Plane waves DFT

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Density Functional Theory

The many-body Hamiltonian

The Hamiltonian of all ions (I) and electrons (e) writes

$$\hat{H} = \hat{T}_I + \hat{T}_e + \hat{V}_{I-I} + \hat{V}_{I-e} + \hat{V}_{e-e}$$

The ion-ion interaction

$$\hat{V}_{I-I} = \frac{1}{2} \sum_{\kappa,\kappa'} \frac{Z_\kappa Z_{\kappa'}}{|\mathbf{R}_\kappa - \mathbf{R}_{\kappa'}|}$$

The ion-electron interaction

$$\hat{V}_{I-e} = \sum_{\kappa,i} -\frac{Z_\kappa}{|\mathbf{R}_\kappa - \mathbf{r}_i|}$$

The electron-electron interaction

$$\hat{V}_{e-e} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

With the kinetic energy operators for the ions $\hat{T}_I$ and electrons $\hat{T}_e$

The Born-Oppenheimer approximation

Assuming that

- Ions move much slower than electrons.
- Ions can be treated classically.

We can write down the Hamiltonian of the electrons

$$\hat{H} = \hat{T} + \hat{V}_{e-e} + V_{\text{ext}}(\mathbf{r})$$

with the external potential

$$V_{\text{ext}}(\mathbf{r}) = \sum_\kappa -\frac{Z_\kappa}{|\mathbf{R}_\kappa - \mathbf{r}|}$$

and the kinetic energy operator

$$\hat{T} = \sum_i -\frac{1}{2}\nabla_i^2$$

The many-body ground state

The many-body Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{e-e} + V_{\text{ext}}(\mathbf{r})$$

It is still an untracktable problem to solve

$$\hat{H}\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

Note, however, that we are interested in the ground state, which is the minimum energy configuration

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

Local potentials and electronic density

Whenever we have a local potential $V(\mathbf{r})$, it really means

$$V(\mathbf{r}) \longrightarrow \hat{V} = \sum_i V(\mathbf{r}_i)$$

The expectation value of this potential is

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r})$$

with the electronic density

$$n(\mathbf{r}) = \sum_{i=1}^{N} \int d\mathbf{r}_1 \ldots d\mathbf{r}_N |\Psi(\mathbf{r}_1, \ldots \mathbf{r}_N)|^2 \delta(\mathbf{r} - \mathbf{r}_i)$$

Non-interacting electrons

If we could somehow replace all interactions with an effective potential that all the electrons see, and write

$$\hat{H} = \hat{T} + \hat{V}_{\text{eff}}(\mathbf{r})$$

Then the wavefunction would be separable as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\ldots\phi_N(\mathbf{r}_N)$$

And we would only need to solve a one-body problem and find the first N eigenvalues of

$$\hat{H}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

And the total energy would be

$$E = \sum_i \epsilon_i$$

The Hartree ansatz

The Hartree ansatz starts by assuming that that the wavefunction is separable,

$$\Psi_H(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\ldots\phi_N(\mathbf{r}_N)$$

The electronic density is simply

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

The Hartree potential

With the Hartree wavefunction, the expectation value for the electron-electron interaction (the Hartree energy) writes

$$E_H = \langle \Psi_H | \hat{V}_{e-e} | \Psi_H \rangle = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

This can be written as

$$E_H = \frac{1}{2} \int d\mathbf{r} V_H(\mathbf{r}) n(\mathbf{r})$$

with the Hartree potential defined as

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

What is a functional?

A **functional** is a mapping between a function and a number, or another function.

The Hartree energy is a functional of the density, so we can write

$$E_H = E_H[n]$$

The Hartree potential is also a functional of the density, and we can write

$$V_H(\mathbf{r}) = V_H[n](\mathbf{r})$$

Functional derivatives

The best way to explain functional derivatives is through example. Define

$$U = \int V(\mathbf{r}')n(\mathbf{r}')d\mathbf{r}'$$

Then the **functional derivative** of U with respect to $n(\mathbf{r})$ gives

$$\frac{\delta U}{\delta n(\mathbf{r})} = V(\mathbf{r})$$

The Hartree potential relates to the Hartree energy through

$$V_H(\mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r})} = \frac{1}{2}\frac{\delta}{\delta n(\mathbf{r})}\left[\int d\mathbf{r}'d\mathbf{r}''\frac{n(\mathbf{r}')n(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|}\right] = \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Self-consistent Hartree method

In the Hatree method, the Hamiltonian is a functional of the density:
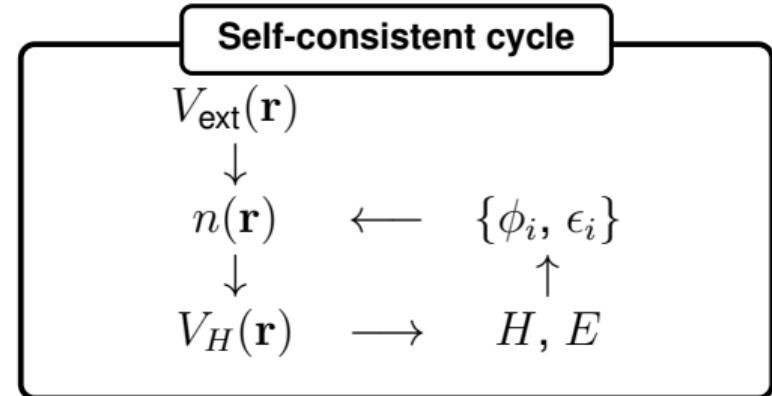
$$\hat{H}[n] = \hat{T} + V_H[n](\mathbf{r}) + V_{\text{ext}}(\mathbf{r})$$

Solving this Hamiltonian yields the one-particle wavefunctions

$$\hat{H}\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

The first N wavefunctions allow to compute the density

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

```
┌─────────────────────────────────────┐
│        Self-consistent cycle         │
│                                      │
│  V_ext(r)                            │
│     ↓                                │
│   n(r)      ⟵      {φ_i, ε_i}        │
│     ↓                 ↑              │
│  V_H(r)     ⟶      H, E             │
│                                      │
└─────────────────────────────────────┘
```

Remarks on the Hartree method

- Actually not a very precise method.
- Each electron sees its own contribution to the electrostatic potential.
- It is missing an important ingredient:
  the wavefunction should be **anti-symmetric** under the exchange of two particles.

The Hartree-Fock method

Since electrons are Fermions, their wavefunction must be anti-symmetric under the exchange of any two electron coordinates

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3, \dots, \mathbf{r}_N)$$

We can construct a totally anti-symmetric wavefunction from one-particle wavefunctions:

$$\Psi_{HF}(\mathbf{r}_1, ... \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_{\{s_i\}} (-1)^s \phi_{s_1}(\mathbf{r}_1) \, \phi_{s_2}(\mathbf{r}_2) \, ... \, \phi_{s_N}(\mathbf{r}_N)$$

The summation runs over the $N!$ possible permutations that change $i \longrightarrow s_i$ and s is the number of two-particle swaps needed to achieve a permutation.

The Hartree-Fock method

With the Hartree-Fock wavefunction, the electron-electron interaction energy is

$$\langle\Psi_{HF}|\hat{V}_{e-e}|\Psi_{HF}\rangle = \frac{1}{2}\sum_{i,j}\int d\mathbf{r}d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi_i(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$-\frac{1}{2}\sum_{i,j}\int d\mathbf{r}d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r})\phi_j(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$=\frac{1}{2}\sum_i\langle\phi_i|V_H|\phi_i\rangle + \frac{1}{2}\sum_i\langle\phi_i|V_F|\phi_i\rangle$$

With the Fock operator (also called "exact exchange")

$$V_F(\mathbf{r},\mathbf{r}') = -\sum_{j=1}^{N}\frac{\phi_j^*(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

which is a non-local operator.
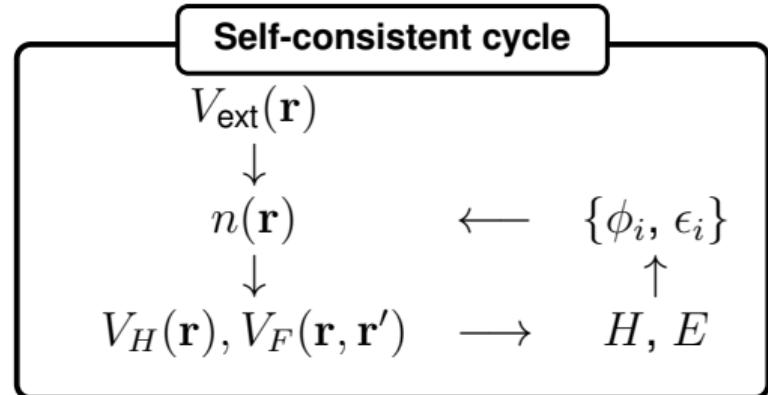
Self-consistent Hartree-Fock method

In the Hatree-Fock method, the Hamiltonian is a functional of both the density and the wavefunctions:

$$H[\phi] = \hat{T} + V_H[n](\mathbf{r}) + V_F[\phi](\mathbf{r}, \mathbf{r}') + V_{\text{ext}}(\mathbf{r})$$

Solving this Hamiltonian yields the one-particle wavefunctions

$$\int d\mathbf{r}' H(\mathbf{r}, \mathbf{r}')\phi_i(\mathbf{r}') = \epsilon_i \phi_i(\mathbf{r})$$

The first N wavefunctions allow to compute the density and the Fock operator.

Self-consistent cycle

$$V_{\text{ext}}(\mathbf{r})$$
$$\downarrow$$
$$n(\mathbf{r}) \qquad \longleftarrow \qquad \{\phi_i, \epsilon_i\}$$
$$\downarrow \qquad\qquad\qquad\qquad \uparrow$$
$$V_H(\mathbf{r}), V_F(\mathbf{r}, \mathbf{r}') \quad \longrightarrow \quad H, E$$

Remarks on the Hartree-Fock method

- Actually used in chemistry.
- Corrects the problem of Coulomb self-interaction in the Hartree method.
- The exchange contribution to the energy is treated exactly.
- It is still missing an important ingredient:
  the electronic wavefunction may be **correlated**.

Hohenberg-Kohn theorem

For a many-body Hamiltonian of N particles

$$\hat{H} = \hat{T} + \hat{V}_{ee} + V_{\text{ext}}(\mathbf{r})$$

The Hohenberg-Kohn theorem states that there is a one-to-one mapping between the ground-state electronic density $n(\mathbf{r})$ and the external potential $V_{\text{ext}}(\mathbf{r})$.

In other words, the external potential is a functional of the ground-state electronic density.

Proof of the Hohenberg-Kohn theorem by contradiction

Suppose that two different potentials $V_{\text{ext}}^1(\mathbf{r})$ and $V_{\text{ext}}^2(\mathbf{r})$ correspond to the same ground-state density $n(\mathbf{r})$.

These two potentials give two different Hamiltonians H^1 and H^2, with different ground state wavefunctions Ψ_1 et Ψ_2 that give the same density $n(\mathbf{r})$.

The minimization principle implies that

$$E_1 = \langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle = \langle \Psi_2 | H_2 | \Psi_2 \rangle + \langle \Psi_2 | H_1 - H_2 | \Psi_2 \rangle$$

$$E_1 < E_2 + \int d\mathbf{r} \big[V_{\text{ext}}^1(\mathbf{r}) - V_{\text{ext}}^2(\mathbf{r}) \big] n(\mathbf{r})$$

But the converse must also be true

$$E_2 < E_1 + \int d\mathbf{r} \big[V_{\text{ext}}^2(\mathbf{r}) - V_{\text{ext}}^1(\mathbf{r}) \big] n(\mathbf{r})$$

Adding the last two equations leads to the contradiction

$$E_1 + E_2 < E_2 + E_1$$

Implications of the Hohenberg-Kohn theorem

This means that the entire Hamiltonian must be a functional of the ground-state electronic density

$$\hat{H}[n] = \hat{T} + \hat{V}_{e-e} + V_{\text{ext}}[n](\mathbf{r})$$

and so is the wavefunction $\Psi[n]$ and the total energy $E[n]$.

We can write

$$E[n] = \langle \Psi | \hat{T} + \hat{V}_{e-e} | \Psi \rangle + \langle \Psi | V_{\text{ext}} | \Psi \rangle = F[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

and we have introduced the **Kohn-Sham functional**

$$F[n] = \langle \Psi | \hat{T} + \hat{V}_{e-e} | \Psi \rangle$$

which is a universal functional of the density.

The Kohn-Sham system

The Kohn-Sham system is a set of non-interacting electrons that produce the same ground-state density as the real system. The wavefunction is thus separable as

$$\Psi_{\mathsf{KS}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dot{\phi}_N(\mathbf{r}_N)$$

Let the Kohn-Sham functional for the non-interacting system be

$$F_s[n] = \langle \Psi_{\mathsf{KS}}|\hat{T} + \hat{V}_{e-e}|\Psi_{\mathsf{KS}}\rangle = \sum_i \langle \phi_i| - \frac{1}{2}\nabla^2|\phi_i\rangle + E_H[n]$$

Define the **exchange-correlation energy**

$$E_{xc}[n] = F[n] - F_s[n]$$

Then, the total energy functional can be written exactly as

$$E[n] = \sum_i \langle \phi_i| - \frac{1}{2}\nabla^2|\phi_i\rangle + E_H[n] + E_{xc}[n] + \int d\mathbf{r} V_{\mathsf{ext}}(\mathbf{r})n(\mathbf{r})$$

Kohn-Sham Hamiltonian

The Kohn-Sham equation is obtained by minimizing the total energy with respect to the wavefunction, and using **Lagrange multipliers** ϵ_i to maintain the normalization

$$\frac{\delta}{\delta\phi_i^*(\mathbf{r})}\Big(E[n] - \epsilon_i \langle\phi_i|\phi_i\rangle \Big) = 0$$

The **exchange-correlation potential** is obtain from the chain derivative

$$\frac{\delta E_{xc}[n]}{\delta\phi_i^*(\mathbf{r})} = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \frac{\delta n(\mathbf{r})}{\delta\phi_i^*(\mathbf{r})} = V_{xc}(\mathbf{r})\phi_i(\mathbf{r})$$

We arrive at the Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Self-consistent Kohn-Sham equations
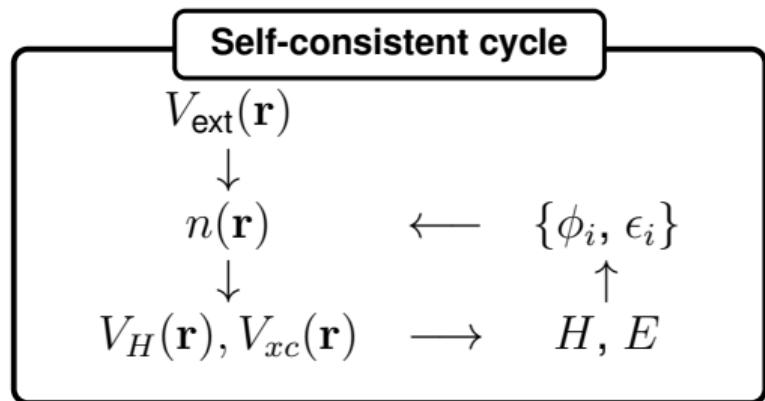
The Kohn-Sham Hamiltonian is

$$\hat{H}[n] = \hat{T} + V_H[n](\mathbf{r}) + V_{xc}[n](\mathbf{r}) + V_{\mathsf{ext}}(\mathbf{r})$$

Solving this Hamiltonian yields the one-particle wavefunctions

$$\hat{H}\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

The first N wavefunctions allow to compute the density.

Self-consistent cycle

$$
\begin{array}{ccc}
V_{\mathsf{ext}}(\mathbf{r}) & & \\
\downarrow & & \\
n(\mathbf{r}) & \longleftarrow & \{\phi_i,\, \epsilon_i\} \\
\downarrow & & \uparrow \\
V_H(\mathbf{r}), V_{xc}(\mathbf{r}) & \longrightarrow & H,\, E
\end{array}
$$

In Abinit, the cycle stops when

- We reach the maximum number of steps `nstep`
- The energy changes by less than `toldfe`
- The potential changes by less than `tolvrs`

Remarks on the Kohn-Sham equations

- In principles, DFT is an exact theory for the ground state.
- However, we don't know the exact form of $E_{xc}[n]$.
- The precision of DFT depends on how well we approximate $E_{xc}[n]$ and $V_{xc}[n]$.
- The Kohn-Sham eigenvalues are just Lagrange multipliers. In principles, they have no physical meaning.
  - Except for the eigenvalue of the highest occupied state, which corresponds to the **ionization potential** (Koopman's theorem).
- In practice, the KS eigenvalues approximate quite well the electronic structure of the occupied states.
- DFT is a ground-state theory. We should't expect it to describe excited states.

Exchange-correlation functionals

The exchange-correlation potential is usually separated as

$$V_{xc}(\mathbf{r}) = V_x(\mathbf{r}) + V_c(\mathbf{r})$$

Those potentials are **parametrized** to fit the results obtained by more advanced techniques (GW, quantum Monte-Carlo, etc.)

Hybrid functionals use a fraction of exact exchange and produce a non-local potential

$$V_{xc}(\mathbf{r}, \mathbf{r}') = \alpha V_F(\mathbf{r}, \mathbf{r}') + V_c(\mathbf{r})\delta(\mathbf{r}, \mathbf{r}')$$
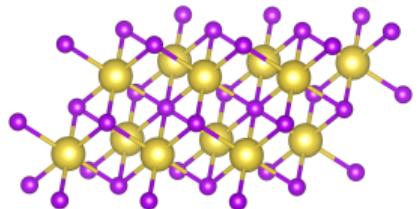
There exists **hundreds** of xc functionals designed for various kinds of systems (molecules, semiconductors, metals) or for specific properties (structural parameters, ionization potential, band gap, ...)

Exchange-correlation functionals
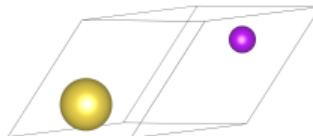
Type	Ingredients	Examples
Local density approximation (LDA)	Density $n(\mathbf{r})$	PW92, PZ
Generalized gradient approximation (GGA)	Density $n(\mathbf{r})$ Gradient of density $\nabla n(\mathbf{r})$	**PBE**, revPBE
Hybrids	Density $n(\mathbf{r})$ Gradient of density $\nabla n(\mathbf{r})$ $V_F[\phi_i]$	HSE06, PBE0, B3LYP
Meta-GGA	Density $n(\mathbf{r})$ Gradient of density $\nabla n(\mathbf{r})$ Kinetic energy density $\kappa(\mathbf{r})$ Wavefunctions $\phi_i(\mathbf{r})$	SCAN, R2SCAN, TB

Plane wave DFT
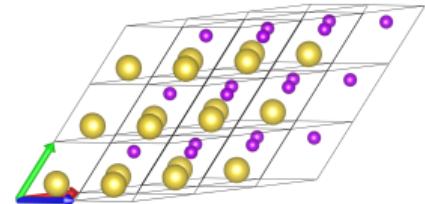
Periodic crystals
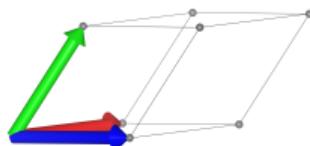
Crystal

Primitive cell

Repeated primitive cells

Primitive vectors
$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$

The volume is

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

Construct the matrix

$$M = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$$

Then, the volume is

$$\Omega = |M|$$
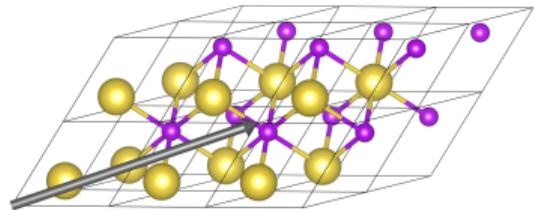
Lattice vectors

A **lattice vector** is a linear combination of lattice vectors multiplied by integer numbers

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

where $n_1, n_2, n_3 \in \mathbb{Z}$.

The set of all $\mathbf{R}$ vectors forms a **Bravais lattice**.

$$\mathbf{R} = 2\mathbf{a}_1 + \mathbf{a}_3$$

Reciprocal lattice

The reciprocal lattice vectors are of the form

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$$
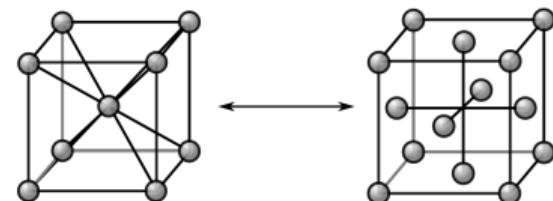
where $m_1, m_2, m_3 \in \mathbb{Z}$.

With the primitive vectors of the reciprocal lattice

$$[\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3]^T = \tilde{M}^T = 2\pi M^{-1}$$

The volume of a primitive cell of the reciprocal lattice is

$$\Omega_{BZ} = |\tilde{M}| = \frac{(2\pi)^3}{\Omega}$$

For any lattice vector $\mathbf{R}$ and reciprocal lattice vector $\mathbf{G}$, we have

$$e^{i\mathbf{G} \cdot \mathbf{R}} = 1$$

Periodic potential

Consider a set of non-interacting electrons subject to a potential $U(\mathbf{r})$. The Schrödinger equation (in natural units $\hbar = m = e = 1$) is

$$H\psi(\mathbf{r}) = \left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

If the potentiel has the periodicity of the crystal

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$$

Then, its Fourier decomposition is

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}$$

The Bloch theorem

In a periodic potential, the wavefunctions have the form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

where the band index n and the wavevector $\mathbf{k}$ are quantum numbers with

$$n \in \mathbb{N} \quad ; \quad \mathbf{k} \in \mathbb{R}^3$$

and the Bloch functions $u_{n\mathbf{k}}$ have the periodicity of the crystal

$$u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$$

which means they have a Fourier decomposition

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}$$

Note that we should also add a spin index: $\sigma n\mathbf{k}$

Wavefunction normalization

Since the wavefunction must be normalized, we have that

$$
\begin{aligned}
1 &= \int d\mathbf{r} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 \\
&= \int d\mathbf{r} \sum_{\mathbf{G}\mathbf{G}'} c_{n\mathbf{k}}(\mathbf{G})^* c_{n\mathbf{k}}(\mathbf{G}') e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}} \\
&= \sum_{\mathbf{G}} |c_{n\mathbf{k}}(\mathbf{G})|^2
\end{aligned}
$$

The $c_{n\mathbf{k}}(\mathbf{G})$ coefficients are also normalized.

Schrödinger equation in plane waves

The Schrödinger equation in a crystal is

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right] e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

Taking the Fourier transform, we get

$$\frac{1}{2}(\mathbf{k}+\mathbf{G})^2 c_{n\mathbf{k}}(\mathbf{G}) + \sum_{\mathbf{G}'} V(\mathbf{G}-\mathbf{G}') c_{n\mathbf{k}}(\mathbf{G}') = \epsilon_{n\mathbf{k}} c_{n\mathbf{k}}(\mathbf{G})$$

This is a matrix equation of the form

$$\sum_{\mathbf{G}'} H_{\mathbf{k}}(\mathbf{G}, \mathbf{G}') c_{n\mathbf{k}}(\mathbf{G}') = \epsilon_{n\mathbf{k}} c_{n\mathbf{k}}(\mathbf{G})$$

It shows that each $\mathbf{k}$ point can be solved independently.

Schrödinger equation in plane waves

The Hamiltonian matrix is

$$H_{\mathbf{k}}(\mathbf{G}, \mathbf{G}') = \frac{1}{2}(\mathbf{k} + \mathbf{G})^2 \delta_{\mathbf{G}, \mathbf{G}'} + V(\mathbf{G} - \mathbf{G}')$$

Since we can enumerate the $\mathbf{G}$ vectors, we can represent the matrix form of the Schrödinger equation as

$$\begin{pmatrix} \frac{1}{2}(\mathbf{k} + \mathbf{G}_1)^2 & V(\mathbf{G}_1 - \mathbf{G}_2) & V(\mathbf{G}_1 - \mathbf{G}_3) & \dots \\ V(\mathbf{G}_2 - \mathbf{G}_1) & \frac{1}{2}(\mathbf{k} + \mathbf{G}_2)^2 & V(\mathbf{G}_2 - \mathbf{G}_3) & \\ V(\mathbf{G}_3 - \mathbf{G}_1) & V(\mathbf{G}_3 - \mathbf{G}_2) & \frac{1}{2}(\mathbf{k} + \mathbf{G}_3)^2 & \\ & \vdots & & \ddots \end{pmatrix} \cdot \begin{pmatrix} c_{n\mathbf{k}}(G_1) \\ c_{n\mathbf{k}}(G_2) \\ c_{n\mathbf{k}}(G_3) \\ \vdots \end{pmatrix} = \epsilon_{n\mathbf{k}} \begin{pmatrix} c_{n\mathbf{k}}(G_1) \\ c_{n\mathbf{k}}(G_2) \\ c_{n\mathbf{k}}(G_3) \\ \vdots \end{pmatrix}$$
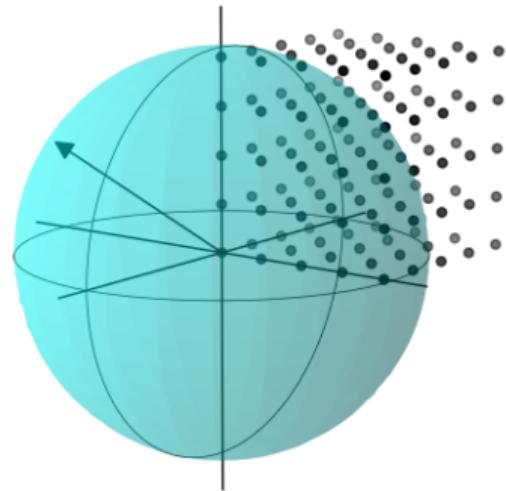
The G sphere

The cut-off energy E_{cut} defines a sphere of radius G_{max}

$$\frac{G_{max}^2}{2} = E_{cut}$$

The planewave basis is the set of $\mathbf{G}$ vectors such that

$$\frac{(\mathbf{k} + \mathbf{G})^2}{2} \leq E_{cut}$$

The number of planewaves insite that sphere
is M_{PW} (`mpw`).

Wavefunction in the plane wave basis

This is how the wavefunctions are stored in memory

$$\psi_{\sigma n \mathbf{k}}(\mathbf{r}) \longrightarrow \begin{pmatrix} c_{\sigma n \mathbf{k}}(G_1) \\ c_{\sigma n \mathbf{k}}(G_2) \\ c_{\sigma n \mathbf{k}}(G_3) \\ \vdots \\ c_{\sigma n \mathbf{k}}(G_{M_{\mathsf{PW}}}) \end{pmatrix}$$

Storing a float number in memory requires 64 bits = 8 bytes. The c coefficients are complex numbers. Hence, the memory needed to store the wavefunctions is

$$\mathsf{Mem} = \mathtt{nspinor} \times \mathtt{nkpt} \times \mathtt{nband} \times \mathtt{mpw} \times 2 \times 8 \text{ bytes}$$

Smearing the borders of the G sphere

When performing structural optimization, the lattice parameters change, and so does the size of the $\mathbf{G}$ vectors. Hence, the number of $\mathbf{G}$ vectors inside the G sphere changes. As a result, the total energy as a function of the lattice parameters may be non-smooth. In Abinit, we solve this problem by defining a smoothing region with the variable `ecutsm`.

If a planewave falls in the region

$$E_{\text{cut}} - \texttt{ecutsm} < \frac{(\mathbf{k} + \mathbf{G})^2}{2} \leq E_{\text{cut}}$$

Then, its kinetic energy contribution is modified as

$$\frac{(\mathbf{k} + \mathbf{G})^2}{2} \longrightarrow f(|\mathbf{k} + \mathbf{G}|)\frac{(\mathbf{k} + \mathbf{G})^2}{2}$$

where $f(x)$ is a function that goes smoothly from 1 to 0 on the edge of the G sphere.

Consider the density

$$n(\mathbf{r}) = \sum_{n\mathbf{k}} f_{n\mathbf{k}} \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

Its Fourier components are

$$n(\mathbf{G}) = \sum_{n\mathbf{k}} f_{n\mathbf{k}} \sum_{\mathbf{G}'} c_{n\mathbf{k}}^*(\mathbf{G}' - \mathbf{G}) c_{n\mathbf{k}}(\mathbf{G}')$$

- The $\mathbf{G}$ vectors needed to describe $n(\mathbf{G})$ can be **twice as large** as those needed to describe $c_{n\mathbf{k}}(\mathbf{G})$
- The density would require a $\mathbf{G}$ sphere with a radius twice as big.
- The same is true for the potential $V(\mathbf{G})$.

The FFT (Fast Fourier Transform) grid

The density and potential are actually stored in **real space**, and the real space grid is called the **FFT grid**. The number of FFT grid points N_{FFT} (nfft) is

$$N_{\mathsf{FFT}} = N_x \times N_y \times N_z$$

Suppose that the $\mathbf{G}$ sphere is contained in a box of size $M_x \times M_y \times M_z$.
Then $n(\mathbf{r})$ and $V(\mathbf{r})$ will be exactly described if

$$\frac{N_x}{M_x} \geq 2 \quad ; \quad \frac{N_y}{M_y} \geq 2 \quad ; \quad \frac{N_z}{M_z} \geq 2$$

Abinit will report the boxcut ratio, defined by

$$\mathtt{boxcut} = \min\left(\frac{N_x}{M_x}, \frac{N_y}{M_y}, \frac{N_z}{M_z}\right)$$

Applying the Hamiltonian on the wavefunctions

When solving the Hamiltonian, we need to apply it on the wavefunctions, which means that we need to compute quantities like

$$w(\mathbf{G}) = \sum_{\mathbf{G}'} V(\mathbf{G} - \mathbf{G}')c_{n\mathbf{k}}(\mathbf{G}')$$

If the number of $\mathbf{G}$ vectors is N, then we need to perform N^2 float operations to compute $w(\mathbf{G})$. But we can do better!

Recall that the FFT algorithm requires only $N \log N$ operations.
It is then faster to compute

$$c_{n\mathbf{k}}(\mathbf{G}) \xrightarrow{\text{FFT}} u_{n\mathbf{k}}(\mathbf{r}) \longrightarrow w(\mathbf{r}) = V(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) \xrightarrow{\text{FFT}} w(\mathbf{G})$$

because the number of operations is $N + 2N \log N$.

Solving the Schrödinger equation

At each self-consistent field (SCF) step, we know the density and the potential, and we perform a non-self-consistent field (NSCF) procedure to solve the eigenvalue problem

$$H_{\mathbf{k}} \left| \psi_{n\mathbf{k}} \right\rangle = \epsilon_{n\mathbf{k}} \left| \psi_{n\mathbf{k}} \right\rangle$$

Several algorithm are available to solve the Hamiltonian, which are selected with the variable `wfoptalg`. In particular:

- State-by-state conjugate gradient (serial algorithm)
- Locally Optimal Block Preconditioned Conjugate Gradient (LOBPCG)
- Chebyshev filtering

We proceed iteratively to solve

$$H \left| \psi \right\rangle = \epsilon \left| \psi \right\rangle$$

Suppose that at step i we have an estimate $\left| \psi^{(i)} \right\rangle$ for the wavefunction, the wavefunction at the next step is obtained by computing

$$\epsilon^{(i)} = \langle \psi^{(i)} | H | \psi^{(i)} \rangle$$
$$\left| r^{(i)} \right\rangle = \left(H - \epsilon^{(i)} \right) \left| \psi^{(i)} \right\rangle$$
$$\left| \psi^{(i+1)} \right\rangle = \alpha^{(i)} \left| \psi^{(i)} \right\rangle + \beta^{(i)} \left| r^{(i)} \right\rangle + \gamma^{(i)} \left| \psi^{(i-1)} \right\rangle$$

where $\alpha^{(i)}$, $\beta^{(i)}$, $\gamma^{(i)}$ are the scalar coefficient that minimize $\epsilon^{(i+1)}$, which can be obtained by the Raleigh-Ritz procedure.

Spin considerations

Spin degrees of freedom

In principle, the one-particle wavefunctions $\psi_{\sigma n \mathbf{k}}$ are described by **spinors**.

However, some simplifications are possible and we distinguish the following cases:

- Unpolarized system
- Antiferromagnetic system
- Collinear spin polarization
- Non-collinear spin

In Abinit, several variables control the treatment of spin

- nsppol : number of spin polarizations.
- nspden : number of spin densities.
- nspinor : number of spinor components.

Unpolarized calculations

The eigenvalues do not depend on spin direction.
The two spin channels are completely independent, and they contribute equally to the density.

This is the default behavior, and corresponds to setting the variables

- `nsppol = 1`
- `nspden = 1`
- `nspinor = 1`

We are ignoring spin degrees of freedom, and we can write

$$\psi_{\sigma n \mathbf{k}} \longrightarrow \psi_{n \mathbf{k}}$$

Collinear spin polarization

There are two independent spin channels. The eigenvalues depend on spin direction.

This is activated by setting the variables

- nsppol = 2
- nspden = 2
- nspinor = 1

The spin index σ refers to the spin channel:

$$\psi_{\sigma n\mathbf{k}} \longrightarrow \quad \psi_{\uparrow n\mathbf{k}} \quad \text{or} \quad \psi_{\downarrow n\mathbf{k}}$$

However, there are no particular direction for spin polarization. It is unspecified.

Antiferromagnetism

There are two independent spin channels, but they are completely equivalent.
The eigenvalues do not depend on spin direction.

This is activated by setting the variables

- `nsppol = 1`
- `nspden = 2`
- `nspinor = 1`

Non-collinear spin

Wavefunctions are represented as spinors.
Allows to include spin-orbit coupling.

This is activated by setting the variables

- `nsppol = 1`
- `nspden = 1 or 4`
- `nspinor = 2`

The spin index σ refers to spinor component:

$$\psi_{\sigma n\mathbf{k}} = \begin{pmatrix} \psi_{\uparrow n\mathbf{k}} \\ \psi_{\downarrow n\mathbf{k}} \end{pmatrix}$$

In this case, there are twice as many bands as in the collinear or non-collinear case.

Brillouin zone sampling

k-point summations

Several quantities require an integral over the first Brillouin zone, such as the density

$$n(\mathbf{r}) = \sum_n \frac{1}{\Omega_{BZ}} \int_{BZ} f(\epsilon_F - \epsilon_{n\mathbf{k}}) |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

or the total kinetic energy

$$E_{kin} = \sum_n \frac{1}{\Omega_{BZ}} \int_{BZ} f(\epsilon_F - \epsilon_{n\mathbf{k}}) \langle \psi_{n\mathbf{k}}(\mathbf{r})| -\frac{1}{2}\nabla^2 |\psi_{n\mathbf{k}}(\mathbf{r})\rangle \, d\mathbf{k}$$

This integration is represented as a discrete sum
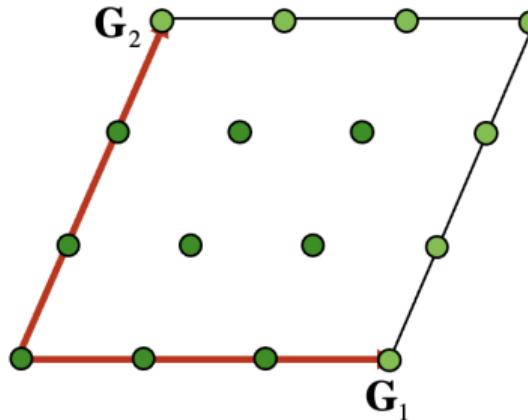
$$\frac{1}{\Omega_{BZ}} \int_{BZ} X_{\mathbf{k}} d\mathbf{k} \longrightarrow \sum_{\mathbf{k}} w_{\mathbf{k}} X_{\mathbf{k}}$$

and we use symmetries to reduce the number of k-points and assign weights $w_{\mathbf{k}}$.
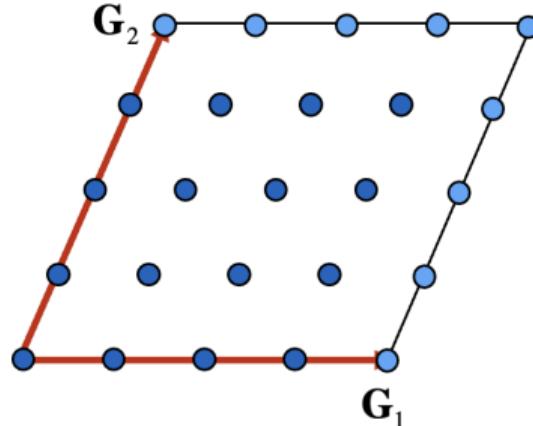
The Monkhorst-Pack grid is a uniform sampling of the Brillouin zone. In Abinit, this is achieved by setting

ngkpt = nk1 nk2 nk3

$n_{k1} = n_{k2} = 3$

$n_{k1} = n_{k2} = 4$
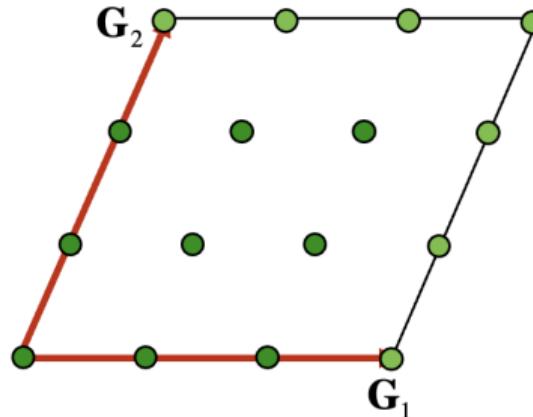
It is usually more efficient to use a shifted Monkhorst-Pack grid, with
```
ngkpt = nk1 nk2 nk3
shiftk = sk1 sk2 sk3
```
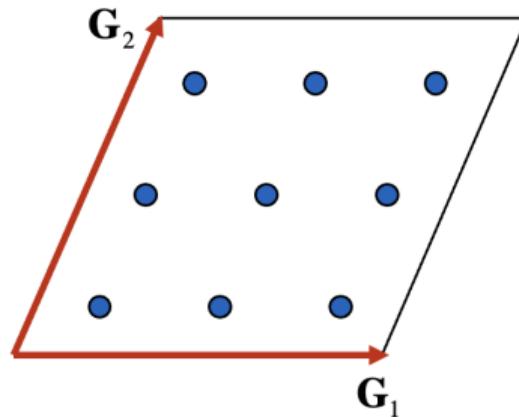

$$n_{k1} = n_{k2} = 3$$
$$s_{k1} = s_{k2} = 0$$
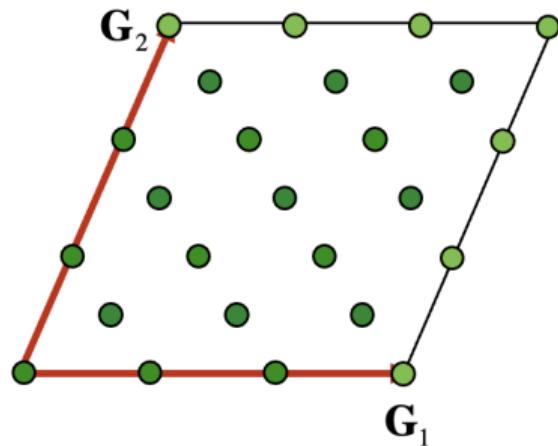
$$n_{k1} = n_{k2} = 3$$
$$s_{k1} = s_{k2} = 0.5$$

It is also possible to combine multiple shifts to create a uniform sampling.

$n_{k1} = n_{k2} = 3$
(unshifted + shifted)

```
ngkpt = nk1 nk2 nk3
nshiftk = nsk
shiftk = sk1(1) sk2(1) sk3(1)
         sk1(2) sk2(2) sk3(2)
         ...
         sk1(nsk) sk2(nsk) sk3(nsk)
```

k-point real space lattice

Internally, Abinit represents the k-point grid with `kptrlatt`
which is a 3×3 scaling matrix for the primitive vectors that defines a supercell
whose reciprocal lattice corresponds to the k-point grid.

The supercell primitive vectors are

$$[\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3]^T = \texttt{kptrlatt} \cdot [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$$

$$\begin{pmatrix} R_{1x} & R_{1y} & R_{1z} \\ R_{2x} & R_{2y} & R_{2z} \\ R_{3x} & R_{3y} & R_{3z} \end{pmatrix} = \begin{pmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{pmatrix} \cdot \begin{pmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{pmatrix}$$
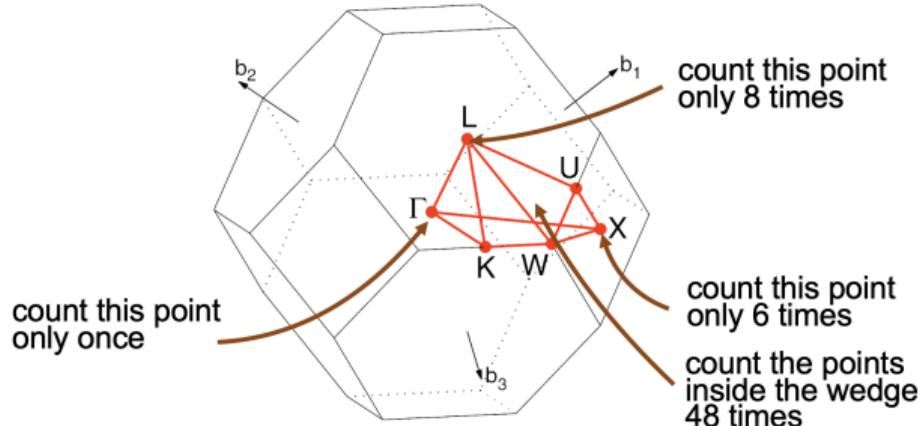
$$[\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3]^T = 2\pi [\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3]^{-1}$$

Reducing the number of k-points

The irreducible Brillouin zone (IBZ) unfolds into the full BZ when we apply all the symmetry operations of the system.

If a homogeneous grid has N points in the full BZ, and if the $\mathbf{k}$ vector in the IBZ is equivalent to $s_{\mathbf{k}}$ points in the full BZ (including itself), then its weight is $w_{\mathbf{k}} = s_{\mathbf{k}}/N$

For example, in a FCC system:
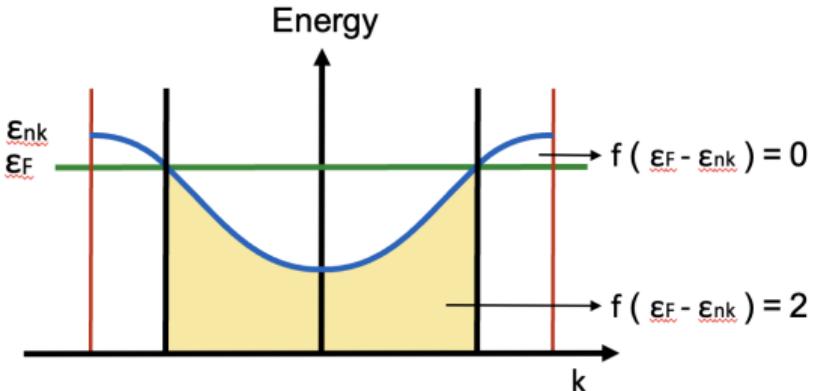
Treatment of metals: Smearing the occupation factors

The occupation factor of fermions are described by Fermi-Dirac statistics

$$f(\epsilon_{n\mathbf{k}}) = \frac{1}{1 + e^{(\epsilon_{n\mathbf{k}} - \epsilon_F)/k_B T}}$$

At $T = 0$ there is a discontinuity in the occupations at the Fermi level.

f goes abruptly from 0 to 2 in an energy range $\sigma = k_B T$.

As a result, an extremely large number of k-points would be needed to describe metallic systems.

Treatment of metals: Smearing the occupation factors

This is solved by using a smearing scheme for the occupation factors with `tsmear` σ

The Fermi-Dirac distribution is replaced with (s = `nsppol`)

$$f(\epsilon_{n\mathbf{k}}) = s \int_{t=(\epsilon_{n\mathbf{k}}-\epsilon_F)/\sigma}^{\infty} \bar{\delta}(t)dt \qquad \text{with} \qquad \int_{-\infty}^{\infty} \bar{\delta}(t)dt = 1$$

Gaussian smearing (`occopt=7`)

$$\bar{\delta}(x) = e^{-x^2}/\sqrt{\pi}$$

Gauss-Hermite smearing (`occopt=6`)

$$\bar{\delta}(x) = \frac{1}{\sqrt{\pi}}\left(\frac{3}{2} - x^2\right)e^{-x^2}$$

Cold smearing (`occopt = 4, 5`)