DFT in practice : Part I
plane wave expansion & the Brillouin zone integration

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Outline

- Plane wave expansion
  - Kohn-Sham equations for periodic systems
  - Potential terms in plane waves
- Brillouin zone integration
  - \( \vec{k} \)-point sampling & Monkhorst-Pack grid
  - Integration in irreducible Brillouin zone
  - Smearing methods
Kohn-Sham equations to be solved self-consistently

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})
\]

\[
V_{\text{eff}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}' - \vec{r}|} + \frac{\delta E_{\text{XC}}[n]}{\delta n(\vec{r})}
\]

\[
n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2
\]

If the exchange-correlation functional is exact the total energy and the density will be exact.

However, Kohn-sham single particle wavefunctions and eigenenergies do not correspond to any exact physical value.
Self-consistent Kohn-Sham loop

Select initial electron density $n_0(\vec{r})$

Construct $V_{KS}(\vec{r}) = v(\vec{r}) + V_H[n] + V_{XC}[n^\uparrow, n^\downarrow]$

Solve $\left[ -\frac{1}{2} \nabla^2 + V_{KS}(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$

Calculate $n(\vec{r}) = \sum_i f_i |\psi_i(\vec{r})|^2$

self-consistent ?

Yes

Output total energy and charge density

No
Basis set representation of Kohn-Sham orbitals

Atomic Orbitals (AO)

\[ \psi_\alpha(\vec{r}) = \psi_\alpha(r) Y_{\ell}^m(\theta, \varphi) \]

where

\[ \psi_\alpha(r) = \begin{cases} 
  e^{-\alpha r^2} & \text{Gaussian} \\
  e^{-\alpha r} & \text{Slater}
\end{cases} \]

molecular structures: slightly distorted atoms

- small basis sets can give good results ✓
- easy to represent vacuum regions ✓
- basis functions are attached to nuclear positions ×
- non-orthogonal ×
- basis set superposition errors (BSSE) ×
Plane waves

\[ \psi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \]

- orthogonal \( \checkmark \)
- periodic \( \checkmark \) (solids)
- nonperiodic \( \times \) (finite systems) \( \Rightarrow \) PBC with supercell approach
- practical for Fourier transform and computation of matrix elements \( \checkmark \)
- atomic wave functions require large number of plane waves \( \times \)
- nonlocalized \( \Rightarrow \) inefficient for parallelization \( \times \)
Bravais lattice, primitive cell & Brillouin zone

Direct lattice: \( \mathbf{a} = [\vec{a}_1, \vec{a}_2, \vec{a}_3] \)

Reciprocal lattice derives from confinement and Fourier analysis of periodic functions:
\[ e^{i\vec{b}_i \cdot \vec{a}_j} = \delta_{ij} \quad \Rightarrow \quad \vec{b}_i \cdot \vec{a}_j = 2\pi \ell \quad (\ell = \text{integer}) \]

Reciprocal latt.: \( \mathbf{b} = 2\pi (\mathbf{a})^{-1} = [\vec{b}_1, \vec{b}_2, \vec{b}_3] \)

Cell volume: \( \Omega_{\text{cell}} = \det(\mathbf{a}) \)

BZ volume: \( \Omega_{\text{BZ}} = \det(\mathbf{b}) = (2\pi)^3 / \Omega_{\text{cell}} \)

Direct lattice vectors: \( \vec{T}(n_1, n_2, n_3) = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \equiv \vec{T}_n \)

Reciprocal latt. vectors: \( \vec{G}(m_1, m_2, m_3) = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \equiv \vec{G}_m \)

1st BZ (Wigner-Seitz cell): boundaries are the bisecting planes of \( \vec{G} \) vectors where Bragg scattering occurs.
Born-von Karman supercell approach

\begin{equation}
\psi_{i,k}(\vec{r} + N_j \vec{a}_j) = \psi_{i,k}(\vec{r})
\end{equation}

Supercell must be sufficiently large to maintain isolation.
Plane wave expansion & the Brillouin zone integration

Plane wave expansion of the single particle wavefunctions

**Bloch’s theorem**

For a periodic Hamiltonian:

\[
\psi_{i,k}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \frac{1}{\sqrt{N_{\text{cell}}}} u_{i,k}(\vec{r}) \quad \left\{ \psi_{i,k}(\vec{r} + \vec{a}_j) = e^{i\vec{k} \cdot \vec{a}_j} \psi_{i,k}(\vec{r}) \right\}
\]

where \( \vec{k} \) is in the first BZ and periodic \( u_{i,k}(\vec{r}) \) can be expanded in a Fourier series:

\[
u_{i,k}(\vec{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}} \sum_m c_{i,m}(\vec{k}) e^{i\vec{G}_m \cdot \vec{r}} \quad \left\{ u_{i,k}(\vec{r} + \vec{a}_j) = u_{i,k}(\vec{r}) \right\}
\]

Equivalently,

\[
\psi_{i,k}(\vec{r}) = \sum_m c_{i,m} \frac{1}{\sqrt{\Omega}} e^{i(\vec{k} + \vec{G}_m) \cdot \vec{r}} \equiv \sum_{\vec{q}} c_{i,\vec{q}} |\vec{q}\rangle \quad (\vec{q} = \vec{k} + \vec{G}_m)
\]
Plane wave expansion & the Brillouin zone integration

Fourier representation of the Kohn-Sham equations

For a crystal,

**Implications of Bloch states**

- $\psi_{i,k}$ is a superposition of PWs with $\vec{q}$ wavevectors which differ by $\vec{G}_m$ to maintain the PBC.

- $\vec{k}$ is well-defined crystal momentum which is conserved.

**Potential has the lattice periodicity as $u_{i,k}(\vec{r})$.**

\[ V_{\text{eff}}(\vec{r}) = \sum_m V_{\text{eff}}(\vec{G}_m) e^{i\vec{G}_m \cdot \vec{r}} \]

Only $\vec{G}_m$ vectors are allowed in the Fourier expansion. The non-zero matrix elements are,

\[ \langle \vec{q}' | V_{\text{eff}} | \vec{q} \rangle = \sum_m V(\vec{G}_m) \langle \vec{q}' | e^{i\vec{G}_m \cdot \vec{r}} | \vec{q} \rangle = \sum_m V_{\text{eff}}(\vec{G}_m) \delta_{\vec{q}'-\vec{q},\vec{G}_m} \]
Substituting these Bloch states into the Kohn-Sham equations, multiplying by $\langle \vec{q}' \rangle$ from the left and integrating over $\vec{r}$ gives a set of matrix equations for any given $\vec{k}$.

$$
\int d\vec{r} \langle \vec{q}' \rangle \times \left\{ \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \sum_{\vec{q}} c_{i,m} |\vec{q}\rangle = \varepsilon_i \sum_{\vec{q}} c_{i,m} |\vec{q}\rangle \right\}
$$

$$
\sum_{m'} \left[ \frac{1}{2} |\vec{k} + \vec{G}_m|^2 \delta_{m,m'} + V_{\text{eff}}(\vec{G}_m - \vec{G}_{m'}) \right] c_{i,m'} = \varepsilon_i c_{i,m}
$$

Matrix diagonalization needed, but still easier to solve.

- Eigenvectors and eigenenergies for each $\vec{k}$ are independent in the 1st BZ.
- In the large $\Omega = N_{\text{cell}} \Omega_{\text{cell}}$ limit, $\vec{k}$ points become a dense continuum and $\varepsilon_i(\vec{k})$ become continuous bands.
Hartree potential in plane waves

\[ V_H(\vec{G}) = \frac{1}{\Omega_{cell}} \int d\vec{r} e^{-i\vec{G} \cdot \vec{r}} \left( \int d\vec{r}' \frac{\sum \tilde{G}_i^* n(\tilde{G}') e^{i\tilde{G}' \cdot \vec{r}'}}{|\vec{r} - \vec{r}'|} \right) \]

\[ = \frac{1}{\Omega_{cell}} \sum_{\tilde{G}'} n(\tilde{G}') \int d\vec{r} e^{i(\tilde{G}' - \tilde{G}) \cdot \vec{r}} \int d\vec{u} e^{i\tilde{G}' \cdot \vec{u}} \frac{1}{|\vec{u}|} \]

\[ = \frac{1}{\Omega_{cell}} \sum_{\tilde{G}'} n(\tilde{G}') \Omega_{cell} \delta_{\tilde{G}, \tilde{G}'} 2\pi \int_0^\infty \int_{-1}^1 \frac{e^{iG' u \cos \theta}}{u} u^2 d(\cos \theta) du \]

\[ = 2\pi n(\vec{G}) \int_0^\infty \frac{e^{iGu} - e^{-iGu}}{iG} du = 4\pi \frac{n(\vec{G})}{G} \int_0^\infty \sin(Gu) du \]

\[ = 4\pi \frac{n(\vec{G})}{G} \lim_{\eta \to 0} \int_0^\infty e^{-\eta u} \sin(Gu) du \]

\[ = 4\pi \frac{n(\vec{G})}{G} \lim_{\eta \to 0} \frac{G}{\eta^2 + G^2} = 4\pi \frac{n(\vec{G})}{G^2} \quad (G \neq 0) \]
Exchange-correlation potential in plane waves

\[ V_{\text{xc}}(\vec{G}) = \frac{1}{\Omega_{\text{cell}}} \int d\vec{r} e^{-i\vec{G} \cdot \vec{r}} \frac{\partial}{\partial n} \left\{ n(\vec{r})\epsilon_{\text{xc}}([n], \vec{r}) \right\} \]

\[ = \frac{1}{\Omega_{\text{cell}}} \int d\vec{r} e^{-i\vec{G} \cdot \vec{r}} \left\{ \sum_{\vec{G}'} \epsilon_{\text{xc}}([n], \vec{G}') e^{i\vec{G}' \cdot \vec{r}} + \sum_{\vec{G}, \vec{G}''} n(\vec{G}'') e^{i\vec{G}'' \cdot \vec{r}} \frac{\partial\epsilon_{\text{xc}}([n], \vec{G}')}{\partial n} e^{i\vec{G}' \cdot \vec{r}} \right\} \]

\[ = \frac{1}{\Omega_{\text{cell}}} \left\{ \sum_{\vec{G}'} \epsilon_{\text{xc}}([n], \vec{G}') \int d\vec{r} e^{i(\vec{G}' - \vec{G}) \cdot \vec{r}} + \sum_{\vec{G}, \vec{G}''} n(\vec{G}'') \frac{\partial\epsilon_{\text{xc}}([n], \vec{G}')}{\partial n} \int d\vec{r} e^{i(\vec{G}'' - \vec{G} + \vec{G}') \cdot \vec{r}} \right\} \]

\[ = \frac{1}{\Omega_{\text{cell}}} \left\{ \sum_{\vec{G}'} \epsilon_{\text{xc}}([n], \vec{G}') \Omega_{\text{cell}} \delta_{\vec{G}, \vec{G}'} + \sum_{\vec{G}, \vec{G}''} n(\vec{G}'') \frac{\partial\epsilon_{\text{xc}}([n], \vec{G}')}{\partial n} \Omega_{\text{cell}} \delta_{\vec{G}''}, \vec{G} - \vec{G}' \right\} \]

\[ = \epsilon_{\text{xc}}([n], \vec{G}) + \sum_{\vec{G}'} n(\vec{G} - \vec{G}') \frac{\partial\epsilon_{\text{xc}}([n], \vec{G}')}{\partial n} \]
Fourier representation of $E_H$ and $E_{XC}$ terms

By similar arguments,

$$E_H = \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} = 2\pi\Omega_{\text{cell}} \sum_{\vec{G} \neq 0} \frac{n(\vec{G})^2}{G^2}$$

$$E_{XC} = \int d\vec{r} n(\vec{r})\epsilon_{xc}(\vec{r}) = \Omega_{\text{cell}} \sum_{\vec{G}} n(\vec{G})\epsilon_{xc}(\vec{G})$$
Plane wave expansion & the Brillouin zone integration

External potential in terms of structure and form factors

Ionic potential as a superposition of isolated atomic potentials

\[ v_{\text{ext}}(\vec{r}) = \sum_{\kappa=1}^{n_{\text{sp}}} \sum_{j=1}^{n_{\kappa}} \sum_{\vec{T}} V^{\kappa}(\vec{r} - \vec{\tau}_{\kappa,j} - \vec{T}) \]

- \( n_{\text{sp}} \) species, \( n_{\kappa} \) atoms at \( \vec{\tau}_{\kappa,j} \) for \( \kappa \), the set of translation vectors \( \vec{T} \)

\[ V_{\text{ext}}(\vec{G}) = \frac{1}{\Omega} \int_{\Omega} d\vec{r} v_{\text{ext}}(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = \frac{1}{\Omega} \sum_{\kappa=1}^{n_{\text{sp}}} \sum_{j=1}^{n_{\kappa}} \int_{\Omega} d\vec{u} V^{\kappa}(\vec{u}) e^{-i\vec{G} \cdot (\vec{u} + \vec{\tau}_{\kappa,j})} \sum_{\vec{T}} e^{-i\vec{G} \cdot \vec{T}} \]

\[ = \frac{1}{\Omega_{\text{cell}}} \sum_{\kappa=1}^{n_{\text{sp}}} \int_{\Omega} d\vec{u} V^{\kappa}(\vec{u}) e^{-i\vec{G} \cdot \vec{u}} \sum_{j=1}^{n_{\kappa}} e^{-i\vec{G} \cdot \vec{\tau}_{\kappa,j}} \equiv \sum_{\kappa=1}^{n_{\text{sp}}} \frac{\Omega^{\kappa}_{\text{cell}}}{\Omega^{\kappa}} S^{\kappa}(\vec{G}) V^{\kappa}(\vec{G}) \]

This form is particularly useful when \( V^{\kappa}(\vec{r}) = V^{\kappa}(|\vec{r}|) \)!
Form factor for a spherically symmetric ionic potential

\[
V_\kappa(\vec{G}) = \frac{1}{\Omega_\kappa} \int_0^\infty \int_{-1}^1 \int_0^{2\pi} V_\kappa(r) e^{-i\vec{G}\cdot\vec{r}} r^2 \, d\phi \, d(cos \theta) \, dr
\]

\[
= \frac{2\pi}{\Omega_\kappa} \int_0^\infty V_\kappa(r) \left. \frac{e^{-iGr(cos \theta)}}{-iGr} \right|_1^{-1} r^2 \, dr
\]

\[
= \frac{2\pi}{\Omega_\kappa} \int_0^\infty \frac{e^{iGr} - e^{-iGr}}{iGr} r^2 \, dr
\]

\[
= \frac{4\pi}{\Omega_\kappa} \int_0^\infty j_0(|\vec{G}|r) V_\kappa(r) r^2 \, dr
\]

\[
= V_\kappa(|\vec{G}|)
\]
Computationally, a complete expansion in terms of infinitely many plane waves is not possible.

The coefficients, \( c_m(\vec{k}) \), for the lowest orbitals decrease exponentially with increasing PW kinetic energy \((\vec{k} + \vec{G}_m)^2/2\).

A cutoff energy value, \( E_{cut} \), determines the number of PWs \( N_{pw} \) in the expansion, satisfying,

\[
\frac{(\vec{k} + \vec{G}_m)^2}{2} < E_{cut} \quad (PW \ sphere) \rightarrow
\]

\( N_{pw} \) is a discontinuous function of the PW kinetic energy cutoff.

Basis set size depends only on the computational cell size and the cutoff energy value.
Electron density in the plane wave basis

\[ n(\mathbf{r}) = \frac{1}{N_k} \sum_{\mathbf{k}, i} n_{i, \mathbf{k}}(\mathbf{r}) \quad \text{where} \quad n_{i, \mathbf{k}}(\mathbf{r}) = |\psi_{i, \mathbf{k}}(\mathbf{r})|^2 \]

Then, in terms of Bloch states,

\[ n_{i, \mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{m, m'} c_{i, m}^*(\mathbf{k}) c_{i, m'}(\mathbf{k}) e^{i(\mathbf{G}_{m'} - \mathbf{G}_m) \cdot \mathbf{r}} \]

and

\[ n_{i, \mathbf{G}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{m} c_{i, m}^*(\mathbf{k}) c_{i, m''}(\mathbf{k}) \]

where \( \mathbf{G}_{m''} = \mathbf{G}_m + \mathbf{G} \implies \text{sphere of } n(\mathbf{G}) \text{ has a double radius.} \)
Properties like the electron density, total energy, etc. can be evaluated by integration over $\mathbf{k}$ inside the BZ.

for the $i^{th}$ band of a function $f_i(\mathbf{k})$

$$\frac{1}{\Omega_{BZ}} \int_{BZ} d\mathbf{k} f_i(\mathbf{k}) \quad \Rightarrow \quad \bar{f}_i = \frac{1}{N_k} \sum_{\mathbf{k}} f_i(\mathbf{k})$$

**Example:**

a 2D square lattice

25 $\mathbf{k}$-points in the BZ

$$\bar{f}_i = f_i(k_1) + \ldots + f_i(k_{25})$$
Moreno and Soler [Phys.Rev.B 45,24] : 
A mesh with uniformly distributed $\vec{k}$-points is preferred.

**Example** : A rectangular lattice

They have nearly the same number of $\vec{k}$-points.

(a) : Isotropic sampling ✓

(b) : finer sampling vertically ✓

poor sampling horizontally ×
Monkhorst-Pack grid

A uniform mesh of $\vec{k}$-points can be generated by Monkhorst-Pack procedure

$$\vec{k}_{n_1,n_2,n_3} = \sum_1^3 \frac{2n_i - N_i - 1}{2N_i} \vec{G}_i$$

where $N_i$ is the number of $\vec{k}$-points in each direction and $n_i = 1, \ldots, N_i$.

**Example**: $4 \times 4 \times 1$ MP grid for 2D square lattice

$$\vec{G}_1 = \vec{b}_1 = \frac{\pi}{a} \hat{k}_x, \quad \vec{G}_2 = \vec{b}_2 = \frac{\pi}{a} \hat{k}_y, \quad \vec{G}_3 = 0$$

$$\vec{k}_{1,1} = \left( -\frac{3}{8}, -\frac{3}{8} \right) \quad \vec{k}_{1,3} = \left( -\frac{3}{8}, \frac{1}{8} \right)$$

$$\vec{k}_{1,2} = \left( -\frac{3}{8}, -\frac{1}{8} \right) \quad \vec{k}_{1,4} = \left( -\frac{3}{8}, \frac{3}{8} \right)$$
**Example**: a 2D square lattice

Centered on $\Gamma$

Centered around $\Gamma$

25 $\vec{k}$-points

[shifted by $(1/8, 1/8, 0)$]

16 $\vec{k}$-points

They both have the same $\vec{k}$-point density in the reciprocal space!
Let the Hamiltonian, $H$, be invariant under time-reversal,

$$THT^{-1} = H \quad \text{(in the absence of magnetic fields!)}$$

then

$$H\psi = \varepsilon\psi$$

$$THT\psi = HT\psi = \varepsilon T\psi$$

$T\psi \equiv \psi^*(\vec{r},-t)$ is also a solution of the same Schrödinger equation with the same eigenvalue.

The solutions $\psi$ and $T\psi$ are orthogonal, $\langle \psi | T\psi \rangle = 0$

Bloch states, $\psi_{i,-\vec{k}}$ and $\psi^*_{i,\vec{k}}$ satisfy the condition $\psi(\vec{r} + \vec{T}_n) = e^{i\vec{k} \cdot \vec{T}_n} \psi(\vec{r})$

$$\implies \varepsilon_{i,-\vec{k}} = \varepsilon_{i,\vec{k}}$$

Kramer's theorem implies inversion symmetry in the reciprocal space!
We use symmetry of the Bravais lattice to reduce the calculation to a summation over $\vec{k}$ inside the IBZ.

**Example**: IBZ of the 2D square lattice

Special $\vec{k}$-points:

- $\Gamma \equiv (0, 0)$: full symmetry of the point group.
- $X \equiv (\frac{1}{2}, 0)$: $E$, $C_2$, $\sigma_x$, $\sigma_y$
- $M \equiv (\frac{1}{2}, \frac{1}{2})$: full symmetry of the point group.

Then, we can unfold the IBZ by the symmetry operations to get the solution for the full BZ.
Preserve symmetry

*Example*: Hexagonal cell

Shift the $\vec{k}$-point mesh to preserve hexagonal symmetry!

In this case, even meshes break the symmetry.

A mesh centered on $\Gamma$ preserves the symmetry.
Integration in the IBZ

- Generate a uniform mesh in reciprocal space
- Shift the mesh if required
- Employ all symmetry operations of the Bravais lattice to each of the \( \vec{k} \)-points
- Select the \( \vec{k} \)-points which fall into the IBZ
- Calculate weights, \( \omega_{\vec{k}} \), for each of the selected \( \vec{k} \)-points

\[
\omega_{\vec{k}} = \frac{\text{number of symmetry connected } \vec{k} \text{-points}}{\text{total number of } \vec{k} \text{-points in the BZ}}
\]

- IBZ integration is then given by

\[
\bar{f}_i = \sum_{\vec{k}}^{\text{IBZ}} \omega_{\vec{k}} f_i(\vec{k})
\]
**Example:** 4×4×1 MP grid for 2D square lattice

4×4×1 MP grid = 16 $\vec{k}$-points in the BZ

4 equivalent $\vec{k}_{4,4} = \left(\frac{3}{8}, \frac{3}{8}\right)$ $\Rightarrow$ $w_k = \frac{1}{4}$

4 equivalent $\vec{k}_{3,3} = \left(\frac{1}{8}, \frac{3}{8}\right)$ $\Rightarrow$ $w_k = \frac{1}{4}$

8 equivalent $\vec{k}_{4,3} = \left(\frac{3}{8}, \frac{1}{8}\right)$ $\Rightarrow$ $w_k = \frac{1}{2}$

Then, the BZ integration reduces to,

$$\bar{f}_i = \frac{1}{4} f_i(\vec{k}_{4,4}) + \frac{1}{4} f_i(\vec{k}_{3,3}) + \frac{1}{2} f_i(\vec{k}_{4,3})$$
Fermi level: the energy of the highest occupied band.

IBZ integration over the filled states: \[ \bar{f}_i = \sum_{\vec{k}} \omega_{\vec{k}} f_i(\vec{k}) \theta(\varepsilon_i(\vec{k}) - \varepsilon_F) \]

For insulators and semiconductors, DOS goes to zero smoothly before the gap.

For metals, the resolution of the step function at the Fermi level is very difficult in plane waves.

Trick is to replace sharp \( \theta(\varepsilon_i(\vec{k}) - \varepsilon_F) \) function with a smoother \( f(\{\varepsilon_i(\vec{k})\}) \) function allowing partial occupancies at the Fermi level.
Fermi-Dirac smearing

In order to overcome the discontinuity of the functions at the Fermi level,

\[
f\{\varepsilon_i(\vec{k})\} = \frac{1}{e^{(\varepsilon_i(\vec{k}) - \varepsilon_F)/\sigma} + 1}
\]

where \(\sigma = k_B T\)

\(T \rightarrow 0\) : Fermi-Dirac distribution approaches to the step function.

Finite temperature \(T\) introduces entropy to the system of non-interacting particles,

\[
S(f) = -[f \ln f + (1 - f) \ln(1 - f)]
\]

and the Free energy is given by,

\[
F = E - \sum_i \sigma S(f_i)
\]

**Drawback** : reduced occupancies below \(\varepsilon_F\) are not compensated new occupancies above \(\varepsilon_F\).
Gaussian smearing

An approximate step function is obtained by integration of a Gaussian-approximated delta function.

\[ f\{(\varepsilon_{i\mathbf{k}})\} = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{\varepsilon_{i\mathbf{k}} - \varepsilon_F}{\sigma} \right) \right] \]

Smearing parameter, \( \sigma \), has no physical interpretation.

Entropy and the free energy cannot be written in terms of \( f \).

\[ S \left( \frac{\varepsilon - \varepsilon_F}{\sigma} \right) = \frac{1}{2\sqrt{\pi}} \exp \left[ - \left( \frac{\varepsilon - \varepsilon_F}{\sigma} \right)^2 \right] \]
To overcome the drawback introduced by the Fermi-Dirac smearing, 
Expand the step function in a complete set of orthogonal Hermite 
functions. (Hermite polynomials multiplied by Gaussians)

\[ \delta(x) \approx D_N = \sum_{n=0}^{N} A_n H_{2n} e^{-x^2} \rightarrow (H_{2n} : \delta(x) \text{ is even}) \]

\[ \theta(x) \approx S_N = 1 - \int_{-\infty}^{\infty} D_N(t)dt \]

\[ S_0 = \frac{1}{2} (1 - \text{erf}(x)) \rightarrow (\text{Gaussian smearing}) \]

\[ S_N = S_0(x) + \sum_{n=1}^{N} A_n H_{2n-1}(x)e^{-x^2} \]

Yields negative occupation numbers!
Marzari-Vanderbilt : cold smearing

Amends the negative occupation numbers introduced by Methfessel-Paxton.

The delta function is approximated by a Gaussian multiplied by a first order polynomial,

\[ \tilde{\delta}(x) = \frac{1}{\sqrt{\pi}} e^{-[x-(1/\sqrt{2})]^2(2 - \sqrt{2}x)} \]

where

\[ x = \frac{\varepsilon_{ik} - \varepsilon_F}{\sigma} \]
Linear tetrahedron method

Divide the BZ into tetrahedra

Interpolate the function $X_i$ within these tetrahedra

Integrate the interpolated function to obtain $\bar{X}_i$