

Mathematical quantum chemistry . . .

. . . and how to apply it in a periodic setting

Michael F. Herbst

Materials team, CERMICS, École des Ponts ParisTech

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→ https://michael-herbst.com/talks/2019.11.07_enpc_math_qchem.pdf

Contents

- 1 Why care about electronic structures?
- 2 Describing chemistry
- 3 Plane-wave density-functional theory

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Why care about electronic structures?

- Electrons glue the world together
- Electrons keep the world apart

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Materials and semiconductors



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Chemical and pharmaceutical industry



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Why “computer chemistry”?

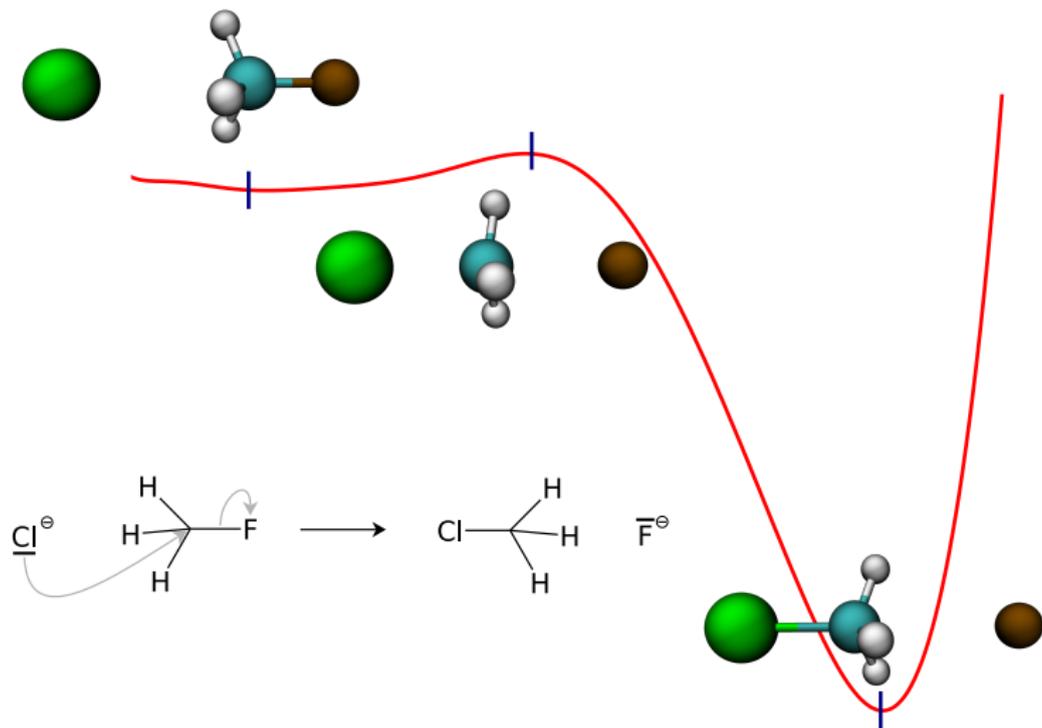
- Experiments are expensive (money, people, time)
 - 1 droplet water¹: $1.7 \cdot 10^{21}$ particles
 - Experiments only measure averages
 - Sometimes hard to link to physical laws
- ⇒ Cooperative research of experiment and theory
- ⇒ Standard practice in industry and research

¹Assume 0.05 ml.

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Describing chemistry



Electronic structure theory

- N electrons in chemical system
- Spectrum of $\hat{\mathcal{H}}_N$

$$\hat{\mathcal{H}}_N \equiv \sum_{i=1}^N -\frac{1}{2}\Delta_i + \sum_{i=1}^N \hat{\mathcal{V}}_{\text{Nuc},i} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{r_{ij}}$$

with

$$-\frac{1}{2}\Delta_i$$

Kinetic energy of electrons

$$\hat{\mathcal{V}}_{\text{Nuc},i}$$

Electron-nuclear interaction

$$\frac{1}{r_{ij}}$$

Electron-electron interaction

Schrödinger operator domain

- N electrons $\Rightarrow 3N$ coords
- Electrons are fermions:

$$D(\hat{\mathcal{H}}_N) = H^2(\mathbb{R}^{3N}, \mathbb{C}) \cap \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C})$$

where

$$\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}) \equiv \text{span} \left\{ \psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_N \mid \right. \\ \left. \psi_i \in L^2(\mathbb{R}^3, \mathbb{C}) \forall i = 1, \dots, N \right\}$$

- **One-particle** function ψ_i (orbitals)

Variational principle

- HVZ theorem: (Usually) $\hat{\mathcal{H}}_N$ has discrete lowest eigenvalue
- Ritz-Galerkin / Courant-Fischer
- Ground state (lowest eigenvalue):

$$E_0 \leq \min_{\Phi \in Q(\hat{\mathcal{H}}_N)} \mathcal{E}(\Phi) = \min_{\Phi \in Q(\hat{\mathcal{H}}_N)} \frac{\langle \Phi | \hat{\mathcal{H}} \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

with the Schrödinger form domain

$$Q(\hat{\mathcal{H}}_N) = \bigwedge^N H^1(\mathbb{R}^3, \mathbb{C})$$

- Derivatives of E_0 give properties
- So just discretise $Q(\hat{\mathcal{H}}_N)$ and we're done?

Curse of dimensionality

$$E_0 \leq \min_{\Phi \in Q(\hat{\mathcal{H}}_N)} \frac{\langle \Phi | \hat{\mathcal{H}} \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

- $\langle \cdot | \cdot \rangle$ is inner product in $H^1(\mathbb{R}^{3N})$
- ⇒ Involves integral over $3N$ -dim. space
- Assume 2 quadrature points only per dim.
- Chloromethane: $N = 26 \Rightarrow 2^{78} \approx 3 \cdot 10^{23}$ quadrature points
- ⇒ Finished in 1 year:
 - We have to be clever in choosing a basis

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The full N -particle basis (Full-CI, FCI)

- Want suitable N -particle basis

$$\mathbb{B}_N \subset \bigwedge^N H^1(\mathbb{R}^3, \mathbb{C})$$

- Exploit Tensor product structure:

- Choose one-particle basis

$$\mathbb{B}_1 = \{\varphi_\nu\}_{\nu \in \mathcal{I}_{\text{bas}}} \subset H^1(\mathbb{R}^3, \mathbb{C})$$

- Somehow* construct orthonormal orbitals

$$\{\psi_i\}_{0 \leq i \leq N} \subset \text{span } \mathbb{B}_1$$

- Get **all** Slater determinants

$$\mathbb{B}_N = \left\{ \varphi_{\sigma(1)} \wedge \varphi_{\sigma(2)} \wedge \cdots \wedge \varphi_{\sigma(N)} \mid \right. \\ \left. \sigma \text{ permutation from } \{1 \dots N\} \text{ to } \mathcal{I}_{\text{bas}} \right\}$$

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The N -particle and one-particle bases

- Want suitable *approximative* N -particle basis

$$\tilde{\mathbb{B}}_N \subset \mathbb{B}_N \subset \bigwedge^N H^1(\mathbb{R}^3, \mathbb{C})$$

- Exploit Tensor product structure:

- Choose **one-particle** basis

$$\mathbb{B}_1 = \{\varphi_\nu\}_{\nu \in \mathcal{I}_{\text{bas}}} \subset H^1(\mathbb{R}^3, \mathbb{C})$$

- Somehow* construct orthonormal orbitals

$$\{\psi_i\}_{1 \dots N_{\text{orb}}} \subset \text{span } \mathbb{B}_1$$

- Get a **selection of** Slater determinants

$$\tilde{\mathbb{B}}_N \subset \left\{ \psi_{\sigma(1)} \wedge \psi_{\sigma(2)} \wedge \cdots \wedge \psi_{\sigma(N)} \mid \right. \\ \left. \sigma \text{ permutation from } \{1 \dots N\} \text{ to } \{1 \dots N_{\text{orb}}\} \right\}$$

Curse of dimensionality solved?

- Yes: $|\tilde{\mathbb{B}}_N|$ is polynomial in N .
- How to construct ψ_i ?
 - Small, meaningful approximation basis $\tilde{\mathbb{B}}_N$ requires suitable one-particle orbitals $\{\psi_i\}_i$
 - Idea: Start from those giving the best single determinant

$$\psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_N.$$

- This needs $H^1(\mathbb{R}^3, \mathbb{C})$ inner product only.
- ⇒ Much simpler problem!
- Hartree-Fock (HF) or density-functional theory (DFT)

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- ⇒ Much simpler problem!
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Recipe for quantum chemistry

- 1 *Somehow* select one-particle basis $\mathbb{B}_1 \subset H^1(\mathbb{R}^3, \mathbb{C})$
- 2 Solve Hartree-Fock (HF) or density-functional theory (DFT):
 - Select $\Phi \equiv \psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_N$ with $\mathcal{E}(\Phi)$ lowest and $\psi_i \in \text{span } \mathbb{B}_1$.
- 3 We found the best $|\tilde{\mathbb{B}}_N| = 1$ for this \mathbb{B}_1 . If satisfied, stop.
- 4 Else use HF or DFT to generate a few more $\{\psi_i\}$ (virtuals)
- 5 Use these to construct more determinants and increase $\tilde{\mathbb{B}}_N$
- 6 Solve the resulting problem (Post-HF)

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The Hartree-Fock problem (Definitions)

- Associated to determinant $\Phi \equiv \psi_1 \wedge \psi_2 \wedge \dots \wedge \psi_N$ are:

Density matrix $\gamma_{\Phi}(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2) = \sum_{i=1}^N \psi_i^*(\underline{\mathbf{r}}_1) \psi_i(\underline{\mathbf{r}}_2)$

Density $\rho_{\Phi}(\underline{\mathbf{r}}) = \gamma_{\Phi}(\underline{\mathbf{r}}, \underline{\mathbf{r}})$

- Define the Coulomb integral

$$D(f, g) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f(\underline{\mathbf{r}}_1) g(\underline{\mathbf{r}}_2)}{\|\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2\|_2} d\underline{\mathbf{r}}_1 d\underline{\mathbf{r}}_2$$

- The electron-nuclear interaction is

$$V_{\text{Nuc}}(\underline{\mathbf{r}}) = - \sum_{A=1}^M \frac{Z_A}{\|\underline{\mathbf{r}} - \underline{\mathbf{R}}_A\|_2}$$

Hartree-Fock problem (Energy functional)

- Energy functional

$$\begin{aligned}\mathcal{E}_{\text{HF}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} \|\nabla \psi_i\|_2^2 d\underline{\mathbf{r}} + \int_{\mathbb{R}^3} \rho_{\Phi}(\underline{\mathbf{r}}) V_{\text{Nuc}}(\underline{\mathbf{r}}) d\underline{\mathbf{r}} \\ &+ D(\rho_{\Phi}, \rho_{\Phi}) - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2)|^2}{\|\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2\|_2} d\underline{\mathbf{r}}_1 d\underline{\mathbf{r}}_2,\end{aligned}$$

- We seek $\Phi_0 = \arg \min_{\Phi} \mathcal{E}_{\text{HF}}(\Phi)$ under

$$\begin{aligned}\Phi &= \psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_N \\ \langle \psi_i | \psi_j \rangle &= \delta_{ij}, \psi_i \in H^1(\mathbb{R}^3, \mathbb{C})\end{aligned}$$

- Solution exists and is unique (up to unitary transformation)
- Last term is non-local

Density-functional theory problem (Energy functional)

- Energy functional

$$\begin{aligned}\mathcal{E}_{\text{DFT}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} \|\nabla \psi_i\|_2^2 \, d\mathbf{r} + \int_{\mathbb{R}^3} \rho_{\Phi}(\mathbf{r}) V_{\text{Nuc}}(\mathbf{r}) \, d\mathbf{r} \\ &+ D(\rho_{\Phi}, \rho_{\Phi}) + \int_{\mathbb{R}^3} \epsilon_{\text{xc}}[\rho_{\Phi}](\mathbf{r}) \, d\mathbf{r}\end{aligned}$$

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- Properties of problem depend on $\epsilon_{\text{xc}}, \dots$
- Last term might capture physics better or worse ...

Density-functional theory (Euler-Lagrange equations)

- Energy functional

$$\mathcal{E}_{\text{DFT}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} \|\nabla \psi_i\|_2^2 d\mathbf{r} + \int_{\mathbb{R}^3} \rho_{\Phi}(\mathbf{r}) V_{\text{Nuc}}(\mathbf{r}) d\mathbf{r} \\ + D(\rho_{\Phi}, \rho_{\Phi}) + \int_{\mathbb{R}^3} \epsilon_{\text{xc}}[\rho_{\Phi}](\mathbf{r}) d\mathbf{r}$$

- Euler-Lagrange equations (depend on Φ_0 , thus $\{\psi_i\}_{1 \leq i \leq N}$):

$$\left\{ \begin{array}{l} \underbrace{\left(-\frac{1}{2} \Delta + V_{\text{Nuc}} + V_{\text{H}}[\rho_{\Phi_0}] + V_{\text{xc}}[\rho_{\Phi_0}] \right)}_{=\hat{\mathcal{F}}_{\Phi}} \psi_i = \epsilon_i \psi_i, \\ \langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \forall i, j \quad 1 \leq i, j \leq N \\ -\Delta V_{\text{H}}[\rho_{\Phi}] = 4\pi \rho_{\Phi} \\ V_{\text{xc}}[\rho_{\Phi}] d\rho_{\Phi} = d \left(\int_{\mathbb{R}^3} \epsilon_{\text{xc}}[\rho_{\Phi}](\mathbf{r}) d\mathbf{r} \right) \quad (\text{Fréchet sense}) \end{array} \right.$$

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- Self-consistent problem
 - Implicit assumption: Relevant spectrum of $\hat{\mathcal{F}}_{\Phi}$ is discrete!
- ⇒ Generalisation: Use density matrix γ_{Φ} as primary descriptor

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Operator traces and Schatten classes

- Let $(\phi_n)_n$ denote a Hilbert basis for $L^2(\mathbb{R}^3)$
- The **trace** of a bounded, non-negative operator \hat{O} is

$$\mathrm{tr}_{L^2(\mathbb{R}^3)}(\hat{O}) = \sum_{n=1}^{\infty} \langle \phi_n | \hat{O} \phi_n \rangle_{L^2(\mathbb{R}^3)}$$

- $\mathfrak{S}_p(L^2(\mathbb{R}^3))$: Set of compact operators on $L^2(\mathbb{R}^3)$ with finite **p -Schatten norm**

$$\|\hat{O}\|_{\mathfrak{S}_p} = \mathrm{tr}_{L^2(\mathbb{R}^3)}(|\hat{O}|^p)^{1/p}.$$

with $|\hat{O}| = (\hat{O}^\dagger \hat{O})^{(1/2)}$

- \mathfrak{S}_1 : **Trace-class operators**
- \mathfrak{S}_2 : **Hilbert-Schmidt operators**

Density-functional theory (Density matrix)

- Converged density matrix γ_0 lives in Grassmannian

$$\{\gamma \in \mathcal{P}_N \mid \sigma(\gamma) = \{0, 1\}\}$$

with corresponding convex hull

$$\mathcal{P}_N = \left\{ \gamma \in \mathfrak{S}_1(L^2(\mathbb{R}^3, \mathbb{C})) \mid 0 \leq \gamma \leq 1, \right. \\ \left. \text{tr}_{L^2(\mathbb{R}^3, \mathbb{C})}(\gamma) = N, \text{tr}_{L^2(\mathbb{R}^3, \mathbb{C})}(|\nabla| \gamma |\nabla|) < \infty \right\}$$

- Energy functional

$$\mathcal{E}_{\text{DFT}}(\gamma) = -\frac{1}{2} \text{tr}_{L^2(\mathbb{R}^3, \mathbb{C})}(\Delta \gamma) + \int_{\mathbb{R}^3} \rho_\gamma(\underline{\mathbf{r}}) V_{\text{Nuc}}(\underline{\mathbf{r}}) d\underline{\mathbf{r}} \\ + D(\rho_\gamma, \rho_\Phi) + \int_{\mathbb{R}^3} \epsilon_{\text{xc}}[\rho_\Phi](\underline{\mathbf{r}}) d\underline{\mathbf{r}}$$

Density-functional theory (Density matrix 2)

- Energy functional

$$\begin{aligned}\mathcal{E}_{\text{DFT}}(\gamma) = & -\frac{1}{2} \text{tr}_{L^2(\mathbb{R}^3, \mathbb{C})} (\Delta \gamma) + \int_{\mathbb{R}^3} \rho_\gamma(\underline{\mathbf{r}}) V_{\text{Nuc}}(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\ & + D(\rho_\gamma, \rho_\Phi) + \int_{\mathbb{R}^3} \epsilon_{\text{xc}}[\rho_\Phi](\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}\end{aligned}$$

- Optimisation problem:

$$\gamma_0 = \arg \min_{\gamma \in \mathcal{P}_N} \mathcal{E}_{\text{DFT}}(\gamma)$$

- Self-consistent problem:

$$\begin{cases} \gamma_0 = \mathbb{1}_{(-\infty, \varepsilon_F)} (\hat{\mathcal{F}}_{\gamma_0}) & \text{with } \varepsilon_F \text{ s.t. } \gamma_0 \in \mathcal{P}_N \\ \hat{\mathcal{F}}_\gamma = -\frac{1}{2} \Delta + V_{\text{Nuc}} + V_{\text{H}}[\rho_\gamma] + V_{\text{xc}}[\rho_\gamma], \\ \rho_\gamma(\underline{\mathbf{r}}) = \gamma(\underline{\mathbf{r}}, \underline{\mathbf{r}}), \gamma \in \mathcal{P}_N \end{cases}$$

Periodic problems

- Assume lattice $\mathcal{R} = (a\mathbb{Z})^3$, unit cell $\Gamma = [-a/2, a/2]^3$
 - Reciprocal lattice $\mathcal{R}^* = (\frac{2\pi}{a}\mathbb{Z})^3$, its unit cell $\mathcal{B} = \Gamma^*$
 - V_{Nuc} is \mathcal{R} -translation invariant
- ⇒ Full Schrödinger operator is \mathcal{R} -translation invariant
- Same holds for ρ and thus $\hat{\mathcal{F}}_{\gamma_0}$!

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Bloch-Floquet transform

- Bloch-Floquet transform \mathcal{Z} allows to identify

$$L^2(\mathbb{R}^3, \mathbb{C}) \cong \frac{1}{|\mathcal{B}|} \int_{\mathcal{B}}^{\oplus} L^2_{\text{per}}(\Gamma) d\underline{\mathbf{k}}$$

$$\hat{\mathcal{F}}_{\gamma} \cong \mathcal{Z}^* \hat{\mathcal{F}}_{\gamma} \mathcal{Z} = \frac{1}{|\mathcal{B}|} \int_{\mathcal{B}}^{\oplus} \hat{\mathcal{F}}_{\underline{\mathbf{k}}, \gamma} d\underline{\mathbf{k}}$$

- **Fibers** $\hat{\mathcal{F}}_{\underline{\mathbf{k}}, \gamma}$ are operators on $L^2_{\text{per}}(\Gamma)$, $\Gamma \subset \mathbb{R}^3$
- Decompositions:

$$\sigma(\hat{\mathcal{F}}_{\gamma}) = \sigma(\mathcal{Z}^* \hat{\mathcal{F}}_{\gamma} \mathcal{Z}) = \bigcup_{\underline{\mathbf{k}} \in \mathcal{B}} \sigma(\hat{\mathcal{F}}_{\underline{\mathbf{k}}, \gamma})$$

$$\mathbb{1}_{(-\infty, \varepsilon_F)}(\hat{\mathcal{F}}_{\gamma}) = \frac{1}{|\mathcal{B}|} \int_{\mathcal{B}}^{\oplus} \mathbb{1}_{(-\infty, \varepsilon_F)}(\hat{\mathcal{F}}_{\underline{\mathbf{k}}, \gamma}) d\underline{\mathbf{k}}$$

⇒ Can solve DFT problem by looking at Fibers independently

Discretising the problem

- Choose a finite subset of \mathbf{k} -Points $\tilde{\mathcal{B}} \subset \mathcal{B}$:

$$\frac{1}{|\mathcal{B}|} \int_{\mathcal{B}}^{\oplus} \hat{\mathcal{F}}_{\underline{\mathbf{k}},\gamma} d\underline{\mathbf{k}} \simeq \bigoplus_{\underline{\mathbf{k}} \in \tilde{\mathcal{B}}} \hat{\mathcal{F}}_{\underline{\mathbf{k}},\gamma}$$

- For each $\underline{\mathbf{k}} \in \tilde{\mathcal{B}}$:
 - Select *suitable* one-particle basis $\mathbb{B}_{1,\underline{\mathbf{k}}} \subset L^2_{\text{per}}(\Gamma)$
 - Discretise $\hat{\mathcal{F}}_{\underline{\mathbf{k}},\gamma}$ and solve discretised DFT
- Sum up results over $\underline{\mathbf{k}} \in \tilde{\mathcal{B}}$

Plane-wave basis sets

- Good for periodic problems: **Plane waves**

$$\varphi_{\underline{\mathbf{G}}}(\underline{\mathbf{r}}) = \frac{1}{\sqrt{|\Gamma|}} e^{i\underline{\mathbf{G}} \cdot \underline{\mathbf{r}}}$$

- For given **energy cutoff** E_{cut} :

$$\mathbb{B}_{1,\underline{\mathbf{k}}} = \left\{ \varphi_{\underline{\mathbf{G}}} \mid \underline{\mathbf{G}} \in \mathcal{R}^*, \|\underline{\mathbf{G}} + \underline{\mathbf{k}}\|^2 \leq 2E_{\text{cut}} \right\}$$

- Notice: One cutoff, but different basis sets per $\underline{\mathbf{k}}$

⇒ Fourier basis ⇒ simple differential operators

⇒ Pointwise computation of Δ , FFTs for fast convolutions, ...

Recipe for plane-wave DFT

0. Select E_{cut} , $\tilde{\mathcal{B}}$ and tolerance $\tau > 0$.
1. Guess an initial density matrix γ , set $i = 1$ and $\gamma^{(0)} = \gamma$.
2. For each $\underline{\mathbf{k}} \in \tilde{\mathcal{B}}$:
 - Build $\mathbb{B}_{1,\underline{\mathbf{k}}}$ using E_{cut} and discretise $\hat{\mathcal{F}}_{\underline{\mathbf{k}},\gamma^{(i-1)}}$ as $\mathbf{F}_{\underline{\mathbf{k}}}^{(i)}$
 - Diagonalise $\mathbf{F}_{\underline{\mathbf{k}}}^{(i)}$ (to allow evaluation of $\mathbb{1}$ below)
3. Determine $\varepsilon_F^{(i)}$, such that

$$N = \text{tr}(\gamma^{(i)}), \quad \gamma^{(i)} = \sum_{\underline{\mathbf{k}} \in \tilde{\mathcal{B}}} \mathbb{1}_{(-\infty, \varepsilon_F^{(i)})} \left(\mathbf{F}_{\underline{\mathbf{k}}}^{(i)} \right)$$

4. If $\left\| \gamma^{(i)} - \gamma^{(i-1)} \right\| < \tau$ stop
5. Else, set $i = i + 1$ and repeat from 2.

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Eric Cancès



Questions?

DFTK: <https://github.com/mfherbst/DFTK.jl>

 mfherbst

 <https://michael-herbst.com/blog>

 michael.herbst@inria.fr



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