An overview of numerical techniques for the simulation of quantum systems

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Numerical simulations: the context

• Electronic structure models used by thousands of physicists, chemists, biologists, materials scientists, nanoscientists on a daily basis

- over 10,000 papers a year and growing;
- about 15% of the resources available in scientific computing centers;
- W. Kohn and J. Pople: 1998 Nobel prize in Chemistry for their contributions to electronic structure calculation methods
- Numbers of hits (April 2014) for "Density Functional Theory"
  - in google scholar: 2,630,000
  - in mathscinet: 251

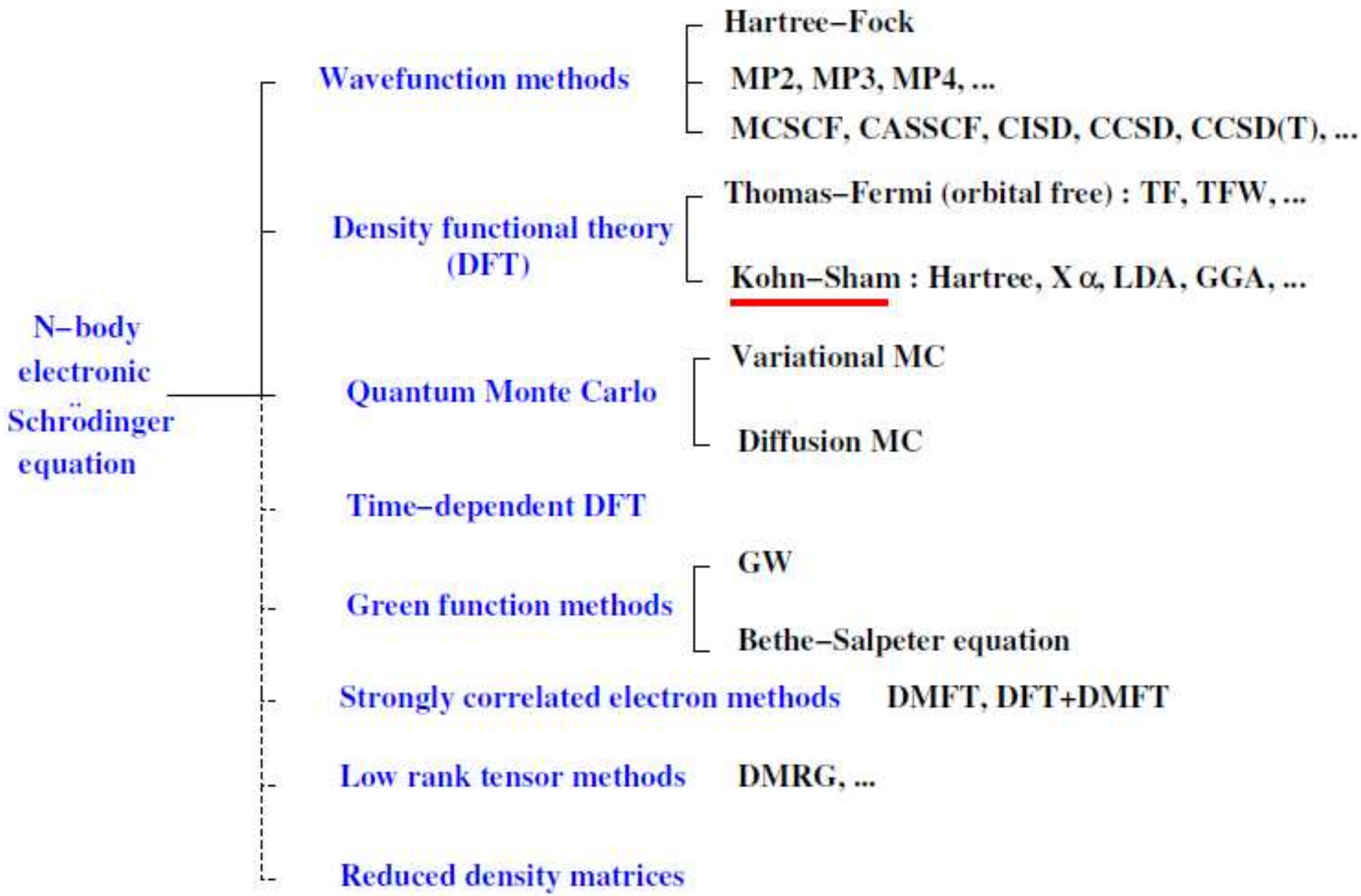
Most of these models are completely, or largely, unexplored from mathematical and numerical points of view.

Numerical simulations: some orders of magnitude

- **Main challenge in first principle molecular simulation:**
  - solve numerically the electronic Schrödinger equation (3N dim. PDE)
  - ...up to chemical accuracy

- **What chemical accuracy can mean...**
  - 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)
  - energy of a hydrogen bond: $\sim$ 0.003 ha (2 kcal/mol)
  - $k_B T$ 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}=29,470 MHz)

Numerical methods: some zoology



Outline

- **Density functional theory**
  - General formulation for finite systems
  - Kohn-Sham approximation
  - Models for crystals
- **Numerical solution of the Kohn-Sham equations**
  - Discretization of effective periodic operators
  - Solution of the nonlinear Euler-Lagrange equations
- **Numerical analysis**
  - Discretization errors for nonlinear eigenvalue problems
  - Open issues and perspectives

Density-functional theory

The Levy-Lieb approach (1)

- Hamiltonian of N electrons in the absence of external potential

$$H_0^N = \sum_{i=1}^{N} -\frac{1}{2}\Delta_{x_i} + \sum_{1\leqslant i<j\leqslant N} \frac{1}{|x_i - x_j|}$$

- Ground state energy: minimization over electronic density

$$\rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \ldots, x_N)|^2 \, dx_2 \ldots dx_N$$

using the following equalities

$$\begin{aligned} E(V) &= \inf_{\psi\in\bigwedge_{i=1}^N H^1(\mathbb{R}^3),\, \|\psi\|=1} \left\langle \psi, \left(H_0^N + \sum_{i=1}^{N} V(x_i) \right) \psi \right\rangle \\ &= \inf_{\psi\in\bigwedge_{i=1}^N H^1(\mathbb{R}^3),\, \|\psi\|=1} \left\{ \langle \psi, H_0\psi \rangle_{L^2(\mathbb{R}^{3N})} + \int_{\mathbb{R}^3} \rho_\psi V \right\} \\ &= \inf_{\rho\in\mathcal{R}_N} \left\{ F_{\mathrm{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V \right\} \end{aligned}$$

The Levy-Lieb approach (2)

- N-representable densities $\mathcal{R}_N = \left\{ \rho \geqslant 0,\ \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \displaystyle\int_{\mathbb{R}^3} \rho = N \right\}$
- Levy-Lieb functional: "universal" functional of ρ

$$F_{\mathrm{LL}}(\rho) = \inf \left\{ \langle \psi, H_0^N \psi \rangle_{L^2(\mathbb{R}^{3N})} \;\middle|\; \psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3),\ \|\psi\| = 1,\ \rho_\psi = \rho \right\}$$

- Mixed-state approach: convex, lower semicontinuous functional

$$F_{\mathrm{L}}(\rho) = \inf_{\Gamma \in \mathcal{D}_N,\, \rho_\Gamma = \rho} \left\{ \mathrm{Tr}_{L^2(\mathbb{R}^{3N})} \left(H_0^N \Gamma \right) \right\} \quad (= +\infty \text{ if } \rho \notin \mathcal{R}_N)$$

with $\mathcal{D}_N = \left\{ 0 \leqslant \Gamma = \Gamma^* \leqslant 1,\ \mathrm{Tr}_{L^2(\mathbb{R}^{3N})}(\Gamma) = 1,\ \mathrm{Tr}_{L^2(\mathbb{R}^{3N})}(-\Delta\Gamma) < \infty \right\}$

$$E(V) = \inf_{\rho \in L^1 \cap L^3(\mathbb{R}^3)} \left\{ F_{\mathrm{L}}(\rho) + \int_{\mathbb{R}^3} \rho V \right\}, \qquad V \in L^{3/2} + L^\infty(\mathbb{R}^3)$$

E. Lieb, Density functional theory for Coulomb systems, *Int. J. Quant. Chem.* **24** (1983)

Approximation of F_{L} (1)

- No explicit expression for F_{L}... Approximations needed:
  - Orbital-free models: reference = homogeneous electron gas
  - Kohn-Sham model: reference = non-interacting electrons

- Approximation of the kinetic part: Janak functional

$$
\begin{aligned}
T_{\mathrm{J}}(\rho) &= \inf_{\Gamma \in \mathcal{D}_N,\, \rho_\Gamma = \rho} \left\{ \mathrm{Tr}_{L^2(\mathbb{R}^{3N})} \left(-\frac{1}{2} \Delta \Gamma \right) \right\} \\
&= \inf_{\gamma \in \mathcal{C}_N,\, \rho_\gamma = \rho} \left\{ \mathrm{Tr}_{L^2(\mathbb{R}^{3})} \left(-\frac{1}{2} \Delta \gamma \right) \right\} \\
&= \inf_{\substack{\{\phi_i\} \subset H^1(\mathbb{R}^3) \\ 0 \leqslant n_i \leqslant 1}} \left\{ \sum_{i=1}^{+\infty} \frac{1}{2}\, n_i \int_{\mathbb{R}^3} |\nabla \phi_i|^2,\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij},\ \sum_{i=1}^{+\infty} n_i |\phi_i|^2 = \rho \right\}
\end{aligned}
$$

where N-representable density matrices (operators on $L^2(\mathbb{R}^3)$) are

$$
\mathcal{C}_N = \left\{ 0 \leqslant \gamma = \gamma^* \leqslant 1,\ \mathrm{Tr}_{L^2(\mathbb{R}^3)}(\gamma) = N,\ \mathrm{Tr}_{L^2(\mathbb{R}^3)}(-\Delta \gamma) < \infty \right\}
$$

Approximation of F_{L} (2)

- Classical Coulomb interation $J(\rho) = \displaystyle\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy$

Exchange-correlation functional

$$E_{\mathrm{xc}}(\rho) = F_{\mathrm{L}}(\rho) - T_{\mathrm{J}}(\rho) - J(\rho)$$

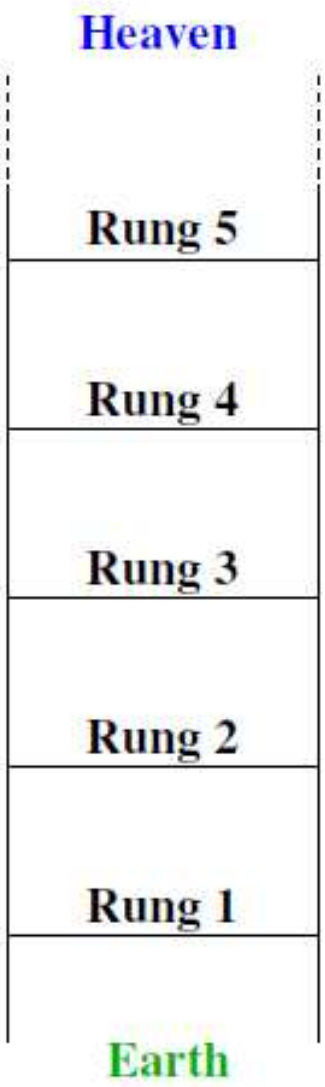
- In practice, $|E_{\mathrm{xc}}(\rho)| \ll T_{\mathrm{J}}(\rho), J(\rho)$
- Simple example: local density approximation (LDA)

$$E_{\mathrm{xc}}(\rho) = \int_{\mathbb{R}^3} e_{\mathrm{xc}}(\rho(x))\,dx, \qquad e_{\mathrm{xc}}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3} + e_{\mathrm{c}}(\rho)$$

where $e_{\mathrm{xc}}(\overline{\rho})$ is the exchange-correlation energy in a homogeneous electron gas (Quantum Monte Carlo computations + fit + asymptotics)

- We will consider this example in the sequel, and denote $v_{\mathrm{xc}} = e'_{\mathrm{xc}}$

A whole zoo of functionals...



Exact exchange–correlation functional

explicit functionals of the Kohn-Sham occupied and unoccupied orbitals
SAOP, ...

explicit functionals of the density matrix (ex: hybrid functionals)
1/2 & 1/2, B3P, B3LYP, PBE0, O3LYP, X3LYP, mPW1PW91, BMK, PWB6K, B1B95, PW6B95, TPS

meta-GGA (explicit in $\rho(\mathrm{r})$, $\nabla\rho(\mathrm{r})$, $\Delta\rho(\mathrm{r})$ and $\tau(\mathrm{r}) = \sum_{i=1}^{N} |\nabla\phi_i(\mathrm{r})|^2$)
BR89, tauPBE, VSXC, BB95, TPSS, PBS00, LAP, ...

GGA (explicit in $\rho(\mathrm{r})$ and $\nabla\rho(\mathrm{r})$)
SIC, PW91, BLYP, mPWPW91, PBE, revPBE, G96LYP, HCTH, OPTX, EDF1, ...

LDA (explicit in $\rho(\mathrm{r})$)

The Kohn-Sham model for crystals (1)

- **Thermodynamic limit**, periodic nuclear density $\rho_{\rm per}^{\rm nuc}$, lattice $\mathcal{R} \simeq (a\mathbb{Z})^3$ with unit cell Γ, reciprocal lattice $\mathcal{R}^* \simeq \left(\frac{2\pi}{a}\mathbb{Z}\right)^3$ with unit cell Γ^*
- **Bloch-Floquet transform:** unitary $L^2(\mathbb{R}^3) \to \int_{\Gamma^*}^{\oplus} L^2_{\rm per}(\Gamma)\, dq$

$$f_q(x) = \sum_{R\in\mathcal{R}} f(x+R)\, \mathrm{e}^{-\mathrm{i}q\cdot(x+R)} = \frac{(2\pi)^{3/2}}{|\Gamma|} \sum_{K\in\mathcal{R}^*} \widehat{f}(q+K)\, \mathrm{e}^{\mathrm{i}K\cdot x}$$

  - Any operator commuting with the spatial translations τ_R $(R \in \mathcal{R})$ can be decomposed as $(Af)_q = A_q f_q$, and $\sigma(A) = \overline{\bigcup_{q\in\Gamma^*} \sigma(A_q)}$
  - Bloch matrices: $A_{K,K'}(q) = \langle e_K, A_q e_{K'} \rangle_{L^2_{\rm per}(\Gamma)}$, $e_K(x) = |\Gamma|^{-1/2} \mathrm{e}^{\mathrm{i}K\cdot x}$

$$\mathcal{F}(Av)(q+K) = \sum_{K'\in\mathcal{R}^*} A_{K,K'}(q) \mathcal{F}v(q+K')$$

[CLL01] I. Catto, C. Le Bris, and P.-L. Lions, *Ann. I. H. Poincaré-An*, 2001
[CDL08] E. Cancès, A. Deleurence and M. Lewin, *Commun. Math. Phys.*, 2008

The Kohn-Sham model for crystals (2)

Nonlinear eigenvalue problem

$$\begin{cases} \gamma^0_{\rm per} = 1_{(-\infty,\varepsilon_{\rm F}]}(H^0_{\rm per}), \qquad \rho^0_{\rm per} = \rho_{\gamma^0_{\rm per}}, \\ H^0_{\rm per} = -\dfrac{1}{2}\Delta + V^0_{\rm per}, \qquad V^0_{\rm per} = W^0_{\rm per} + v_{\rm xc}(\rho^0_{\rm per}), \\ -\Delta W^0_{\rm per} = 4\pi(\rho^0_{\rm per} - \rho^{\rm nuc}_{\rm per}), \qquad \displaystyle\int_\Gamma \rho^0_{\rm per} = \int_\Gamma \rho^{\rm nuc}_{\rm per} = N \end{cases}$$

More explicit expressions using the Bloch decomposition

$$\left(H^0_{\rm per}\right)_q = -\frac{1}{2}\Delta - {\rm i}q\cdot\nabla + \frac{|q|^2}{2} + V^0_{\rm per} = \sum_{n=1}^{+\infty} \varepsilon_{n,q} |u_{n,q}\rangle\langle u_{n,q}|$$

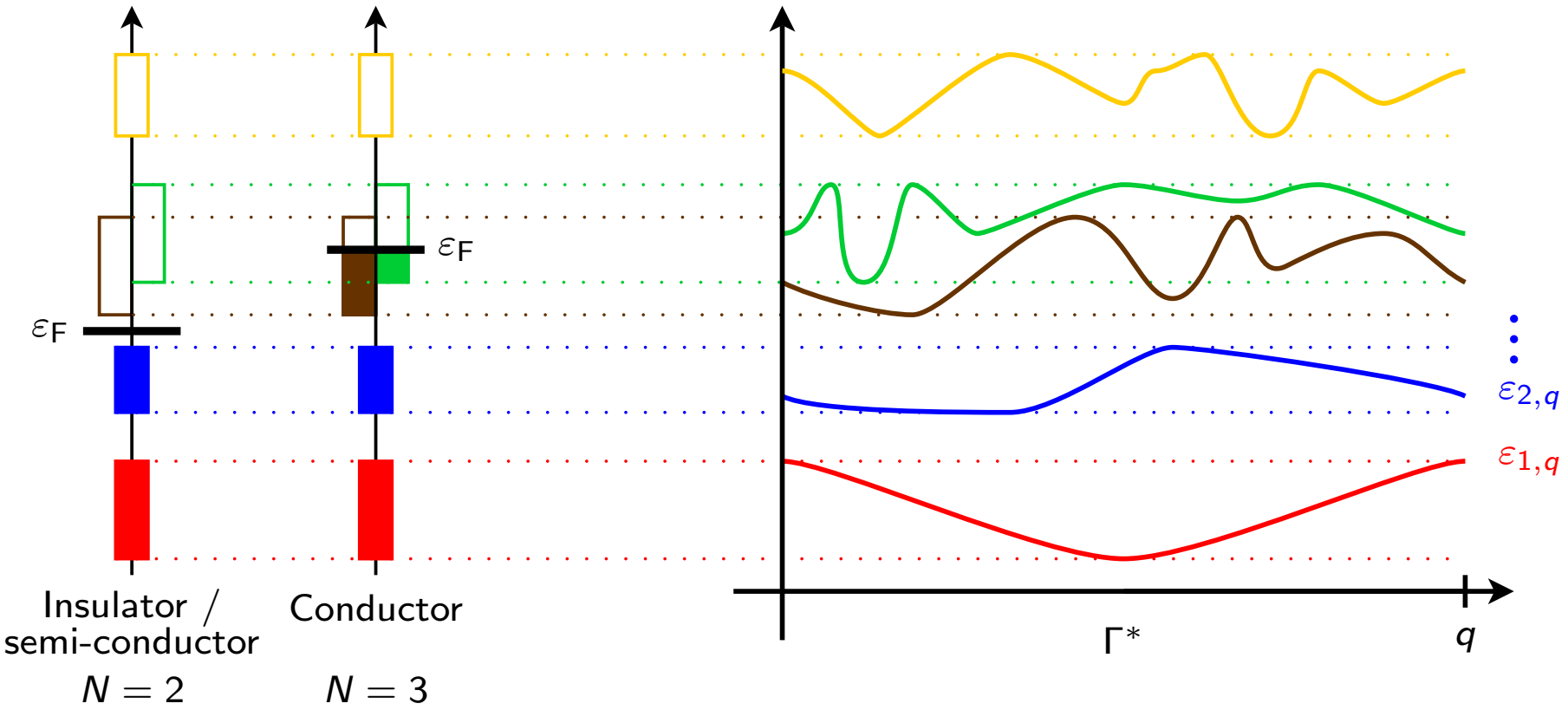
$$\left(\gamma^0_{\rm per}\right)_q = \sum_{n=1}^{+\infty} 1_{\{\varepsilon_{n,q}\leqslant\varepsilon_{\rm F}\}} |u_{n,q}\rangle\langle u_{n,q}|$$

Fermi level obtained from $N = \dfrac{1}{|\Gamma^*|}\displaystyle\sum_{n=1}^{+\infty} |\{q\in\Gamma^* \mid \varepsilon_{n,q}\leqslant\varepsilon_{\rm F}\}|$

The Kohn-Sham model for crystals (3)

The spectrum of the periodic Hamiltonian is composed of bands

$$\sigma(H) = \bigcup_{n\geq 1} \left[\Sigma_n^-, \Sigma_n^+\right], \qquad \Sigma_n^- = \min_{q\in\overline{\Gamma^*}} \varepsilon_{n,q}, \quad \Sigma_n^+ = \max_{q\in\overline{\Gamma^*}} \varepsilon_{n,q}$$



Numerical solution of the Kohn-Sham equations

Practical computation of the ground state: linear operator

- Consider a periodic operator $H = -\frac{1}{2}\Delta + V_{\mathrm{per}}$
- **Discretization of the Brillouin zone** with M points in Γ_M^* (symmetries)

$$\fint_{\Gamma^*} f(q)\,dq \simeq \sum_{q\in\Gamma_M^*} w_q\, f(q), \qquad \sum_{q\in\Gamma_M^*} w_q = 1$$

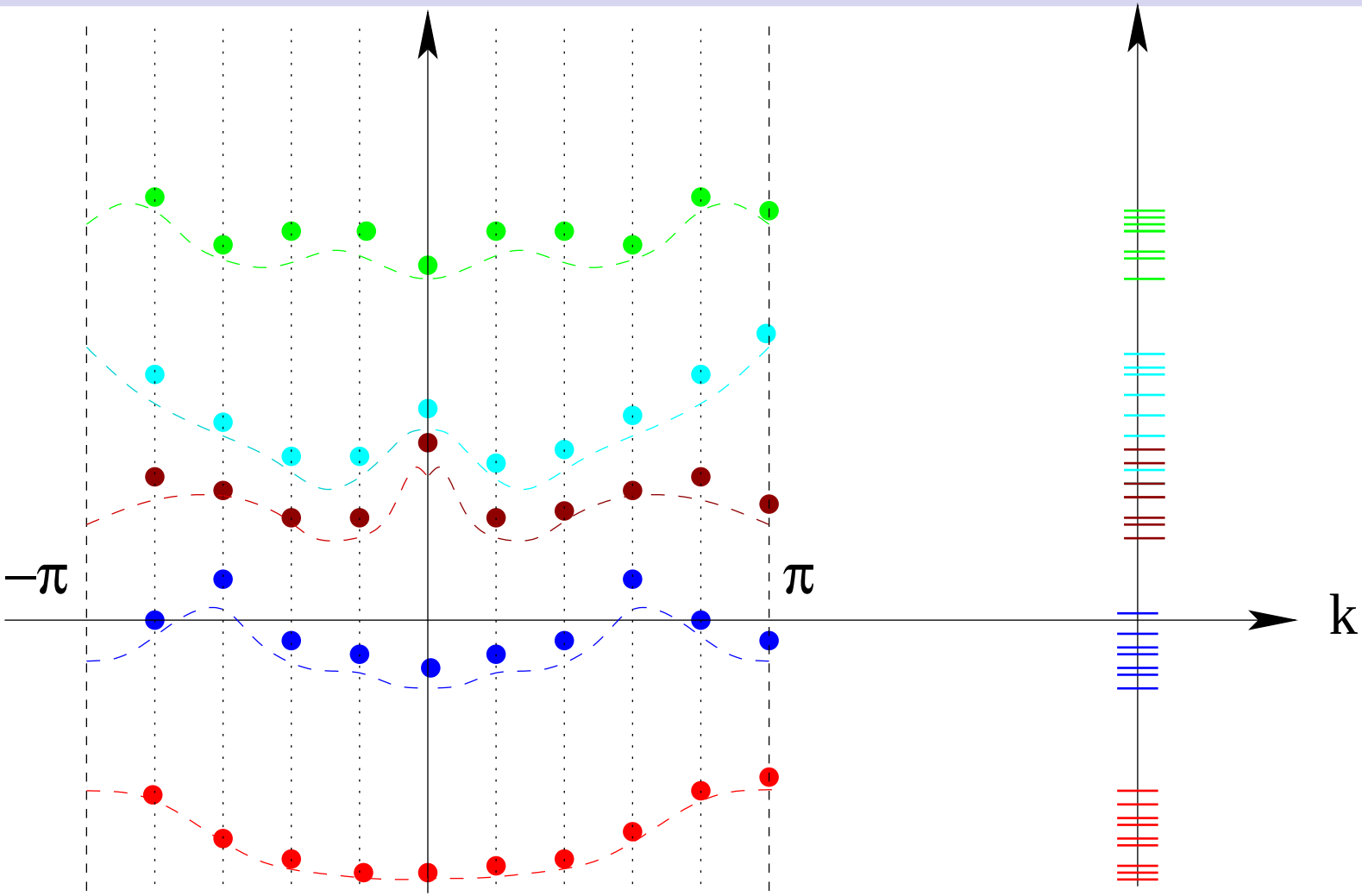
- **Galerkin discretization of the operator** H_q
  - Localized orbitals, wavelets, discontinuous Galerkin, ...
  - Planewaves $e_K(x) = |\Gamma|^{-1/2}\,\mathrm{e}^{-\mathrm{i}K\cdot x}$, energy cut-off $|K| \leqslant K_{\max}$
    $\rightarrow n_{\max}$ elements

$$[H_q]_{K,K'} = \langle e_K, H_q e_{K'}\rangle_{L^2_{\mathrm{per}}(\Gamma)} = \frac{1}{2}|K+q|^2\delta_{K,K'} + \fint_\Gamma V^0_{\mathrm{per}}(x)\mathrm{e}^{\mathrm{i}(K-K')\cdot x}\,dx$$

  - **Quadrature rules** needed to evaluate matrix elements (or FFT)

- Diagonalize the matrices $[H_q]_{K,K'}$ to obtain eigenvectors $\Psi_{n,q}^{K_{\max}} \in \mathbb{C}^{n_{\max}}$ and eigenvalues $\varepsilon_{n,q}^{K_{\max}}$

Discretization of the Brillouin zone



Construct $\gamma^0_{\mathrm{per}}(x,y) \simeq \displaystyle\sum_{q\in\Gamma^*_M} w_q \sum_{n=1}^{n_{\max}} \mathbf{1}_{\{\varepsilon^{K_{\max}}_{n,q}\leqslant\varepsilon_{\mathrm{F}}\}}\psi^{K_{\max}}_{n,q}(x)\overline{\psi^{K_{\max}}_{n,q}(y)}\,\mathrm{e}^{\mathrm{i}q\cdot(x-y)}$

Practical computation of the ground state: general topics

- **Pseudo-potentials:** Many flavors...
  - Core electrons not significantly affected by the chemical surrounding
  - Reduce the computational cost: only valence electrons
  - Smoother wavefunctions, less planewaves needed
  - Effective potential: modify $V_{\mathrm{per}}^{\mathrm{nuc}}$, add a non-local operator

- Solution of the nonlinear eigenvalue problem: **fixed-point iterations**
  - compute the potential V^n associated with ρ_{γ^n}
  - diagonalize the Hamiltonian $-\frac{1}{2}\Delta + V^n$
  - construct $\widetilde{\gamma}^{n+1}$ using the lowest energy eigenfunctions
  - obtain $\rho_{\gamma^{n+1}}$ by mixing ρ_{γ^n} and $\rho_{\widetilde{\gamma}^{n+1}}$
  - Some results from numerical analysis (Cancès/Lebris, Levitt)
- **Direct minimization** for large basis sets (planewaves)

- Other topic: fast resolution of linear subproblems (preconditioning, etc)

Elements of numerical analysis

E. Cancès, R. Chakir and Y. Maday, Numerical analysis of nonlinear eigenvalue problems, *J. Sci. Comput.* **45** (2010) 90-117

E. Cancès, R. Chakir and Y. Maday, Numerical analysis of the planewave discretization of orbital-free and Kohn-Sham models, *M2AN* **46** (2012) 341-388

Nonlinear eigenvalue problem

- Results for Kohn-Sham models quite technical $\rightarrow$ simplified model

Minimization problem

Domain $\Omega = (0, L)^d$, with $d = 1, 2, 3$

$$I = \inf \left\{ E(v),\ v \in H^1_0(\Omega),\ \int_\Omega v^2 = 1 \right\},$$

$$E(v) = \int_\Omega |\nabla v|^2 + \int_\Omega V|v|^2 + \frac{\mu}{2}\int_\Omega |v|^4, \qquad \mu > 0, \quad V \in L^2(\Omega)$$

- Properties
  - exactly two minimizers: u (with $u \geqslant 0$ in Ω) and $-u$
  - $\exists ! \lambda \in \mathbb{R}$ such that (λ, u) satisfies the nonlinear eigenvalue problem

$$-\Delta u + Vu + \mu u^3 = \lambda u, \qquad \|u\|_{L^2} = 1$$

  - $u \in H^2(\Omega) \hookrightarrow C^{0,\alpha}(\overline{\Omega})$ for some $\alpha > 0$ and $u > 0$ in Ω

Variational approximation

- Family of finite dimensional subspaces $(X_\delta)_{\delta>0}$ of $H_0^1(\Omega)$ with

$$\min\left\{\|u-u_\delta\|_{H^1},\ u_\delta\in X_\delta\right\}\xrightarrow[\delta\to 0^+]{}0$$

- Variational approximation $I_\delta=\inf\left\{E(v_\delta),\ v_\delta\in X_\delta,\ \int_\Omega v_\delta^2=1\right\}$
- At least one minimizer u_δ such that $(u_\delta,u)_{L^2}\geqslant 0$. Uniquess for δ small
- A priori error estimators in the linear case ($\mu=0$)

$$\|u_\delta-u\|_{H^1}\leqslant C\min_{v_\delta\in X_\delta}\|v_\delta-u\|_{H^1}$$

$$c\|u_\delta-u\|_{H^1}^2\leqslant E(u_\delta)-E(u)\leqslant C\|u_\delta-u\|_{H^1}^2$$

$$|\lambda_\delta-\lambda|\leqslant C\|u_\delta-u\|_{H^1}^2$$

I. Babuška and J. Osborn, *Eigenvalue problems*, in: Handbook of numerical analysis. Volume II (1991) 641-787

Proof for the linear case ($\mu = 0$)

- Find a solution of $-\Delta u + Vu = \lambda u$ with $\|u\|_{L^2} = 1$, λ minimal

$$a(u,v) = \int_\Omega \nabla u \cdot \nabla v + \int_\Omega Vuv, \qquad E(u) = a(u,u) = \lambda$$

- Approximate minimizer u_δ satisfies $\|u_\delta\|_{L^2} = 1$ and λ_δ minimal

$$\forall v_\delta \in X_\delta, \qquad a(u_\delta, v_\delta) = \lambda_\delta (u_\delta, v_\delta)_{L^2}$$

- Energy of the approximate minimizer $E(u_\delta) = a(u_\delta, u_\delta) = \lambda_\delta$
- Error estimate on the energies

$$\begin{aligned}
\lambda_\delta - \lambda = E(u_\delta) - E(u) &= a(u_\delta, u_\delta) - a(u,u) \\
&= a(u_\delta - u, u_\delta - u) + 2a(u, u_\delta) - 2a(u,u) \\
&= a(u_\delta - u, u_\delta - u) + 2\lambda(u, u_\delta)_{L^2} - 2\lambda(u,u)_{L^2} \\
&= a(u_\delta - u, u_\delta - u) - 2\lambda(1 - (u, u_\delta)_{L^2}) \\
&= a(u_\delta - u, u_\delta - u) - \lambda \|u_\delta - u\|_{L^2}^2
\end{aligned}$$

- Conclusion: $0 \leqslant \lambda_\delta - \lambda = E(u_\delta) - E(u) \leqslant C \|u_\delta - u\|_{H^1}^2$

A priori error estimators in the nonlinear case

- Nonlinear setting $\mu > 0$: general results

A priori error estimates

$$\|u_\delta - u\|_{H^1} \leqslant C \min_{v_\delta \in X_\delta} \|v_\delta - u\|_{H^1} \xrightarrow[\delta \to 0^+]{} 0$$

$$c\|u_\delta - u\|_{H^1}^2 \leqslant E(u_\delta) - E(u) \leqslant C\|u_\delta - u\|_{H^1}^2$$

$$|\lambda_\delta - \lambda| \leqslant C\|u_\delta - u\|_{H^1}^2 + \mu \left| \int_\Omega u_\delta^2 (u_\delta + u)(u_\delta - u) \right|$$

$$\|u_\delta - u\|_{L^2}^2 \leqslant C\|u_\delta - u\|_{H^1} \min_{\psi_\delta \in X_\delta} \|\psi_{u_\delta - u} - \psi_\delta\|_{H^1}$$

- For any $w \in L^2(\Omega)$, the element ψ_w is the unique solution in

$$u^\perp = \left\{ v \in H_0^1(\Omega) \;\middle|\; (v,u)_{L^2} = 0 \right\}$$

to the adjoint problem

$$\forall v \in u^\perp, \quad \left\langle \left(E''(u) - \lambda\right) \psi_w, v \right\rangle_{H^{-1}, H_0^1} = (w,v)_{L^2}$$

Aubin-Nitsche argument for a simple linear elliptic equation

- **Aim:** obtain good estimates on the L^2 norm of $u - u_\delta$
- General setting
  - a bilinear, continuous, coercive on $H_0^1(\Omega) \times H_0^1(\Omega)$
  - L linear, continuous on $H_0^1(\Omega)$
  - unique solutions $u \in H_0^1(\Omega)$ and $u_\delta \in X_\delta$ of

$$\forall v \in H_0^1(\Omega),\ a(u,v) = L(v), \qquad \forall v_\delta \in X_\delta,\ a(u_\delta, v_\delta) = L(v_\delta)$$

- Adjoint problem with corrector $u - u_\delta$ on the right-hand side

$$\exists! \psi \in H_0^1(\Omega) \quad \text{such that} \quad \forall v \in H_0^1(\Omega), \quad a(v,\psi) = (u_\delta - u, v)_{L^2}$$

- Then, introducing the projection $\pi_\delta \psi$ of ψ onto X_δ, in the H^1 norm:

$$\begin{aligned} \|u_\delta - u\|_{L^2}^2 &= a(u_\delta - u, \psi) = a(u_\delta - u, \psi - \pi_\delta \psi) \\ &\leqslant C \|u_\delta - u\|_{H^1} \|\psi - \pi_\delta \psi\|_{H^1} \\ &= C \|u_\delta - u\|_{H^1} \min_{\psi_\delta \in X_\delta} \|\psi - \psi_\delta\|_{H^1} \end{aligned}$$

Planewave discretization

- Periodic boundary conditions on $\Omega = (0, 2\pi)^d$ and V periodic

$$I = \inf \left\{ E(v),\ v \in H^1_{\#}(\Omega),\ \int_\Omega |v|^2 = 1 \right\}$$

- Variational space $V_N = \left\{ \sum_{k \in \mathbb{Z}^d,\, |k| \leqslant N} c_k e_k \,\middle|\, c_{-k} = c_k^* \right\}$ with $e_k(x) = \dfrac{\mathrm{e}^{\mathrm{i}k\cdot x}}{(2\pi)^{d/2}}$

- $u_N = \operatorname{argmin} \left\{ E(v_N),\ v \in V_N,\ \int_\Omega |v_N|^2 = 1 \right\}$ with $(u_N, u)_{L^2} \geqslant 0$

- **Strategy for better a priori estimates for $|\lambda - \lambda_\delta|$:**
  - prove regularity of u, u_δ (assumptions on V and nonlinearity)
  - bound $\displaystyle\int_\Omega w_{u,u_\delta}(u - u_\delta)$ by $\|u - u_\delta\|_{H^{-r}_{\#}} = \sup_{w \neq 0} \frac{1}{\|w\|_{H^r_{\#}}} \int_\Omega w(u - u_\delta)$
  - Aubin-Nitsche like treatment of $\displaystyle\int_\Omega w(u - u_\delta)$

Spectral approximation

Convergence result

Assume that $V \in H^\sigma_\#(\Omega)$ for some $\sigma > d/2$. Then $(u_N)_{N\in\mathbb{N}}$ converges to u in $H^{\sigma+2}_\#(\Omega)$ and there exists $0 < c \leqslant C < \infty$ such that for all $N \in \mathbb{N}$,

$$\|u_N - u\|_{H^s_\#} \leqslant \frac{C}{N^{\sigma+2-s}} \qquad \text{for all } -\sigma \leqslant s < \sigma + 2$$

$$c\|u_N - u\|^2_{H^1_\#} \leqslant E(u_N) - E(u) \leqslant C\|u_N - u\|^2_{H^1_\#}$$

$$|\lambda_N - \lambda| \leqslant \frac{C}{N^{2(\sigma+1)}}$$

- Note that $|\lambda_N - \lambda|$ is of the same order as $\|u_N - u\|^2_{H^1_\#}$
- Results for the pseudo-spectral approximation (numerical integration)
- Results for the planewave approximation of Kohn-Sham: convergence rate depends in particular on the regularity of the pseudo-potential

Some open issues and perspectives

A lot remains to be done!

- Numerical analysis (compare with e.g. computational fluid dynamics)
  - A priori error estimations: discretization of the Brillouin zone (metals), numerical quadratures, ...
  - A posteriori error estimators: adaptivity and load balancing
  - More efficient methods: "linear scaling"
- For some models, even the theoretical study is missing!
  - Post-DFT methods such as GW for instance
  - Nonlinear models of electronic transport