Planewave DFT calculations

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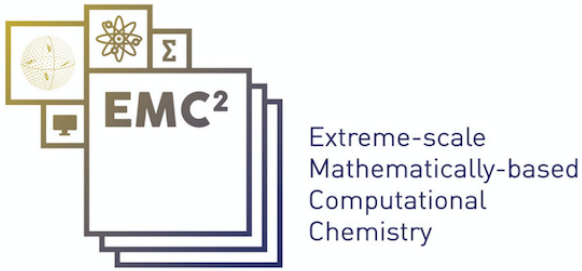
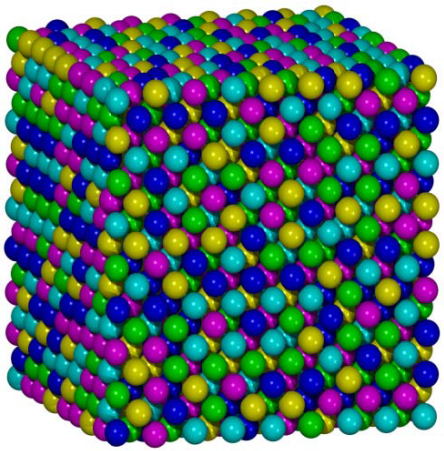
DFTK Summer School, August 29-31, 2022



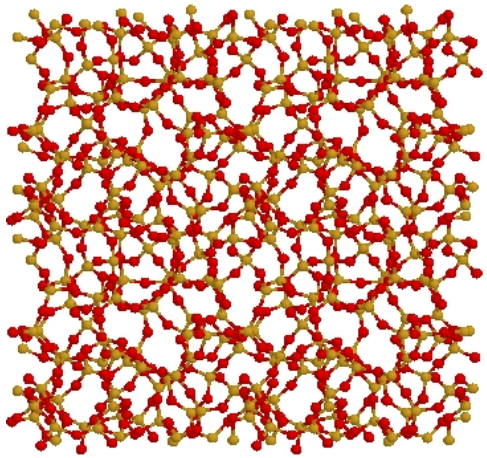
1 - Calculations on periodic simulation cells

Periodic simulation cell $\Omega = [0, L)^3$, periodic lattice $\mathbb{L} = L\mathbb{Z}^3$

Spin-unpolarized system with M ionic cores and N valence electron pairs

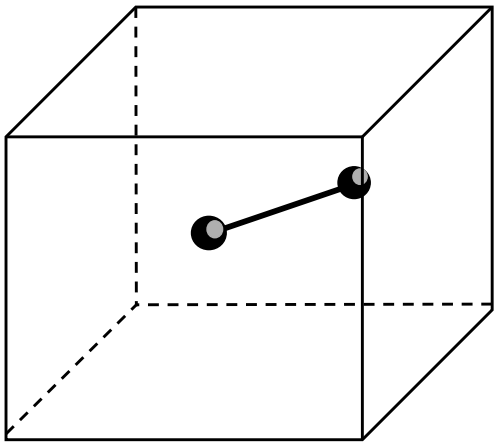


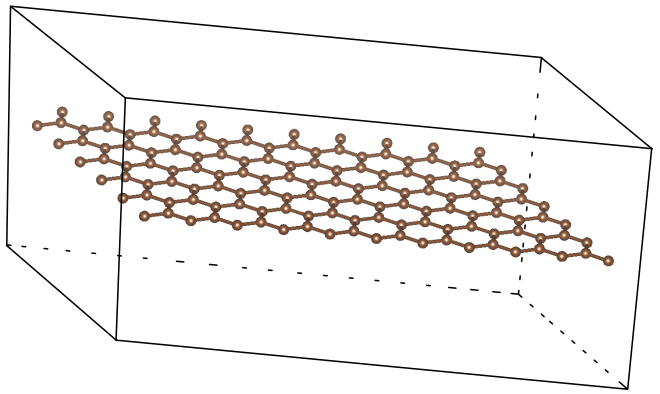
High entropy alloy



Amorphous system

but also...





Periodic simulation cell $\Omega = [0, L)^3$, periodic lattice $\mathbb{L} = L\mathbb{Z}^3$

Spin-unpolarized system with M ionic cores and N valence electron pairs

Kohn-Sham equations on the periodic simulation cell (PSC-KS)

$$
\begin{cases}
\left[\left(-\frac{1}{2}\Delta + v_{\mathrm{loc}} + v_{\mathrm{nl}} + v^{\mathrm{H}}_{\rho^0} + v^{\mathrm{xc}}_{\rho^0}\right)\psi^0_i\right](\mathbf{r}) = \varepsilon^0_i \psi^0_i(\mathbf{r}) & \psi^0_i \ \mathbb{L}\text{-periodic} \\
\displaystyle\int_\Omega \psi^0_i(\mathbf{r})^* \psi^0_{i'}(\mathbf{r})\, d\mathbf{r} = \delta_{ii'}, \quad \varepsilon^0_1 \le \varepsilon^0_2 \le \cdots & \\
\rho^0(\mathbf{r}) = 2\displaystyle\sum_{i=1}^{N} |\psi^0_i(\mathbf{r})|^2 & \\
-\Delta v^{\mathrm{H}}_{\rho^0}(\mathbf{r}) = 4\pi\left(\rho^0(\mathbf{r}) - \langle\rho^0\rangle\right) & v^{\mathrm{H}}_{\rho^0}\ \mathbb{L}\text{-periodic s.t. } \langle v^{\mathrm{H}}_{\rho^0}\rangle = 0 \\
v^{\mathrm{xc}}_{\rho^0}(\mathbf{r}) = -C_{\mathrm{D}}\rho^0(\mathbf{r})^{1/3} & \text{(X}\alpha\text{ model - just for simplicity)}
\end{cases}
$$

- $H_\rho := -\frac{1}{2}\Delta + v_{\mathrm{loc}} + v_{\mathrm{nl}} + v^{\mathrm{H}}_\rho + v^{\mathrm{xc}}_\rho$**: Kohn-Sham Hamiltonian associated to ρ**
- **Aufbau principle: for most systems, $\varepsilon^0_1 \le \cdots \le \varepsilon^0_N$ lowest N eigenvalues of H_{ρ^0}**

Fourier (planewave) expansions of $\mathbb{L}$-periodic functions

The main unknown functions in the PSC-KS equations (ρ, v_ρ^{H}, ψ_i) are $\mathbb{L}$-periodic functions and can therefore be expanded in Fourier series

$$u(\mathbf{r}) = \sum_{\mathbf{G}\in\mathbb{L}^*} \widehat{u}_{\mathbf{G}} e_{\mathbf{G}}(\mathbf{r})$$

with

$\mathbb{L}^* := \dfrac{2\pi}{L}\mathbb{Z}^3$ **(dual lattice)**, $\quad e_{\mathbf{G}}(\mathbf{r}) := \dfrac{e^{i\mathbf{G}\cdot\mathbf{r}}}{|\Omega|^{1/2}}$ **(Fourier mode with momentum $\mathbf{G}$)**,

$$\widehat{u}_{\mathbf{G}} := \langle e_{\mathbf{G}}, u\rangle_{L^2_{\mathrm{per}}(\Omega)} = \frac{1}{|\Omega|^{1/2}}\int_\Omega u(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}\, d\mathbf{r} \quad \textbf{($\mathbf{G}$-Fourier coeff. of u)}$$

We have in particular

$$\int_\Omega |u(\mathbf{r})|^2\, d\mathbf{r} = \sum_{\mathbf{G}\in\mathbb{L}^*} |u_{\mathbf{G}}|^2 \qquad \textbf{(Parseval relation)}$$

$$\widehat{[-i\nabla u]}_{\mathbf{G}} = \mathbf{G}\widehat{u}_{\mathbf{G}}, \qquad \widehat{[-\Delta u]}_{\mathbf{G}} = |\mathbf{G}|^2\widehat{u}_{\mathbf{G}}$$

Fourier (planewave) expansions of $\mathbb{L}$-periodic functions (continued)

Since the Goedecker-Teter-Hutter (GTH) pseudopotentials used in DFTK are very smooth, so are the functions ρ^0, $v^{\mathrm{H}}_{\rho^0}$, ψ^0_i (elliptic regularity). As a consequence, their Fourier coefficients decay very fast

Consequence: for an energy cut-off E_{c} 'not too large',

$$\sum_{\mathbf{G}\in\mathbb{L}^* \,|\, \frac{|\mathbf{G}|^2}{2}\leq E_{\mathrm{c}}} [\psi^0_i]_{\mathbf{G}} e_{\mathbf{G}}$$

are excellent approximations of the ψ^0_i's

More about that

- **proof in 1D for linear Schrödinger equations (blackboard)**
- **hands-on sessions (this afternoon)**
- **Geneviève's lecture (tomorrow morning)**

Planewave discretization of ρ, v_ρ^{H} and ψ_i

We introduce the finite subsets of Fourier modes

$$\mathbb{L}^{*\bigcirc}_{E_{\mathrm{c}}} := \left\{ \mathbf{G} \in \mathbb{L}^* \,|\, |\mathbf{G}| \leq \sqrt{2E_{\mathrm{c}}} \right\} \quad \textbf{and} \quad \mathbb{L}^{*\square}_{E'_{\mathrm{c}}} := \left\{ \mathbf{G} \in \mathbb{L}^* \,|\, |\mathbf{G}|_\infty \leq \sqrt{2E'_{\mathrm{c}}} \right\}$$

and the associated finite-dimensional subspaces of $\mathbb{L}$-periodic functions

$$\mathcal{X}^{\bigcirc}_{E_{\mathrm{c}}} := \mathbf{Span}(e_{\mathbf{G}},\, \mathbf{G} \in \mathbb{L}^{*\bigcirc}_{E_{\mathrm{c}}}) \quad \textbf{and} \quad \mathcal{X}^{\square}_{E'_{\mathrm{c}}} := \mathbf{Span}(e_{\mathbf{G}},\, \mathbf{G} \in \mathbb{L}^{*\square}_{E'_{\mathrm{c}}})$$

We will see that

- **Kohn-Sham orbitals ψ_i are discretized in $\mathcal{X}^{\bigcirc}_{E_{\mathrm{c}}}$ spaces**
- **densities ρ and Hartree potentials V^{H} should then be discretized in $\mathcal{X}^{\square}_{E'_{\mathrm{c}}}$ spaces with $E'_{\mathrm{c}} \geq 4E_{\mathrm{c}}$**

We have

- $N^{\bigcirc}_{E_{\mathrm{c}}} := \#\mathbb{L}^{*\bigcirc}_{E_{\mathrm{c}}} = \dim \mathcal{X}^{\bigcirc}_{E_{\mathrm{c}}} \sim \frac{\sqrt{2}}{3\pi^2} \,|\Omega|\, E_{\mathrm{c}}^{3/2}$
- $N^{\square}_{E'_{\mathrm{c}}} := \#\mathbb{L}^{*\square}_{E'_{\mathrm{c}}} = \dim \mathcal{X}^{\square}_{E'_{\mathrm{c}}} \sim \frac{2\sqrt{2}}{\pi^3} \,|\Omega|\, E'^{3/2}_{\mathrm{c}}$

Planewave discretization of ρ, v_ρ^{H} and ψ_i (continued)

We seek approximations ψ_i , ρ, v^{H} of ψ_i^0, ρ^0, $v_{\rho^0}^{\mathrm{H}}$ of the form

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}\in\mathbb{L}^{*\bigcirc}_{E_{\mathrm{c}}}} \widehat{[\psi_i]}_{\mathbf{G}} e_{\mathbf{G}}(\mathbf{r}) \quad (\in \mathcal{X}^{\bigcirc}_{E_{\mathrm{c}}})$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_{\mathrm{c}}}} \widehat{\rho}_{\mathbf{G}} e_{\mathbf{G}}(\mathbf{r}) \quad (\in \mathcal{X}^{\square}_{E'_{\mathrm{c}}}) \quad \textbf{and} \quad v^{\mathrm{H}}(\mathbf{r}) = \sum_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_{\mathrm{c}}}} \widehat{[v^{\mathrm{H}}]}_{\mathbf{G}} e_{\mathbf{G}}(\mathbf{r}) \quad (\in \mathcal{X}^{\square}_{E'_{\mathrm{c}}})$$

and impose that these quantities fulfill the conditions

$$\langle \psi_i, \psi_{i'} \rangle_{L^2_{\mathrm{per}}(\Omega)} = \delta_{ii'}, \quad -\Delta v^{\mathrm{H}}(\mathbf{r}) = 4\pi\left(\rho(\mathbf{r}) - \langle\rho\rangle\right) \textbf{ with } \langle v^{\mathrm{H}}\rangle = 0, \quad \rho(\mathbf{r}) = 2\sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

The first two conditions are very easy to handle:

$$\langle \psi_i, \psi_{i'} \rangle_{L^2_{\mathrm{per}}(\Omega)} = \delta_{ii'} \quad \Leftrightarrow \quad \widehat{\Psi}_i^* \widehat{\Psi}_{i'} = \delta_{ii'}$$

$$-\Delta v^{\mathrm{H}}(\mathbf{r}) = 4\pi\left(\rho(\mathbf{r}) - \langle\rho\rangle\right) \textbf{ with } \langle v^{\mathrm{H}}\rangle = 0 \quad \Leftrightarrow \quad \widehat{[v^{\mathrm{H}}]}_{\mathbf{G}} = \frac{4\pi}{|\mathbf{G}|^2} \widehat{\rho}_{\mathbf{G}} \delta_{\mathbf{G}\neq\mathbf{0}}$$

where $\widehat{\Psi}_i \in \mathbb{C}^{N^{\bigcirc}_{E_{\mathrm{c}}}}$ is a column vector collecting the Fourier coefficients of ψ_i

Planewave discretization of ρ, v_ρ^{H} and ψ_i (continued)

The relation $\rho(\mathrm{r}) = 2\sum_{i=1}^{N} |\psi_i(\mathrm{r})|^2$ **reads in momentum space**

$$\widehat{\rho}_{\mathbf{G}} = 2|\Omega|^{-1/2} \sum_{i=1}^{N} \sum_{\mathbf{G}' \in \mathbb{L}_{E_{\mathrm{c}}}^{*\bigcirc}} \widehat{[\psi_i]}_{\mathbf{G}'}^{*} \widehat{[\psi_i]}_{\mathbf{G}+\mathbf{G}'} \qquad (1)$$

Consequences:

1. for consistency, densities must be discretized on larger planewave basis sets

$$\psi_i \in \mathcal{X}_{E_{\mathrm{c}}}^{\bigcirc} \quad \Rightarrow \quad \rho \in \mathcal{X}_{4E_{\mathrm{c}}}^{\bigcirc}$$

We must choose $E_{\mathrm{c}}' = \lambda_{\mathrm{sc}}^2 E_{\mathrm{c}}$ **with** $\lambda_{\mathrm{sc}} \geq 2$ **(supersampling parameter)**

2. computing ρ **from the** ψ_i**'s by directly implementing** (1) **is very expensive**

computational cost: $O(N\lambda_{\mathrm{sc}}^3 |\Omega|^2 E_{\mathrm{c}}^3)$

A much more efficient way is to use zero padding and FFT (see below)

Fast Fourier Transform (FFT)

$$\mathcal{X}^{\square}_{E'_{\rm c}} := \mathbf{Span}(e_{\mathbf{G}},\, \mathbf{G} \in \mathbb{L}^{*\square}_{E'_{\rm c}}) \quad \textbf{where} \quad \mathbb{L}^{*\square}_{E'_{\rm c}} := \left\{ \mathbf{G} \in \mathbb{L}^* \,|\, |G|_\infty \leq \sqrt{2E'_{\rm c}} \right\}$$

$$N^{\square}_{E'_{\rm c}} := \#\mathbb{L}^{*\square}_{E'_{\rm c}} = \dim \mathcal{X}^{\square}_{E'_{\rm c}} = n^3_{E'_{\rm c}} \quad \textbf{with } n_{E'_{\rm c}} \in \mathbb{N}$$

Uniform real-space grid $\frac{L}{n_{E'_{\rm c}}}\mathbb{Z}^3$ **allowing one to discretize of** $\mathbb{L}$**-periodic functions with** $n^3_{E'_{\rm c}} = N^{\square}_{E'_{\rm c}}$ **d.o.f.** **Let** $(\mathbf{r}_j)_{1\leq j\leq N^{\square}_{E'_{\rm c}}} := (\frac{L}{n_{E'_{\rm c}}}\mathbb{Z}^3) \cap \Omega$**.** **The map**

$$\mathcal{F}^{-1}_{N^{\square}_{E'_{\rm c}}} : \mathbb{C}^{N^{\square}_{E'_{\rm c}}} \ni (\widehat{u}_{\mathbf{G}})_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_{\rm c}}} \mapsto \left(u_j := \sum_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_{\rm c}}} \widehat{u}_{\mathbf{G}} e_{\mathbf{G}}(\mathbf{r}_j) \right)_{1\leq j\leq N^{\square}_{E'_{\rm c}}} \in \mathbb{C}^{N^{\square}_{E'_{\rm c}}}$$

is bijective with explicit inverse given by

$$\mathcal{F}_{N^{\square}_{E'_{\rm c}}} : \mathbb{C}^{N^{\square}_{E'_{\rm c}}} \ni (u_j)_{1\leq j\leq N^{\square}_{E'_{\rm c}}} \mapsto \left(\widehat{u}_{\mathbf{G}} := \frac{|\Omega|}{N^{\square}_{E'_{\rm c}}} \sum_{1\leq j\leq N^{\square}_{E'_{\rm c}}} u_j e_{-\mathbf{G}}(\mathbf{r}_j) \right)_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_{\rm c}}} \in \mathbb{C}^{N^{\square}_{E'_{\rm c}}}$$

The maps $\mathcal{F}_{N^{\square}_{E'_{\rm c}}}$ **and** $\mathcal{F}^{-1}_{N^{\square}_{E'_{\rm c}}}$ **can be applied to a vector in** $\mathbb{C}^{N^{\square}_{E'_{\rm c}}}$ **in** $O(N^{\square}_{E'_{\rm c}} \log N^{\square}_{E'_{\rm c}})$ **operations thanks to the Fast Fourier Transform (FFT) algorithm**

Application to the computation of the map $(\psi_i) \to \rho$

1. **Zero padding: embed the N functions ψ_i originally in $\mathcal{X}^{\bigcirc}_{E_c}$ and stored in memory in the momentum representation in the largest space $\mathcal{X}^{\square}_{E'_c}$ by adding Fourier coefficients equal to zero for $\mathbf{G} \in \mathbb{L}^{*\square}_{E'_c} \setminus \mathbb{L}^{*\bigcirc}_{E_c}$**

2. **Transform the ψ_i's in the real-space representation using inverse FFT**

$$(\widehat{[\psi_i]_{\mathbf{G}}})_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_c}} \xrightarrow{\text{FFT}^{-1}} ([\psi_i]_j)_{1\le j\le N^{\square}_{E'_c}} \qquad \textbf{cost: } O(NN^{\square}_{E'_c}\log N^{\square}_{E'_c})$$

3. **Compute ρ in the real-space representation**

$$\rho_j = 2\sum_{i=1}^{N} |[\psi_i]_j|^2 \qquad \textbf{cost: } O(NN^{\square}_{E'_c})$$

4. **Transform ρ back to momentum space using FFT**

$$(\rho_j)_{1\le j\le N^{\square}_{E'_c}} \xrightarrow{\text{FFT}} (\widehat{\rho}_{\mathbf{G}})_{\mathbf{G}\in\mathbb{L}^{*\square}_{E'_c}} \qquad \textbf{cost: } O(NN^{\square}_{E'_c}\log N^{\square}_{E'_c})$$

Total cost $O(N\lambda_{\text{sp}}^3|\Omega|E_c^{3/2}\log(\ldots))$ to be compared with $O(N|\Omega|^2E_c^3)$

The Kohn-Sham map in the spaces $(\mathcal{X}_{E_c}^{\bigcirc}, \mathcal{X}_{E_c'}^{\square})$

- **most algorithms to solve the (nonlinear) KS equations are based on the Kohn-Sham map $T = g \circ f$ (see Michael's talk)**

$$\rho_{\text{in}} \xrightarrow{f} (\psi_i)_{1 \le i \le N} \text{ lowest eigenmodes of } H_{\rho_{\text{in}}} \xrightarrow{g} \rho_{\text{out}} = 2 \sum_{i=1}^{N} |\psi_i|^2$$

- **at the discrete level, $\psi_i \in \mathcal{X}_{E_c}^{\bigcirc}$ and $\rho_{\text{in}}, \rho_{\text{out}} \in \mathcal{X}_{E_c'}^{\square}$ with $E_c' = \lambda_{\text{sp}}^2 E_c$**
- **the map g is implemented using zero padding and 2 FFTs (see above)**
- **the map f is computed using iterative Krylov methods (see Michael's talk) which boil down to evaluating matrix-vector products**

Remaining question: how to compute efficiently an approximation $\widetilde{H_\rho \psi}$ of $H_\rho \psi$ in $\mathcal{X}_{E_c}^{\bigcirc}$ for $\rho \in \mathcal{X}_{E_c'}^{\square}$ and $\psi \in \mathcal{X}_{E_c}^{\bigcirc}$ with

- **ρ known in both real space $(\rho_j)_{1 \le j \le N_{E_c'}^{\square}}$ and momentum space $(\widehat{\rho}_{\mathbf{G}})_{\mathbf{G} \in \mathbb{L}_{E_c'}^{*\square}}$**
- **ψ given in momentum space $(\widehat{\psi}_{\mathbf{G}})_{\mathbf{G} \in L_{E_c}^{*\bigcirc}}$**
- **$\widetilde{H_\rho \psi}$ computed in momentum space**

Computation of an approximation $\widetilde{H_\rho\psi} \in \mathcal{X}_{E_c}^{\bigcirc}$ of $H_\rho\psi$ for $\rho \in \mathcal{X}_{E'_c}^{\square}$ and $\psi \in \mathcal{X}_{E_c}^{\bigcirc}$

$$H_\rho = -\frac{1}{2}\Delta + v_{\mathrm{loc}} + v_{\mathrm{nl}} + v_\rho^{\mathrm{H}} + v_\rho^{\mathrm{xc}} \quad \textbf{in real-space representation}$$

1. Kinetic energy operator: super easy! $-\frac{1}{2}\Delta\psi \in \mathcal{X}_{E_c}^{\bigcirc}$ **and** $\left[\widehat{-\frac{1}{2}\Delta\psi}\right]_{\mathbf{G}} = \frac{|\mathbf{G}|^2}{2}\widehat{\psi}_{\mathbf{G}}$

2. $v_\rho^{\mathrm{H}} \in \mathcal{X}_{E'_c}^{\square}$ **is computed explicitly in momentum space using** $\left[\widehat{v_\rho^{\mathrm{H}}}\right]_{\mathbf{G}} = \frac{4\pi}{|\mathbf{G}|}^2\widehat{\rho}_{\mathbf{G}}$ **and mapped to real-space by inverse FFT**

3. $(v_\rho^{\mathrm{xc}}(\mathbf{r}_j))_{1\le j\le N_{E'_c}^{\square}}$ **is computed in real space from** $(\rho_j)_{1\le j\le N_{E'_c}^{\square}}$

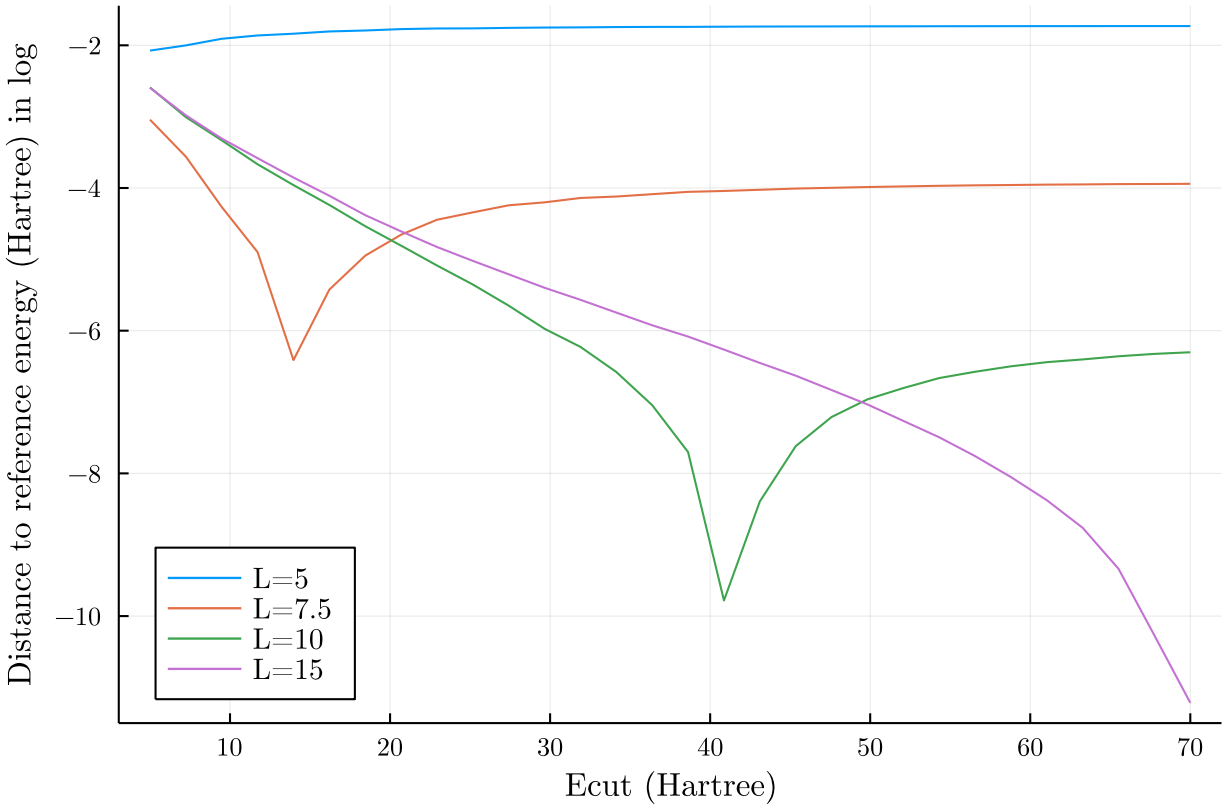
4. the term $(v_{\mathrm{loc}} + v_\rho^{\mathrm{H}} + v_\rho^{\mathrm{xc}})\psi$ **is approximated by**

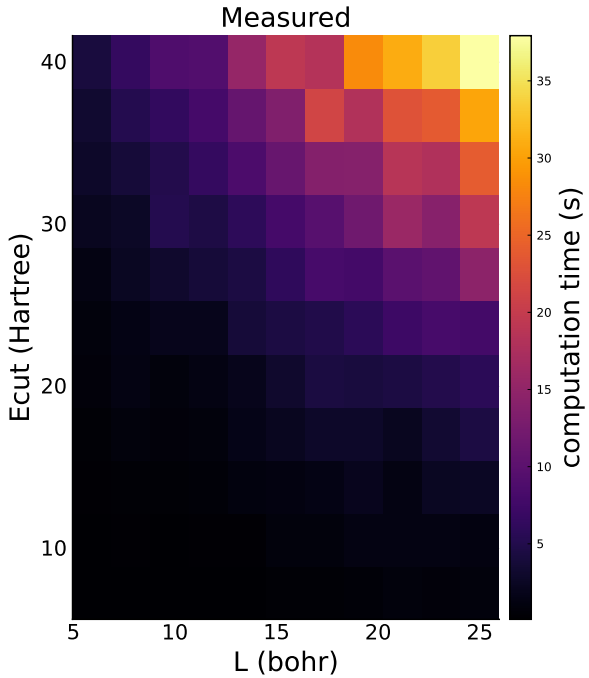
$$\left[\widehat{(v_{\mathrm{loc}} + v_\rho^{\mathrm{H}} + v_\rho^{\mathrm{xc}})\psi}\right]_{\mathbf{G}} = \mathbb{1}_{\mathbf{G}\in\mathbb{L}_{E_c}^{*\bigcirc}}\left[\mathcal{F}_{N_{E'_c}^{\square}}\left[\left((v_{\mathrm{loc}}(\mathbf{r}_j) + v_\rho^{\mathrm{H}}(\mathbf{r}_j) + v_\rho^{\mathrm{xc}}(\mathbf{r}_j))\psi(\mathbf{r}_j)\right)_{1\le j\le N_{E'_c}^{\square}}\right]\right]_{\mathbf{G}}$$

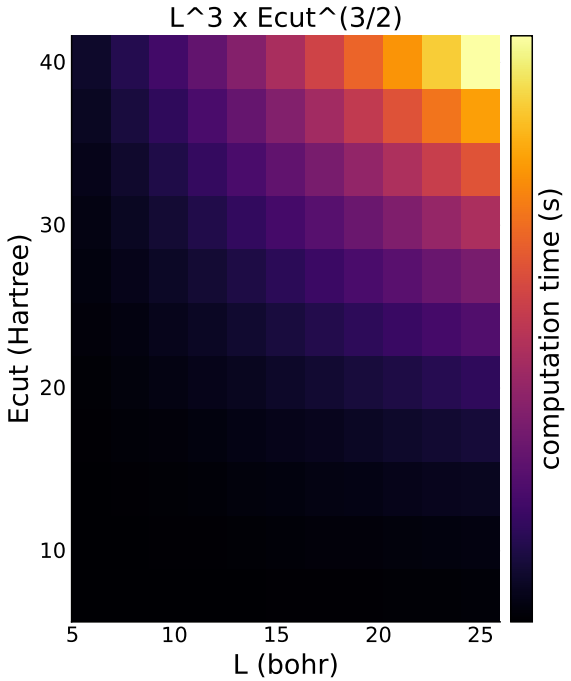
5. $v_{\mathrm{nl}}\psi$ **is approximated directly in momentum space**

A very simple example: the H_2 molecule

Cubic box of size L
Energy cut-off E_c,
Default $\lambda_{sc} = 2$







Variational interpretation

- **at each SCF iteration, we have a density $\rho = \rho_{\text{in}} \in \mathcal{X}_{E'_{\text{c}}}^{\square}$ and we would like to compute approximations in $\mathcal{X}_{E_{\text{c}}}^{\bigcirc}$ of the lowest eigenmodes of H_ρ**

- **a standard way is to use a variational approximation consisting in solving the eigenvalue problem: seek $(\varepsilon, \psi) \in \mathbb{R} \times \mathcal{X}_{E_{\text{c}}}^{\bigcirc}$ such that**

$$\forall \phi \in \mathcal{X}_{E_{\text{c}}}^{\bigcirc}, \quad \langle \phi, H_\rho \psi \rangle = \varepsilon \langle \phi, \psi \rangle$$

- **this is equivalent to seeking the lowest eigenmodes of the Hermitian matrix $\mathbf{H}_\rho \in \mathbb{C}^{N_{E_{\text{c}}}^{\bigcirc} \times N_{E_{\text{c}}}^{\bigcirc}}$ with entries**

$$[\mathbf{H}_\rho]_{\mathbf{G}\mathbf{G}'} := \langle e_{\mathbf{G}} | H_\rho | e_{\mathbf{G}'} \rangle, \qquad \mathbf{G}, \mathbf{G}' \in \mathbb{L}_{E_{\text{c}}}^{*\bigcirc}$$

- **the matrix-vector product defined in the previous slide is equivalent to approximating the matrix $\mathbf{H}_\rho$ as follows**

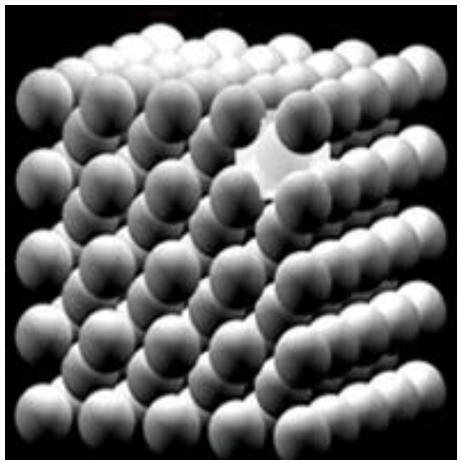
$$[\mathbf{H}_\rho]_{\mathbf{G}\mathbf{G}'} = \underbrace{\langle e_{\mathbf{G}} | -\frac{1}{2}\Delta | e_{\mathbf{G}'} \rangle}_{= \frac{|\mathbf{G}|^2}{2}\delta_{\mathbf{G}\mathbf{G}'} \text{ (exact)}} + \underbrace{\langle e_{\mathbf{G}} | v_\rho^{\text{H}} | e_{\mathbf{G}'} \rangle}_{\text{exact whenever } \lambda_{\text{sc}} \geq 2} + \underbrace{\langle e_{\mathbf{G}} | v_{\text{loc}} + v_{\text{nl}} + v_\rho^{\text{xc}} | e_{\mathbf{G}'} \rangle}_{\text{approximated by numerical quadrature}}$$

better and better when $E_{\text{c}} \to \infty$ and/or $\lambda_{\text{sc}} \to \infty$

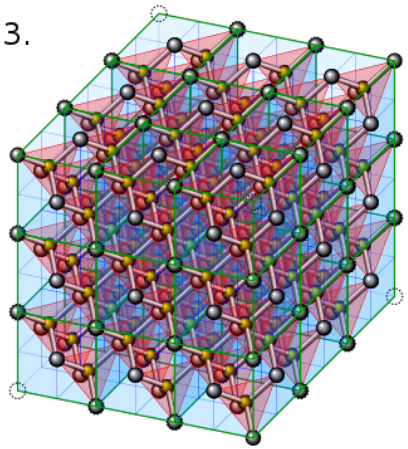
2 - Calculations on periodic crystals using k-points

Perfect crystal

- **Bravais lattice $\mathbb{L} := a\mathbb{Z}$ and unit cell $\Omega := [0, a)^3$, reciprocal lattice $\mathbb{L}^*$**
- **N valence electron pairs per unit cell**



BCC structure

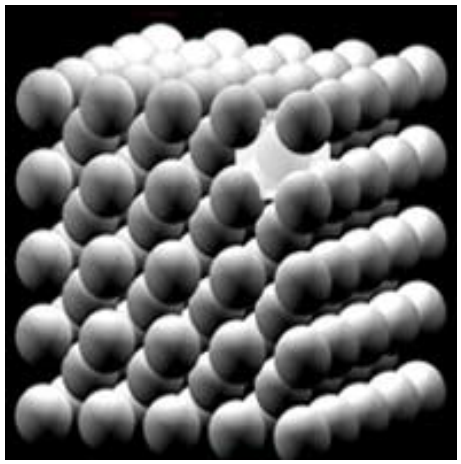


Diamond structure

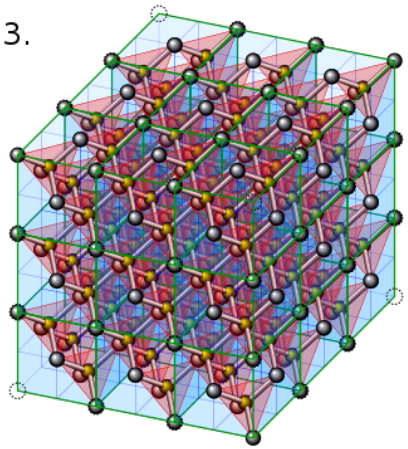
Using the method described in Part I with $\Omega = [0, a)^3$ and PBC at the boundary of Ω would lead to completely wrong results

Perfect crystal

- **Bravais lattice** $\mathbb{L} := a\mathbb{Z}$ **and unit cell** $\Omega := [0, a)^3$**, reciprocal lattice** $\mathbb{L}^*$
- N **valence electron pairs per unit cell**



BCC structure



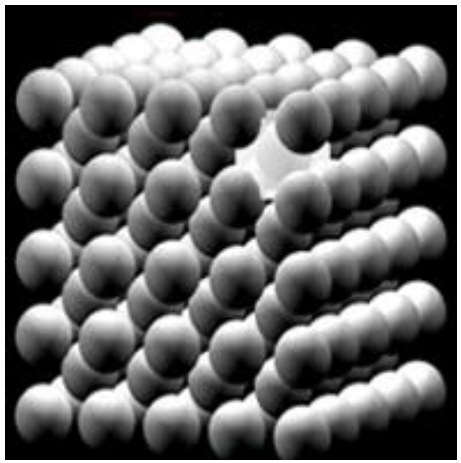
Diamond structure

Periodic simulation cell: supercell made of M^3 copies of the unit cell

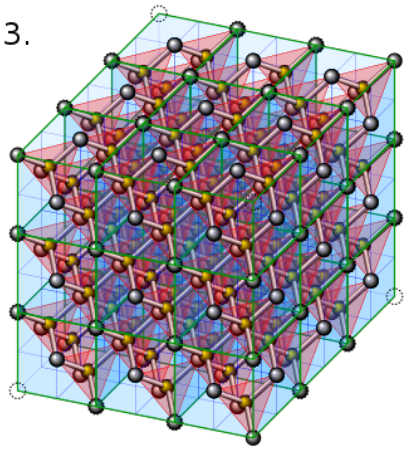
- $\Omega_M = [0, Ma)^3$**,** $\mathbb{L}_M = (aM)\mathbb{Z}^3$
- $N_M = NM^3$ **valence electron pairs in the simulation cell**
- **computational cost scales as** $O(M^6(Na^3)E_{\mathrm{c}}^{3/2}\log(\ldots))$

Perfect crystal

- **Bravais lattice** $\mathbb{L} := a\mathbb{Z}$ **and unit cell** $\Omega := [0, a)^3$**, reciprocal lattice** $\mathbb{L}^*$
- N **valence electron pairs per unit cell**



BCC structure



Diamond structure

Example: BCC iron

- **2 atoms per unit cell, 8 valence electrons per atom,** $N = 8$**,** $a \simeq 5.42$ **bohr**
- $E_{\mathrm{c}} = 20$ **Ha and** $M = 8$ **are reasonable parameters**
- **number of planewaves/grid points for the discretization of** ρ**:** $\sim 10^6$

From supercell to unit cell calculations using symmetries

In this case, the external potential $v_{\rm loc} + v_{\rm nl}$ is not only $\mathbb{L}_M$-translation invariant, but also $\mathbb{L}$-translation invariant

Assuming there is no spontaneous symmetry breaking, ρ^0 and $v^{\rm H}_{\rho^0}$ are $\mathbb{L}$-periodic

We can thus assume that at each SCF iteration $\rho_{\rm in}$ and $\rho_{\rm out}$ are $\mathbb{L}$-periodic

$$\underbrace{\rho_{\rm in}}_{\mathbb{L}-\text{per}} \xrightarrow{f} \underbrace{(\psi_i)_{1\le i\le N}}_{\mathbb{L}_M-\text{per}} \text{ lowest eigenmodes of } H_{\rho_{\rm in}} \xrightarrow{g} \underbrace{\rho_{\rm out}}_{\mathbb{L}-\text{per}} = 2\sum_{i=1}^{N} |\psi_i|^2$$

$H_{\rho_{\rm in}}$ is invariant w.r.t. the $\mathbb{L}$-translation group, an abelian group $\mathfrak{G}$ of order M^3 acting on $L^2_{\rm per}(\Omega_M)$

We denote by $\mathbf{H}_M$ the matrix of $H_{\rho_{\rm in}}$ in the approximation space

$$\mathcal{X}_{M,E_{\rm c}} := \mathbf{span}(e_{\mathbf{G}_M},\ \mathbf{G}_M \in \mathbb{L}^{*\bigcirc}_{M,E_{\rm c}}), \quad \mathbb{L}^{*\bigcirc}_{M,E_{\rm c}} := \{\mathbf{G}_M \in \mathbb{L}^*_M \mid \frac{|\mathbf{G}_M|^2}{2} \le E_{\rm c}\},$$

set $N_{M,E_{\rm c}} = \#\mathbb{L}^{*\bigcirc}_{M,E_{\rm c}} = \dim \mathcal{X}_{M,E_{\rm c}}$, and ignore num. quadrature errors ($\lambda_{\rm sc} = \infty$)

From supercell to unit cell calculations (the pedestrian way)

- **For $\mathbf{R} \in \mathbb{L}$, denote by $\tau_{\mathbf{R}} : L^2_{\rm per}(\Omega_M) \to L^2_{\rm per}(\Omega_M)$ the R-translation operator**

$$\forall \psi \in L^2_{\rm per}(\Omega_M), \quad (\tau_{\mathbf{R}}\phi)(\mathbf{r}) = \phi(\mathbf{r}-\mathbf{R})$$

  Note that if $\mathbf{R} \in \mathbb{L}$ and $\mathbf{R}_M \in \mathbb{L}_M$, $\tau_{\mathbf{R}+\mathbf{R}_M} = \tau_{\mathbf{R}}$ so that there are in fact M^3 such operators

- **We have for all $\mathbf{R} \in \mathbb{L}$ and $\mathbf{G}_M \in \mathbb{L}^*_M$,**

$$(\tau_{\mathbf{R}} e_{\mathbf{G}_M})(\mathbf{r}) = \frac{e^{i\mathbf{G}_M\cdot(\mathbf{r}-\mathbf{R})}}{|\Omega_M|^{1/2}} = e^{-i\mathbf{G}_M\cdot\mathbf{R}} e_{\mathbf{G}}(\mathbf{r})$$

  So $e_{\mathbf{G}}$ is an eigenfunction of $\tau_{\mathbf{R}}$ associated with the eigenvalue $e^{-i\mathbf{G}_M\cdot\mathbf{R}}$

- **Any $\mathbf{G}_M \in \mathbb{L}^*_M$ can be decomposed in a unique way as**

$$\mathbf{G}_M = \mathbf{G}+\mathbf{k} \quad \textbf{with} \quad \mathbf{G} \in \mathbb{L}^* \quad \textbf{and} \quad \mathbf{k} \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right)^3 \quad \textbf{and} \quad e^{-i\mathbf{G}_M\cdot\mathbf{R}} = e^{-i\mathbf{k}\cdot\mathbf{R}}$$

- **We observe that**
  - **$\Omega^* := \left[-\frac{\pi}{a}, \frac{\pi}{a}\right)^3$ is in fact the first Brillouin zone of the crystal**
  - **$\mathbf{k}$ belongs to the regular grid $\mathbb{L}^*_M \cap \Omega^*$, which contains M^3 points**

From supercell to unit cell calculations (the pedestrian way, continued)

- It follows from the previous argument that $\mathcal{X}^{\bigcirc}_{M,E_{\rm c}}$ is $\tau_{\mathbf{R}}$-invariant for any $\mathbf{R} \in \mathbb{L}$, and that the joint eigenspaces of the $\tau_{\mathbf{R}}$'s in $\mathcal{X}^{\bigcirc}_{M,E_{\rm c}}$ are

$$\mathcal{X}^{\bigcirc}_{E_{\rm c},\mathbf{k}} := \mathbf{span}(e_{\mathbf{k}+\mathbf{G}},\ \mathbf{G} \in \mathbb{L}^*_{E_{\rm c},\mathbf{k}}), \quad \mathbb{L}^{*\bigcirc}_{E_{\rm c},\mathbf{k}} := \{\mathbf{G} \in \mathbb{L}^* \mid \frac{|\mathbf{G}+\mathbf{k}|^2}{2} \leq E_{\rm c}\}$$

$$\forall \mathbf{R} \in \mathbb{L}, \quad \forall \psi_{\mathbf{k}} \in \mathcal{X}^{\bigcirc}_{E_{\rm c},\mathbf{k}}, \quad (\tau_{\mathbf{R}}\psi_k)(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r})$$

- Any $\psi_{\mathbf{k}} \in \mathcal{X}^{\bigcirc}_{E_{\rm c},\mathbf{k}}$ is of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}) \quad \textbf{with} \quad u \in \mathcal{X}^{\rm per}_{E_{\rm c},\mathbf{k}} := \mathbf{span}(e_{\mathbf{G}},\ \mathbf{G} \in \mathbb{L}^*_{E_{\rm c},\mathbf{k}}) \subset L^2_{\rm per}(\Omega)$$

- Since H_ρ is $\mathbb{L}$-translation invariant, it commutes with the $\tau_{\mathbf{R}}$, $\mathbf{R} \in \mathbb{L}$, and its variational approximation in $\mathcal{X}^{\bigcirc}_{M,E_{\rm c}}$ is therefore block-diagonal in the decomposition

$$\mathcal{X}^{\bigcirc}_{M,E_{\rm c}} = \bigoplus_{\mathbf{k}\in\mathbb{L}^*_M\cap\Omega^*} \mathcal{X}^{\rm per}_{E_{\rm c},\mathbf{k}}$$

- Instead of diagonalizing one big Hermitian matrix of size $N^{\bigcirc}_{M,E_{\rm c}} \times N^{\bigcirc}_{M,E_{\rm c}}$, we just have to diagonalize M^3 small Hermitian matrices of sizes $N^{\rm per}_{E_{\rm c},\mathbf{k}} \times N^{\rm per}_{E_{\rm c},\mathbf{k}}$

From supercell to unit cell calculations (the pedestrian way, continued)

- **Using the decomposition**

$$\mathcal{X}^{\bigcirc}_{M,E_{\rm c}} = \bigoplus_{\mathbf{k}\in\mathbb{L}^*_M\cap\Omega^*} \mathcal{X}^{\rm per}_{E_{\rm c},\mathbf{k}}$$ **(i.e. gathering the $\mathbf{G}_M$'s with same $\mathbf{k}$)**

the matrix $\mathbf{H}_M$ can be block diagonalized

$$\mathbf{H}_M = \begin{pmatrix} \mathbf{H}_{\mathbf{k}_1} & \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{H}_{\mathbf{k}_2} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ . & . & . & \ldots & . & . \\ . & . & . & \ldots & . & . \\ . & . & . & \ldots & . & . \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{H}_{\mathbf{k}_{M^3}} \end{pmatrix}$$

- **The entries of the matrices $\mathbf{H}_{\mathbf{k}}$ are**

$$[\mathbf{H}_{\mathbf{k}}]_{\mathbf{G}\mathbf{G}'} = \langle e_{\mathbf{k}+\mathbf{G}}|H_\rho|\, e_{\mathbf{k}+\mathbf{G}'}\rangle \qquad \mathbf{G},\mathbf{G}' \in \mathbb{L}^{*\bigcirc}_{E_{\rm c},\mathbf{k}}$$

$$= \delta_{\mathbf{G}\mathbf{G}'}\frac{|\mathbf{G}+\mathbf{k}|^2}{2} + \langle e_{\mathbf{k}+\mathbf{G}}|v_{\rm nl}|\, e_{\mathbf{k}+\mathbf{G}'}\rangle + \underbrace{\langle e_{\mathbf{G}}|\, v_{\rm loc} + v^{\rm H}_\rho + v^{\rm xc}_\rho|e_{\mathbf{G}'}\rangle}_{\text{independent of k}}$$

From supercell to unit cell calculations (the abstract way)

The theory of group representation tells us that

- **the (very large) matrix H_M is unitary equivalent to a block diagonal matrix, each block corresponding to an irreducible representation of the group**
- **since $\mathfrak{G}$ is abelian, it has $\#\mathfrak{G} = M^3$ irreducible representations, which can be labeled by the characters of the group**
- **in the present case, the characters are the functions $\chi_{\mathbf{k}} : \mathfrak{G} \to \mathbb{C}$ defined by**

$$\forall \mathbf{k} \in \mathbb{L}_M^*/\mathbb{L}^* \equiv L_M^* \cap \Omega^*, \quad \forall \mathbf{R} \in \mathbb{L}/\mathbb{L}_M, \quad \chi_{\mathbf{k}}(\tau_{\mathbf{R}}) = e^{-i\mathbf{k}\cdot\mathbf{R}}$$

- **the unitary transform block-diagonalizing the Hamiltonian matrix has an explicit expression involving the characters of the group**

Discrete Bloch transform

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\tau_{\mathbf{R}} \in \mathfrak{G}} \chi_{\mathbf{k}}(\tau_{\mathbf{R}})^* \, (\tau_{\mathbf{R}} u)(\mathbf{r}) = \sum_{\tau_{\mathbf{R}} \in \mathfrak{G}} e^{i\mathbf{k}\cdot\mathbf{R}} \, u(\mathbf{r} - \mathbf{R}) = \sum_{\mathbf{R} \in \mathbb{L} \cap \Omega_M} u(\mathbf{r} + \mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}}$$

Thermodynamic limit: what happens when $M \to \infty$?

Assuming there is no spontaneous symmetry breaking (proven for rHF)

$$\begin{cases} H^{\rho^0} := -\frac{1}{2}\Delta + v_{\mathrm{loc}} + v_{\mathrm{nl}} + v^{\mathrm{H}}_{\rho^0} + v^{\mathrm{xc}}_{\rho^0} & \mathbb{L}\text{-periodic self-adjoint op. on } L^2(\mathbb{R}^3) \\ \gamma^0 = \mathbb{1}_{(-\infty,\varepsilon_{\mathrm{F}}]}(H_{\rho^0}) \quad \text{(GS density matrix)}, \quad \rho^0(\mathbf{r}) = 2\gamma^0(\mathbf{r},\mathbf{r}), & \int_\Omega \rho^0(\mathbf{r})\,d\mathbf{r} = N \end{cases}$$

Using Bloch transform

$$\begin{cases} H^{\rho^0}_{\mathbf{k}} := \frac{1}{2}(-i\nabla + \mathbf{k})^2 + v_{\mathrm{loc}} + v_{\mathrm{nl},\mathbf{k}} + v^{\mathrm{H}}_{\rho^0} + v^{\mathrm{xc}}_{\rho^0} & \text{self-adjoint op. on } L^2_{\mathrm{per}}(\Omega) \\ H^{\rho^0}_{\mathbf{k}} = \sum_{n=1}^{+\infty} \varepsilon_{n\mathbf{k}} |u_{n\mathbf{k}}\rangle\langle u_{n\mathbf{k}}| \quad \text{with} \quad \langle u_{n\mathbf{k}}|u_{n'\mathbf{k}}\rangle_{L^2_{\mathrm{per}}(\Omega)} = \delta_{nn'}, & \varepsilon_{1\mathbf{k}} \le \varepsilon_{2\mathbf{k}} \le \cdots \\ \rho^0(\mathbf{r}) = 2 \fint_{\Omega^*} \sum_{n=1}^{+\infty} \mathbb{1}_{\varepsilon_{n\mathbf{k}} \le \varepsilon_{\mathrm{F}}} |u_{n\mathbf{k}}(\mathbf{r})|^2 \, d\mathbf{k}, & \int_\Omega \rho^0(\mathbf{r})\,d\mathbf{r} = N \end{cases}$$

The supercell method with $\Omega_M = [0, Ma)^3$, E_{c} and $\lambda_{\mathrm{sc}} = \infty$, amounts to discretizing the Brillouin zone Ω^* with the grid $\mathbb{L}^*_M \cap \Omega^*$, and using for each $\mathbf{k} \in \mathbb{L}^*_M \cap \Omega^*$ a variational approximations of $H^{\rho^0}_{\mathbf{k}}$ in the space $\mathcal{X}^{\mathrm{per}}_{E_{\mathrm{c}},\mathbf{k}}$