi_I)(x)\,\phi(t,x)\,dx}{\displaystyle\int_{\mathbb{R}^3} \Psi_I(x)\phi(t,x)\,dx} = \frac{\displaystyle\int_{\mathbb{R}^3} E_L(x)\,f_1(t,x)\,dx}{\displaystyle\int_{\mathbb{R}^3} f_1(t,x)\,dx}$$

and that f_1 solves

$$\begin{cases} \dfrac{\partial f}{\partial t} = \dfrac{1}{2}\Delta f - \mathrm{div}\ (bf) - E_L f \\ \\ f(0,x) = \Psi_I^2(x), \end{cases}$$

with

$$b(x) = \frac{\nabla\Psi_I(x)}{\Psi_I(x)} \qquad \text{and} \qquad E_L(x) = \frac{(H_N\Psi_I)(x)}{\Psi_I(x)} = -\frac{1}{2}\frac{\Delta\Psi_I(x)}{\Psi_I(x)} + V(x)$$

Interpretation of the equation on f_1 in terms of stochastic process

$$\frac{\partial f}{\partial t} = \underbrace{\frac{1}{2}\Delta f}_{\text{diffusion}} - \underbrace{\operatorname{div}\,(bf)}_{\text{drift}} - \underbrace{E_L f}_{\text{birth-death}}$$

One can then try to approximate $E(t)$ by

$$E^{\mathrm{DMC}}(t) = \frac{\mathbb{E}\left(E_L(X_t)\ \exp\left(-\int_0^t E_L\left(X_s\right)\right)\ ds\right)}{\mathbb{E}\left(\ \exp\left(-\int_0^t E_L\left(X_s\right)\ ds\right)\right)}$$

where $(X_t)_{t\geq 0}$ is the stochastic process defined by

$$\begin{cases} dX_t = b\left(X_t\right)\ dt + dW_t \\ X_0 \sim \Psi_I^2. \end{cases}$$

With B. Jourdain et T. Lelièvre, we have proved the following results (M3AS 2006) : under some technical assumptions,

1. Because of the singularity of the drift $b(x) = \dfrac{\nabla \Psi_I(x)}{\Psi_I(x)}$, the trajectories defined by

$$\begin{cases} dX_t^x = b\left(X_t^x\right)\, dt + dW_t \\ X_0^x = x \end{cases}$$

cannot cross the nodal surfaces $\Psi_I^{-1}(0)$.

The random variable X_t^x has a density $p(t,x,y)$ and the function

$$(x,y) \quad \longmapsto \quad \Psi_I(x)^2 p(t,x,y)$$

is symmetric.

2. It holds

$$E(t) = \frac{\displaystyle\int_{\mathbb{R}^3} E_L(x)\, f_1(t,x)\, dx}{\displaystyle\int_{\mathbb{R}^3} f_1(t,x)\, dx} \qquad E^{\mathrm{DMC}}(t) = \frac{\displaystyle\int_{\mathbb{R}^3} E_L(x)\, f_2(t,x)\, dx}{\displaystyle\int_{\mathbb{R}^3} f_2(t,x)\, dx}$$

where f_1 and f_2 are two different weak solutions of

$$\begin{cases} \dfrac{\partial f}{\partial t} = \dfrac{1}{2}\Delta f - \mathrm{div}\ (bf) - E_L f \\[2ex] f(0,x) = \Psi_I^2(x), \end{cases}$$

More precisely

$$f_1(t,x) = \Psi_I(x)\,\phi(t,x) \qquad \begin{cases} \dfrac{\partial\phi}{\partial t} = \dfrac{1}{2}\Delta\phi - V\phi \\[2ex] \phi(0,x) = \Psi_I(x), \end{cases}$$

$$f_2(t,x) = \Psi_I(x)\,\phi_2(t,x) \qquad \begin{cases} \dfrac{\partial\phi_2}{\partial t} = \dfrac{1}{2}\Delta\phi_2 - V\phi_2 \\[2ex] \phi_2(0,x) = \Psi_I(x) \\[2ex] \phi_2(t,x) = 0 \qquad \textbf{on } \Psi_I^{-1}(0) \end{cases}$$

3. The function $E^{\mathrm{DMC}}(t)$ converges when t goes to $+\infty$ to

$$\inf\left\{\langle\Psi, H_N\Psi\rangle, \quad \Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3), \quad \|\Psi\|_{L^2} = 1, \quad \Psi = 0 \text{ on } \Psi_I^{-1}(0)\right\}.$$

which is an upper bound of the exact ground state energy

$$E^0 = \inf\left\{\langle\Psi, H_N\Psi\rangle, \quad \Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3), \quad \|\Psi\|_{L^2} = 1\right\}.$$

This mathematical analysis points out one of the main limitations of the Diffusion Monte Carlo method, well known by its users : using an importance function Ψ_I introduces a systematic error, except in the peculiar case when the nodal surfaces of Ψ^0 and Ψ_I exactly coincide

Mathematical and numerical challenges :

1. Analysis and improvement of the existing numerical schemes (stochastic particle methods)
2. Computation of interatomic forces
3. How to go beyond the fixed node approximation ?

The (Fixed Node) Diffusion Monte Carlo method remains to date the reference method for accurate Quantum Monte Carlo simulations on large systems

$S_0 \rightarrow S_2$

$\pm$