Planewaves, Brillouin zone sampling, Pseudopotentials, PAW and other basis sets

Mojtaba Alaei

Skoltech

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2 Periodic Solids

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Differences in DFT codes

Theoretical Frameworks:

- Orbital-Dependent (Kohn-Sham) DFT (very common)
- Orbital-Free DFT (OF-DFT)

Numerical Implementation Methods:

- Basis Set Methods (e.g., Gaussian, Plane Waves)
- Real-Space / Grid-Based Methods (e.g., Finite Element, Finite Difference)

Basis set KS-DFT methods

Expansion of wave-functions using a basis set $\{\phi_i(\mathbf{r})\}_{i=1}^{M}$:

$$\boxed{\psi(\mathbf{r}) = \sum_{i=1}^{M} c_i \phi_i(\mathbf{r})}$$

Basis set KS-DFT methods

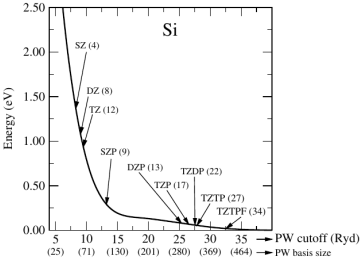
$\phi_i(\mathbf{r})$ Types and Codes:

- **Plane-waves**: $e^{i\mathbf{k}\cdot\mathbf{r}}$
  - Codes: VASP, Quantum ESPRESSO (QE), ABINIT, CASTEP
- **Local basis sets**:
  - Gaussian-type orbitals (GTOs): Gaussian, GAMESS, ORCA, NWChem
  - Numerical Atomic Orbitals (NAOs): FHI-aims, SIESTA, FPLO
  - Slater-type orbitals (STOs): ADF (Amsterdam Density Functional)
- **Mixed / Augmented basis sets**:
  - (L)APW + local orbitals: ELK, WIEN2k, FLEUR
  - Gaussian + Plane Waves (GPW): CP2K
  - Projector Augmented Wave (PAW): GPAW, QE, VASP

Basis set KS-DFT methods

Note

Optimize M (number of basis functions) when performing DFT calculations.



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Nitty-gritty of plane-wave DFT codes!

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- Crystal structure
- Reciprocal Lattice and Brillouin Zone

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Crystal structure

Crystal structure = Bravais lattice + basis.

Bravais lattice

Infinite array of discrete points: $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$

- n_i are integers
- $\mathbf{a}_i$ are primitive vectors

Bravais lattice

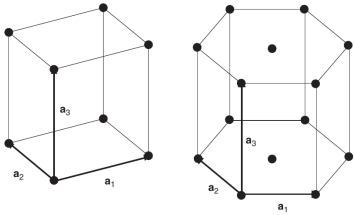

Figure 1: Simple cubic (left) and simple hexagonal (right) Bravais lattices.

basis

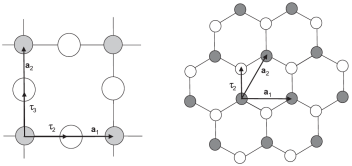

Figure 2: Left: square lattice for CuO_2 planes, Right: honeycomb lattice for a single plane of graphite (graphene) or hexagonal BN.

Graphene lattice (2D crystal)

- primitive (lattice) vectors: $\mathbf{a}_1 = (1,0)a$, $\mathbf{a}_2 = (\frac{1}{2}, \frac{\sqrt{3}}{2})a$, a is lattice parameter.
- basis: $\boldsymbol{\tau}_1 = (0,0)$, $\boldsymbol{\tau}_2 = (0, \frac{1}{\sqrt{(3)}})a$

Primitive Vectors

Note

Primitive vectors are not unique!

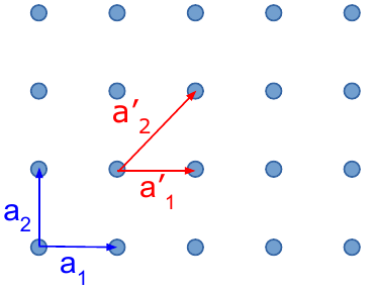

Figure 3: Different primitive vectors used to represent a square lattice.

Cell Volume

The cell volume Ω_{cell} for dimensionality d:

- $d = 1$: $\Omega = |a_1|$
- $d = 2$: $\Omega = |\mathbf{a}_1 \times \mathbf{a}_2|$
- $d = 3$: $\Omega = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$

For any dimension, it can be written simply as:

$$\Omega_{\text{cell}} = |\det(\mathbf{A})|$$

where $\mathbf{A}$ is the basis matrix in row-vector form:

$$\mathbf{A} = \begin{bmatrix} — & \mathbf{a}_1 & — \\ — & \mathbf{a}_2 & — \\ — & \mathbf{a}_3 & — \end{bmatrix} = \begin{bmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{bmatrix}$$

Symmetry Operations

- **Crystalline Order** is defined by symmetry operations:
  - **Translations:** Form a group (closed under addition).
  - **Point Operations:** Rotations, reflections, and inversions that leave the crystal invariant.

$$\text{Space Group} = \text{Translation Group} \times \text{Point Group}$$

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Translational Symmetry

Crystal properties, such as electron density $n(\mathbf{r})$, must satisfy:

$$f(\mathbf{r} + \mathbf{T}) = f(\mathbf{r})$$

where the translation vector $\mathbf{T}$ is defined as:

$$\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (n_i \in \mathbb{Z})$$

Physical Implication

The environment at $\mathbf{r}$ is identical to the environment at $\mathbf{r} + \mathbf{T}$.

Fourier Representation & Periodic Boundary Conditions

A periodic function $f(\mathbf{r})$ can be expressed as a discrete sum of Fourier components:

$$f(\mathbf{r}) = \sum_{\mathbf{q}} f(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

Born–von Karman Boundary Conditions

For a crystal of $N = N_1 \times N_2 \times N_3$ cells, we require:

$$e^{i\mathbf{q}\cdot N_i \mathbf{a}_i} = 1 \qquad \Longrightarrow \qquad \mathbf{q}\cdot\mathbf{a}_i = \frac{2\pi \times \text{integer}}{N_i}$$

- **Reciprocal Space:** The wavevectors $\mathbf{q}$ are restricted to a discrete set.
- **Thermodynamic Limit:** As $N_i \to \infty$, the results become independent of the specific choice of boundary conditions.

Fourier Transform & Periodicity

The Fourier transform over the entire crystal volume Ω is:

$$f(\mathbf{q}) = \frac{1}{\Omega} \int_{\text{crystal}} f(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \, d\mathbf{r}$$

For a periodic function $f(\mathbf{r} + \mathbf{T}) = f(\mathbf{r})$, this simplifies to:

$$f(\mathbf{q}) = \underbrace{\frac{1}{N_{\text{cell}}} \sum_{\mathbf{T}} e^{i\mathbf{q}\cdot\mathbf{T}}}_{\text{Interference Term}} \times \underbrace{\frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} f(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \, d\mathbf{r}}_{\text{Cell Form Factor}}$$

The Selection Rule

The sum over lattice points $\mathbf{T}$ vanishes **unless**:

$$\mathbf{q} \cdot \mathbf{T} = 2\pi \times \text{integer} \quad \text{for all } \mathbf{T}$$

The Reciprocal Lattice

The set of vectors $\{\mathbf{G}\}$ satisfying the selection rule forms the **reciprocal lattice**.

- **Reciprocal Basis Vectors:** Defined by $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$
- **Reciprocal Lattice Vector:** $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$

Fourier Coefficients

The only non-zero Fourier components occur at $\mathbf{q} = \mathbf{G}$:

$$f(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} f(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}}\, d\mathbf{r}$$

The reciprocal lattice is the Fourier transform of the real-space lattice.

Reciprocal Basis and Volume

Reciprocal Basis Vectors ($d = 3$)

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|} \quad (+ \text{ cyclic permutations})$$

Geometric Forms:

- **1D:** $|b_1|$
- **2D:** $|\mathbf{b}_1 \times \mathbf{b}_2|$
- **3D:** $|\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|$

BZ Volume Relation

The Brillouin Zone volume follows:

$$\Omega_{\mathrm{BZ}} = |\det(\mathbf{B})| = \frac{(2\pi)^d}{\Omega_{\mathrm{cell}}}$$

Note the mutual reciprocal relationship between Ω_{BZ} and Ω_{cell}.

Reciprocal Basis in 2D

For a 2D lattice in the xy-plane with primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$:

The 2D Formulas

The reciprocal vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are defined as:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \hat{\mathbf{z}}}{|\mathbf{a}_1 \times \mathbf{a}_2|}, \quad \mathbf{b}_2 = 2\pi \frac{\hat{\mathbf{z}} \times \mathbf{a}_1}{|\mathbf{a}_1 \times \mathbf{a}_2|}$$

where $\hat{\mathbf{z}}$ is the unit vector perpendicular to the plane.

- **Orthogonality:** $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$
- **Direction:** $\mathbf{b}_1$ is perpendicular to $\mathbf{a}_2$, and $\mathbf{b}_2$ is perpendicular to $\mathbf{a}_1$.
- **Area:** The 2D Brillouin Zone area is:

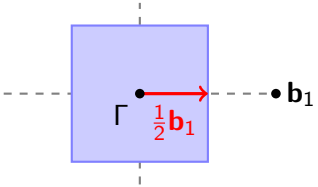
$$\Omega_{\mathrm{BZ}} = |\mathbf{b}_1 \times \mathbf{b}_2| = \frac{(2\pi)^2}{\Omega_{\mathrm{cell}}}$$

The First Brillouin Zone (BZ)

Definition

The **First Brillouin Zone** is the Wigner–Seitz cell of the reciprocal lattice.

- **Construction:** Formed by the perpendicular bisector planes of the vectors from the origin to reciprocal lattice points.
- **Physics (Bragg Condition):** Elastic scattering occurs **only** on the BZ boundaries.
- **Scattering-Free Region:** Wavevectors **k** strictly *inside* the BZ cannot satisfy the Bragg condition.



BZ in 2D

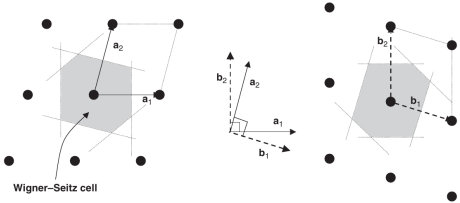


Figure 4: Bravais lattices are defined by primitive vectors and can be represented by either conventional parallelograms or the **unique**, symmetric Wigner–Seitz cell. The corresponding first Brillouin zone is defined as the Wigner-Seitz cell within the reciprocal lattice.

Symmetry and Translation Operators

- **Periodic Hamiltonian:** For independent particles, $\hat{H}$ is invariant under lattice translations $\mathbf{T}_n$:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(\mathbf{r}), \quad \text{where } V(\mathbf{r} + \mathbf{T}_n) = V(\mathbf{r})$$

- **Translation Operator $\hat{T}_n$:** Acts on a function by displacing its argument:

$$\hat{T}_n \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{T}_n)$$

- **Commutation:** Since V is periodic, $[\hat{H}, \hat{T}_n] = 0$.

Mathematical Consequence

$\hat{H}$ and $\hat{T}_n$ share a common set of eigenstates. We can classify energy states by their eigenvalues of the translation operator.

Eigenvalues of Translation

Translations form a group: $\hat{T}_{n1}\hat{T}_{n2} = \hat{T}_{n1+n2}$. Thus, their eigenvalues t_n must satisfy:

$$t_{n1}t_{n2} = t_{n1+n2}$$

- **Boundedness:** To keep the wavefunction finite in an infinite crystal, $|t_i| = 1$.
- **Phase Form:** This implies $t(a_i) = e^{i2\pi y_i}$.
- **Reciprocal Space:** Using periodic boundary conditions, we find:

$$t_n = e^{i\mathbf{k}\cdot\mathbf{T}_n}$$

where $\mathbf{k} = \sum \frac{n_i}{N_i}\mathbf{b}_i$ is a wavevector in reciprocal space.

The Bloch Theorem

The eigenstates of a periodic potential satisfy:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}_n) = e^{i\mathbf{k}\cdot\mathbf{T}_n}\psi_{\mathbf{k}}(\mathbf{r})$$

The Bloch Form

Equivalently, the wavefunction can be written as a plane wave modulated by a **cell-periodic** function $u_{\mathbf{k}}(\mathbf{r})$:

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

where $u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}_n) = u_{\mathbf{k}}(\mathbf{r})$.

This theorem applies to all excitations: electrons, phonons, and more.

Key Physical Consequences

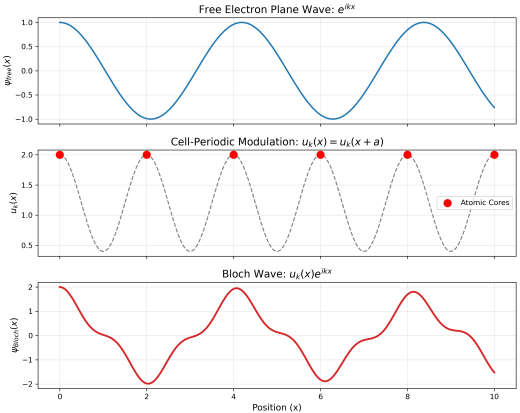
1. **Energy Bands:** For each $\mathbf{k}$, there is a discrete set of eigenvalues $\epsilon_{i,\mathbf{k}}$, forming continuous energy bands.
2. **Crystal Momentum:** $\mathbf{k}$ is conserved modulo a reciprocal lattice vector $\mathbf{G}$.
3. **Umklapp Scattering:** Scattering events where momentum is "reset" by adding $\mathbf{G}$ to stay within the BZ.
4. **Brillouin Zone:** All unique physics is contained within the first BZ. Energies $\epsilon(\mathbf{k})$ are analytic inside but can be non-analytic at the boundaries (Bragg planes).

Visualizing the Bloch Wave

- **Free Electron:** A simple plane wave $\psi \propto e^{i\mathbf{k}\cdot\mathbf{r}}$ with constant amplitude.
- **Bloch Electron:** The amplitude is "reshaped" by the atoms, but the wave nature remains.

The Formula

$$\psi_{\mathbf{k}}(\mathbf{r}) = \underbrace{u_{\mathbf{k}}(\mathbf{r})}_{\text{Atomic}} \times \underbrace{e^{i\mathbf{k}\cdot\mathbf{r}}}_{\text{Wave}}$$



Red dots represent atomic nuclei where the electron is most likely to be found.

Energy Bands and the Brillouin Zone

- **Continuous Limit:** In macroscopic crystals, the spacing between k-points goes to zero; k becomes a continuous variable.
- **Band Structure:** For each k, there is a discrete set of eigenstates labeled by index i, leading to energy bands $\epsilon_{i,\mathbf{k}}$ and **energy gaps**.
- **Role of the BZ:** The Brillouin Zone is the cell of choice for representing excitations.
  - $\epsilon_{i,\mathbf{k}}$ is **analytic** inside the BZ.
  - Non-analytic behavior occurs only at **boundaries** (Bragg planes).

Symmetry Points

High-symmetry points and lines (e.g., Γ, X, L) are used to define directions for electron bands and phonon dispersion curves.

Integrals in k-space

To find intrinsic properties (e.g., total energy per cell), we must sum over all k-states.

- **Discrete Sum:** In a crystal with $N_{\text{cell}}(= N_k)$ cells, there is exactly one k-value per cell:

$$\bar{f}_i = \frac{1}{N_k} \sum_{\mathbf{k}} f_i(\mathbf{k})$$

Key Principle

Under periodic boundary conditions for a crystal of $N_{\text{cell}} = N_1 \times N_2 \times N_3$ cells, there is **exactly one k-value per unit cell**.

Physical Meaning: A denser k-mesh corresponds to simulating a larger crystal with more extended periodic boundary conditions. As $N_k \to \infty$, we recover the macroscopic limit.

Application: Calculating Charge Density

The total electron density $\rho(\mathbf{r})$ is found by summing over all occupied bands i and wavevectors $\mathbf{k}$ in the Brillouin Zone:

$$\rho(\mathbf{r}) = \sum_{i,\text{occ}} \frac{1}{N_k} \sum_{\mathbf{k}\in\text{BZ}} |\psi_{i,\mathbf{k}}(\mathbf{r})|^2$$

Continuous Limit (Thermodynamic Limit)

Converting the discrete sum into a k-space integral:

$$\rho(\mathbf{r}) = \sum_{i,\text{occ}} \frac{\Omega_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} |\psi_{i,\mathbf{k}}(\mathbf{r})|^2 \, d\mathbf{k}$$

Crystal Space Groups

The total **Space Group** of a crystal is the combination of the Translation Group and the Point Group.

- **Point Symmetries:** Rotations, inversions, and reflections that leave the system invariant.
- **Nonsymmorphic Operations:** Combinations of point symmetries with fractional translations (e.g., "glides" or "screws").

Symmetry Operation on a Function

Any function of the crystal (density $n(\mathbf{r})$ or energy E) transforms as:

$$\mathcal{R}_n g(\mathbf{r}) = g(\mathbf{R}_n \mathbf{r} + \mathbf{t}_n)$$

where $\mathbf{R}_n$ is the point operation and $\mathbf{t}_n$ is the fractional translation.

Symmetry and the Schrödinger Equation

Since the Hamiltonian $\hat{H}$ is invariant under symmetry operations, if $\psi_{i,\mathbf{k}}$ is an eigenstate, then $\psi_{i,\mathbf{R}_n\mathbf{k}}$ is also an eigenstate with the **same eigenvalue**:

$$\epsilon_{i,\mathbf{R}_n\mathbf{k}} = \epsilon_{i,\mathbf{k}}$$

- **High-Symmetry Points:** At points where $\mathbf{R}_n\mathbf{k} = \mathbf{k}$ (e.g., the Γ point), eigenstates are classified by group representations.
- **Degeneracy:** Symmetry forces certain states to have the same energy.
  - *Example:* In cubic crystals at $\mathbf{k} = 0$, states often have 2-fold or 3-fold degeneracy.
- **Time-Reversal Symmetry:** Relates states at $\mathbf{k}$ and $-\mathbf{k}$, further reducing unique calculations by a factor of 2.

The Irreducible Brillouin Zone (IBZ)

The **IBZ** is the smallest fraction of the Brillouin Zone sufficient to determine all excitations of the crystal.

- Information at all other k-points can be generated via symmetry operations.
- **Efficiency:** DFT codes only calculate wavefunctions in the IBZ to save time.
- **Reduction Factors:**
  - Square Lattice: IBZ $= 1/8$ of BZ.
  - Cubic (High Symmetry): IBZ $=$ **1/48** of BZ.

Computational Tip

Most plane-wave codes automatically detect the point group to minimize the number of k-points sampled.

IBZ

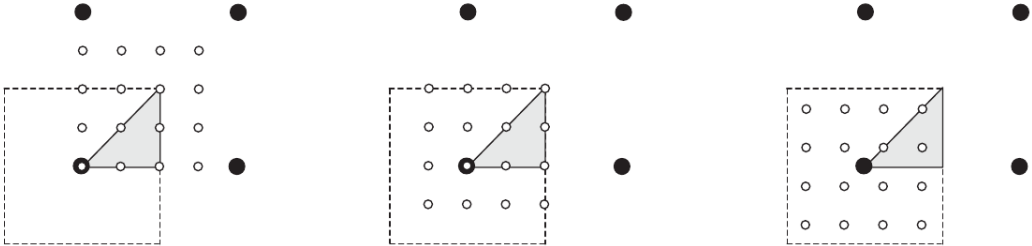


Figure 5: Integration grids for a 2D square lattice (density). Left/Center: Unshifted grid with 6 inequivalent IBZ points (gray). Right: Shifted special-point grid with only 3 inequivalent points.

The Monkhorst-Pack (MP) Method

The most widely used method for BZ integration, defined by a simple uniform grid:

$$\mathbf{k}_{n_1,n_2,n_3} = \sum_{i=1}^{3} \frac{2n_i - N_i - 1}{2N_i} \mathbf{b}_i$$

where $n_i = 1, 2, \ldots, N_i$ and $\mathbf{b}_i$ are reciprocal basis vectors.

Main Features

- **Uniformity:** Points are scaled versions of the reciprocal lattice.
- **Exact Integration:** Perfectly integrates Fourier components up to $N_i\mathbf{a}_i$.
- **Symmetry:** The grid is centered around the origin, covering the primitive cell of the reciprocal lattice.

Practical k-point Sampling: Metals vs. Insulators

The required mesh density ($N_1 \times N_2 \times N_3$) depends on the complexity of the **Fermi surface**:

Insulators & Semiconductors

Occupied bands are fully separated from empty ones by a gap.

- **Convergence:** Very fast with k-points.
- **Typical Mesh:** $4 \times 4 \times 4$ or $6 \times 6 \times 6$.
- **Logic:** Functions are smooth in k-space.

Metals

Bands cross the Fermi level (E_F), creating a sharp discontinuity.

- **Convergence:** Very slow; requires a dense mesh.
- **Typical Mesh:** $12 \times 12 \times 12$ to $40 \times 40 \times 40$.
- **Method:** Often requires **Smearing** (Gaussian or Methfessel-Paxton).

Convergence Rule: Always perform a *total energy vs. k-points* test to ensure accuracy.

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The Plane-Wave Basis Set

Philosophy

Treat assemblies of atoms as **slight distortions** to a free-electron gas.

$$\phi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

Advantages (+)

- **Orthogonal** by construction.
- **Independent** of atomic positions (no "Pulay forces").
- **No BSSE:** Basis Set Superposition Error is absent.

Challenges (± / −)

- **Periodic:** Naturally fits crystal symmetry (±).
- **Efficiency:** Requires a **large number** of functions to describe core electrons (−).

Expansion of Kohn-Sham Orbitals

According to the **Bloch Theorem**, the electronic wavefunctions (Kohn-Sham orbitals) in a periodic potential can be expanded in a **plane-wave basis**:

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

The Computational Goal

The Schrödinger equation is transformed into a **matrix eigenvalue problem**. The primary task of a DFT code is to solve for the unknown coefficients: $c_{i,\mathbf{k}}(\mathbf{G})$

- i**:** Band index.
- **k:** Wavevector in the first Brillouin Zone.
- **G:** Reciprocal lattice vectors.

Plane Waves: Kinetic Energy

The kinetic energy operator is **diagonal** in the plane-wave basis set, which is a major computational advantage.

Action on a Basis Function

Applying the kinetic energy operator $-\frac{1}{2}\nabla^2$ to a plane-wave basis function:

$$-\frac{1}{2}\nabla^2\phi_{\mathbf{G}}(\mathbf{r}) = -\frac{1}{2}(i\mathbf{G})^2\frac{1}{\sqrt{\Omega}}e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{1}{2}G^2\phi_{\mathbf{G}}(\mathbf{r})$$

- **Eigenvalues:** The kinetic energy for a given **G** vector is simply:

$$E_{\text{kin}}(\mathbf{G}) = \frac{1}{2}G^2$$

- **Efficiency:** In this basis, the kinetic energy matrix is **strictly diagonal**.

Note: Atomic units ($m_e = 1, \hbar = 1$) are used here.

The Kinetic Energy Cutoff (E_{cut})

To make the basis set finite, we truncate the infinite expansion:

The Cut-off Sphere

Include **G** satisfying:

$$\frac{1}{2}G^2 \leq E_{\text{cut}}$$

This defines a sphere with radius:

$$G_{\text{max}} = \sqrt{2E_{\text{cut}}}$$

Key Properties:

- **Size (N_{PW}):** Scales with volume:

$$N_{PW} \approx \frac{\Omega}{2\pi^2} E_{\text{cut}}^{3/2}$$

- **Independence:** Depends **only** on Ω and E_{cut}.
- **Variational:** Increasing E_{cut} monotonically lowers total energy.

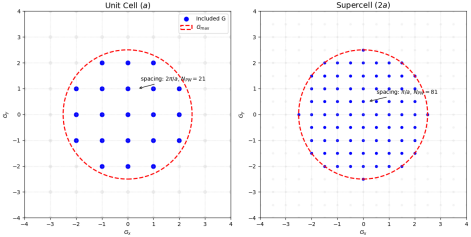
Effect of Volume on Basis Set Size

For a fixed energy cutoff E_{cut}, N_{PW} scales linearly with the real-space volume Ω.

Reciprocal Space Scaling

As volume Ω increases:

- Reciprocal spacing **decreases**.
- G-point grid becomes **denser**.
- More points fit inside the fixed G_{max} sphere.



Computational Cost

$N_{PW} \propto \Omega \cdot E_{\text{cut}}^{3/2}$. Linear scaling means vacuum regions or large supercells significantly increase memory usage.

Plane Wave Expansion: The Hamiltonian

The Hamiltonian H for a periodic system is:

$$H(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

Periodic Potential $V(\mathbf{r})$

Since the potential follows the periodicity of the lattice, we expand it in terms of reciprocal lattice vectors $\mathbf{G}$:

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

- The Fourier coefficients $V_{\mathbf{G}}$ are calculated via integration:

$$V_{\mathbf{G}} = \frac{1}{N_u}\int V(\mathbf{r}')e^{-i\mathbf{G}\cdot\mathbf{r}'}d\mathbf{r}'$$

- N_u represents the number of unit cells in the crystal.

The Schrödinger Equation in **G**-space

Substituting the plane wave expansion into $H\Psi = E\Psi$ yields:

Substituted Equation

$$\sum_{\mathbf{G}} \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 C_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G}',\mathbf{G}''} V_{\mathbf{G}'} C_{\mathbf{G}''} e^{i(\mathbf{k}+\mathbf{G}'+\mathbf{G}'')\cdot\mathbf{r}} = E \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

By setting $\mathbf{G} = \mathbf{G}' + \mathbf{G}''$ and extracting the coefficient for each $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$ term, we obtain the central equation:

$$\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 C_{\mathbf{G}} + \sum_{\mathbf{G}''} V_{\mathbf{G}-\mathbf{G}''} C_{\mathbf{G}''} = E C_{\mathbf{G}}$$

The Hamiltonian Matrix

The problem is solved numerically by constructing an $N \times N$ matrix $H_{\mathbf{GG}'}$ and solving the eigenvalue problem:

$$\mathbf{HC} = E\mathbf{C}$$

Matrix Elements

The elements of the Hamiltonian matrix are defined as:

$$H_{\mathbf{GG}'} = \begin{cases} \frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 + V_0 & \text{if } \mathbf{G} = \mathbf{G}' \\ V_{\mathbf{G}-\mathbf{G}'} & \text{if } \mathbf{G} \neq \mathbf{G}' \end{cases}$$

- **Diagonal:** Kinetic energy + average potential.
- **Off-Diagonal:** Potential components that "couple" different plane waves.
- **Solution:** Diagonalize $\mathbf{H}$ to find energies E and coefficients $C_{\mathbf{G}}$.

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The Challenge of Full-Potential Calculations

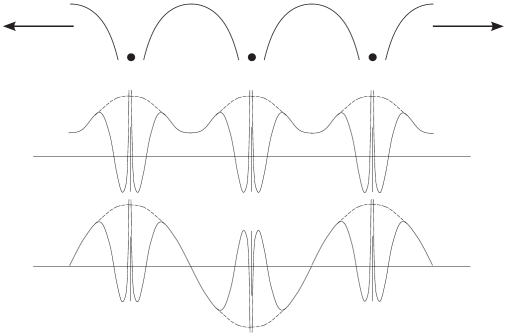


Figure 6: Schematic illustration of a periodic potential in a crystal extending to the left and right and two examples of Bloch states

The Challenge of Full-Potential Calculations

1. Physical Reality: Core vs. Valence

- **Chemical Bonding:** Core electrons are tightly bound and generally do not contribute to chemical bonding between atoms.
- **Computational Waste:** Treating inert core electrons with the same precision as valence electrons is often unnecessary.

2. The "Near-Nucleus" Problem

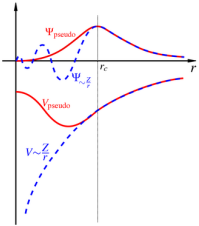
- **Rapid Oscillations:** Near the nucleus, wavefunctions oscillate rapidly to maintain orthogonality to core states.
- **Basis Set Explosion:** To describe these sharp features, a massive number of plane waves (N_{PW}) is required.

Result: Extremely high computational cost for relatively little gain in chemical accuracy.

The Philosophy of Pseudopotentials

The Core Idea

Replace the complex potential with a **pseudopotential**. Outside a cutoff radius (r_c), the valence electrons behave as if they see the real potential.



Real (blue) vs. Pseudo (red) wavefunctions.

Analogy: Decoy cars create the same behavior as real ones!

- **Benefit:** Smoother functions require fewer plane waves (N_{PW}).

The Origins: Orthogonalized Plane Waves (OPW)

The pseudopotential formalism grew out of the **OPW method**, where plane waves are made orthogonal to all core wavefunctions $|\psi_c\rangle$.

Defining the OPW Basis

An Orthogonalized Plane Wave $|\text{OPW}, \mathbf{G}\rangle$ is constructed from a standard plane wave $|\text{PW}, \mathbf{G}\rangle$ and core states $|\psi_c\rangle$:

$$|\text{OPW}, \mathbf{G}\rangle = |\text{PW}, \mathbf{G}\rangle - \sum_{c}^{\text{core}} |\psi_c\rangle\langle\psi_c|\text{PW}, \mathbf{G}\rangle$$

- **Result:** The expansion now accounts for the rapid oscillations near the nucleus.
- **Goal:** Use these "wiggly" basis functions to describe valence states while keeping the plane-wave simplicity.

Constructing the Smooth Pseudostate

We define a **smooth pseudostate** $|\phi_v\rangle$ by subtracting the core orthogonality "wiggles" from the true valence state $|\psi_v\rangle$:

$$|\phi_v\rangle = |\psi_v\rangle + \sum_c \alpha_{cv}|\psi_c\rangle \tag{1}$$

where the coefficients are given by the projection: $\alpha_{cv} = \langle\psi_c|\phi_v\rangle$.

- $|\psi_v\rangle$ is the true, oscillating valence state.
- $|\phi_v\rangle$ is the smooth, computationally efficient pseudo-state.
- The summation acts as a **repulsive term** that cancels the strong nuclear attraction in the core region.

The Pseudo-Hamiltonian

Applying the original Hamiltonian H to our pseudostate $|\phi_v\rangle$ leads to an effective eigenvalue problem:

The Pseudo-Schrödinger Equation

$$H^{ps}(E)|\phi_v\rangle = E_v|\phi_v\rangle$$

where the **Pseudo-Hamiltonian** is defined as:

$$H^{ps}(E) = H + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c|$$

- **Non-locality:** The potential now depends on the projectors $|\psi_c\rangle\langle\psi_c|$.
- **Energy Dependence:** The effective potential depends on the eigenvalue E.
- **Trade-off:** We have removed the "wiggles" (lowering N_{PW}) at the expense of introducing a more complex, non-local operator.

Connection to the PAW Method

The construction of the smooth pseudostate can be viewed as a **linear transformation** between the physical and auxiliary wavefunctions.

The Linear Transformation $\mathcal{T}$

We can define an operator $\mathcal{T}$ that maps the smooth pseudo-state $|\phi_v\rangle$ back to the true, oscillating valence state $|\psi_v\rangle$:

$$|\psi_v\rangle = \mathcal{T}|\phi_v\rangle$$

Based on our previous derivation:

$$|\psi_v\rangle = |\phi_v\rangle - \sum_c \alpha_{cv}|\psi_c\rangle$$

- **PAW Approach:** This is exactly the foundational form used in the **Projector Augmented-Wave (PAW)** method.

The Phillips-Kleinman Pseudopotential

The Phillips-Kleinman (PK) approach defines the pseudopotential as the sum of the true atomic potential and a repulsive projection term.

The PK Potential Formulation

$$V^{PK} = V_{real} + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c|$$

Where:

- V_{real}: The strong, attractive nuclear potential.
- $(E - E_c)|\psi_c\rangle\langle\psi_c|$: The repulsive "cancellation" term.

The Critical Limitation: Energy Dependence

The big issue with the PK pseudopotential is its explicit dependence on the eigenvalue E:

Goals of Modern Pseudopotentials

The evolution beyond Phillips-Kleinman has been driven by three primary, often conflicting, objectives:

1. **Softness:** The potential should be "soft" enough to allow expansion of valence wavefunctions using as few plane waves as possible.
2. **Transferability:** A pseudopotential generated for an atom must accurately reproduce different chemical environments (molecules, crystals).
3. **Charge Accuracy:** The pseudo-charge density must reproduce the true valence charge density as accurately as possible.

The Norm-Conserving Advance

Norm-conservation (Hamann, Schlüter, and Chiang) represented the breakthrough in reconciling these goals by matching the true wavefunction beyond a core radius r_c.

The Norm-Conservation Condition

For $r > r_c$, we enforce $\phi_{PS}(r) = \psi_{AE}(r)$. Inside r_c, the functions differ, but the total charge (the "norm") is constrained to be identical.

Mathematical Constraint

For a given angular momentum l:

$$\int_0^{r_c} |\phi_{PS}(r)|^2 r^2 dr = \int_0^{r_c} |\psi_{AE}(r)|^2 r^2 dr$$

- **Semi-local Form:** Because eigenvalues and wavefunctions differ for different angular momenta l, the pseudopotential must be l-dependent.
- **Electrostatics:** Matching the norm ensures the total charge within the core is correct, leading to an accurate electrostatic potential outside r_c.

Transferability and Scattering

Transferability is measured by the **logarithmic derivatives** at r_c of the all-electron (ψ) and pseudo (ϕ) wavefunctions:

$$\frac{1}{\phi(r_c, E)} \frac{d\phi(r_c, E)}{dr} = \frac{1}{\psi(r_c, E)} \frac{d\psi(r_c, E)}{dr}$$

- **First-Order Matching:** Norm-conservation (via Green's Theorem) ensures that the **first derivative with respect to energy** also matches at the reference E.
- **Accuracy:** This implies that the difference between the pseudo and all-electron scattering is only **second-order** in $(E - E_{ref})$.
- **Result:** High reliability across different chemical environments and energy scales.

Note

Matching the logarithmic derivative ensures that the scattering properties are identical. Matching its energy derivative (via norm-conservation) ensures those properties stay accurate even when the environment shifts the electron's energy.

The Generation Procedure (BHS Method)

The Bachelet, Hamann, and Schlüter (BHS) procedure follows a rigorous path to create transferable potentials:

1. **Atomic Calculation:** Solve the all-electron radial Schrödinger equation.
2. **Construct ϕ_{PS}:** Smooth the core while imposing norm-conservation.
3. **Inversion:** Solve the radial equation backwards to obtain V^{PS}.
4. **Unscreening:** Subtract valence Hartree/XC to get the **Ionic Pseudopotential**.

Transferability

The final ionic potential is what is used in solid-state codes like Quantum ESPRESSO or ABINIT.

Generating Pseudopotentials: The `ld1.x` Module

The **Atomic** package (`ld1.x`) solves the radial Schrödinger (or Dirac) equation for isolated atoms to generate pseudopotentials.

Input: Physical Parameters

- **Configuration:** Atomic number and valence states (e.g., $2s^2 2p^4$).
- **Method:** Norm-Conserving, Ultrasoft, or PAW.
- **Functional:** LDA, PBE, etc.
- **Radii (r_c):** Cutoff for each l-channel.

Output: UPF & Validation

- **.upf file:** The Unified Pseudopotential Format.
- **Log-derivatives:** Plotting to verify **transferability**.

Command Line Execution

```
ld1.x < atom_input.in > atom_output.out
```

Beyond Norm-Conservation

For "hard" elements (Oxygen, Transition Metals), Norm-Conserving (NC) potentials require a very high $E_{\mathbf{cut}}$ because their wavefunctions are naturally tight and nodeless.

The USPP Philosophy

Instead of forcing the smooth wavefunction to carry the correct charge (**Norm-Conservation**), we prioritize **smoothness** and "fix" the charge later using an auxiliary function.

The Trade-off:

- **NC:** High accuracy, but "hard" (needs many plane waves).
- **USPP:** Extremely "soft" (needs fewer plane waves), but requires a more complex mathematical framework.

Relaxing the Norm Constraint

In USPP, we define a smooth function $|\tilde{\phi}\rangle$ that is **not** norm-conserving. The charge difference is captured by the **Augmentation Charge** $Q_{ss'}$.

The Charge Correction

The difference between the all-electron (ϕ) and smooth ($\tilde{\phi}$) norm is:

$$Q_{ss'} = \langle \phi_s | \phi_{s'} \rangle_{R_c} - \langle \tilde{\phi}_s | \tilde{\phi}_{s'} \rangle_{R_c}$$

- **Flexibility:** Since we don't constrain the norm of $\tilde{\phi}$, we can choose a much larger cutoff radius R_c.
- **Smoothness:** This results in a wavefunction significantly flatter than any NC version (e.g., for Oxygen $2p$).

The Generalized Eigenvalue Problem

Because the smooth functions are not orthonormal, the standard Schrödinger equation transforms into a **generalized eigenvalue problem**.

Modified Wave Equation

$$\hat{H}|\tilde{\psi}_n\rangle = \epsilon_n \hat{S}|\tilde{\psi}_n\rangle$$

Where $\hat{S}$ is the **Overlap Operator**:

$$\hat{S} = \mathbf{1} + \sum_{i,j,I} q_{ij}|\beta_i^I\rangle\langle\beta_j^I|$$

- **Local Impact:** $\hat{S}$ is only different from unity inside the core radius R_c.
- **Projectors:** The $|\beta\rangle$ functions "pick out" the parts of the wavefunction that need charge correction.

Practical Advantages of USPP

Why do large-scale simulations (chemistry/materials science) prefer Ultrasoft potentials?

- **Efficiency:** For Oxygen, E_{cut} can drop from $\sim$**80 Ry** (NC) to $\sim$**30 Ry** (USPP).
- **Large Systems:** Lower E_{cut} leads to smaller Hamiltonian matrices, enabling the study of thousands of atoms.
- **Accuracy:** By matching the all-electron calculation at multiple energies, USPP maintains high transferability.

USPP is the "standard" for transition metals and first-row elements in plane-wave codes.

The PAW Transformation

The Projector Augmented-Wave (PAW) method is a linear transformation from computationally efficient pseudo wavefunctions to physical all-electron wavefunctions.

Linear Transformation

The all-electron wavefunction $|\psi_k\rangle$ is recovered from the smooth auxiliary wavefunction $|\tilde{\psi}_k\rangle$ via the operator $\hat{T}$:

$$|\psi_k\rangle = \hat{T}|\tilde{\psi}_k\rangle$$

- **Pseudo Wavefunction ($|\tilde{\psi}_k\rangle$):** Smooth, nodeless, and expanded in a plane-wave basis.
- **All-Electron Wavefunction ($|\psi_k\rangle$):** Contains the rapid oscillations (nodes) near the nucleus.
- **Frozen Core:** PAW typically assumes that core electrons are "frozen" in their atomic state.

The Transformation Operator $\hat{T}$

The operator $\hat{T}$ is designed to be the identity except within the **augmentation spheres** centered on each atom a.

Operator Definition

$$\hat{T} = 1 + \sum_{a,i} \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \right) \langle \tilde{p}_i^a|$$

Definitions of Components:

- $|\phi_i^a\rangle$: **All-electron atomic orbital** (The "real" wiggly function).
- $|\tilde{\phi}_i^a\rangle$: **Pseudo atomic orbital** (The smooth version).
- $\langle \tilde{p}_i^a|$: **Projector function** (Matches the smooth function to the atomic site).

Inside vs. Outside the Augmentation Sphere

The transformation effectively "swaps" the smooth part for the real part inside the core radius r_c.

The Summation Logic

$$|\psi_k\rangle = |\tilde{\psi}_k\rangle + \sum_{a,i} c_i^a \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \right)$$

where the coefficients are determined by the projector: $c_i^a = \langle \tilde{p}_i^a | \tilde{\psi}_k \rangle$.

Outside r_c:
Since $|\phi_i^a\rangle = |\tilde{\phi}_i^a\rangle$ by construction, the terms cancel out:

$$|\psi_k\rangle = |\tilde{\psi}_k\rangle$$

Inside r_c:
The "fake" smooth part is subtracted and the "real" nodal structure is added back.

Expectation Values in PAW: Total Energy

In the PAW method, physical observables are calculated by combining a global smooth part with local atomic corrections.

Total Energy Decomposition

The total energy E is partitioned into a global smooth energy and local atomic contributions:

$$E = \tilde{E} + \sum_a (E^a - \tilde{E}^a)$$

- $\tilde{E}$ **(Smooth):** Energy calculated from the smooth auxiliary density on the global plane-wave grid.
- E^a **(All-Electron):** The energy of the isolated atom a calculated on a high-resolution radial grid.
- $\tilde{E}^a$ **(Pseudo-Atomic):** The energy of the smooth pseudo-atom.

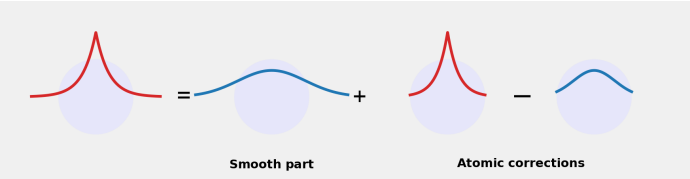
The local diff

Electron Density Reconstruction

The electron density $n(\vec{r})$ follows the same three-part logic to restore all-electron accuracy near the nucleus.

Electron Density Equation

$$n(\vec{r}) = \tilde{n}(\vec{r}) + \sum_a \left[n^a(\vec{r} - \vec{R}^a) - \tilde{n}^a(\vec{r} - \vec{R}^a) \right]$$



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Simulating Low-Dimensional Systems in Periodic Codes

Plane-wave codes (QE, VASP, CP2K) are **naturally periodic** in 3D. To simulate non-bulk systems, we use the **Supercell Technique**:

- **0D (Molecules/Clusters):** Isolated by vacuum in all 3 directions.
- **1D (Nanowires):** Vacuum in 2 directions.
- **2D (Slabs/Surfaces):** Vacuum in the direction normal to the surface (Z).
- **Defects:** Large supercells isolate the defect from its periodic images.

Crucial: A **convergence study** of vacuum size/cell volume is mandatory to eliminate unphysical image-image interactions.

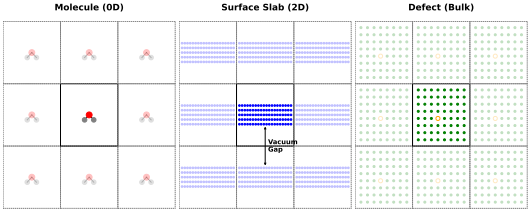

Figure 7: Periodic images in 0D, 2D, and defect systems.

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Key Learning Resources

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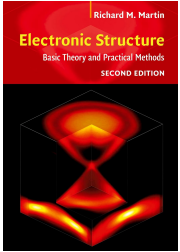
Electronic Structure

Basic Theory & Practical Methods

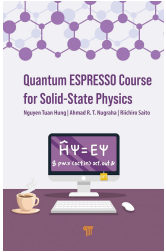


Read: Ch. 4 & 11

Practice and Theory

Quantum ESPRESSO

For Solid-State Physics



Hands-on DFT Tutorial, Theory of DFT, Plane-wave Methods

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The Reciprocal Lattice as a Fourier Transform

Consider a 3D lattice represented as a sum of Dirac delta functions:

$$\rho(\mathbf{r}) = \sum_{\mathbf{T}} \delta(\mathbf{r} - \mathbf{T})$$

The Fourier transform $\rho(\mathbf{q})$ is given by:

$$\rho(\mathbf{q}) = \int e^{-i\mathbf{q}\cdot\mathbf{r}} \left[\sum_{\mathbf{T}} \delta(\mathbf{r} - \mathbf{T}) \right] d\mathbf{r} \tag{2}$$

$$= \sum_{\mathbf{T}} \int e^{-i\mathbf{q}\cdot\mathbf{r}} \delta(\mathbf{r} - \mathbf{T})\, d\mathbf{r} = \sum_{\mathbf{T}} e^{-i\mathbf{q}\cdot\mathbf{T}} \tag{3}$$

Interference and the Selection Rule

The sum $S(\mathbf{q}) = \sum_{\mathbf{T}} e^{-i\mathbf{q}\cdot\mathbf{T}}$ acts as an interference filter:

- **Constructive Interference:** If $\mathbf{q} = \mathbf{G}$, then $\mathbf{q} \cdot \mathbf{T} = 2\pi n$. Every term is $e^{-i(2\pi n)} = 1$. For N cells, the sum is exactly N.
- **Destructive Interference:** If $\mathbf{q} \neq \mathbf{G}$, the phases $e^{-i\mathbf{q}\cdot\mathbf{T}}$ point in different directions in the complex plane. For a large crystal, they **sum to zero**.

Defining the Reciprocal Lattice

The condition for survival defines the reciprocal vectors $\mathbf{G}$:

$$\mathbf{G} \cdot \mathbf{T} = 2\pi \times \text{integer}$$

The Poisson Summation Formula

In the limit of an infinite crystal ($N \to \infty$):

$$\sum_{\mathbf{T}} \delta(\mathbf{r} - \mathbf{T}) \quad \xrightarrow{\mathcal{F}} \quad \frac{(2\pi)^3}{\Omega_{\text{cell}}} \sum_{\mathbf{G}} \delta(\mathbf{q} - \mathbf{G})$$

Understanding the Prefactor

- $(2\pi)^3$**:** Standard normalization for a 3D Fourier Transform.
- $1/\Omega_{\text{cell}}$**:** Represents the **density** of points. A larger real-space cell (Ω_{cell}) leads to a "tighter" and less dense reciprocal lattice.

The Fourier transform of a real-space is a reciprocal-space.

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Basis Set Superposition Error (BSSE)

The Problem

BSSE occurs in **localized basis sets** (e.g., Gaussians, Orbitals) when two atoms (A and B) approach each other.

- **Basis "Borrowing":** Atom A gains access to its own functions *plus* those of Atom B as they overlap.
- **Artificial Flexibility:** This effectively increases the basis set size only in the region where atoms interact.
- **False Stability:** Since a larger basis always lowers the total energy, the system appears **artificially more stable**.

The Artifact

Leads to artificial attraction and overestimation of binding energies.

The Solution can be

Plane Waves fill all space uniformly; they don't move with atoms, so **BSSE is exactly**

Thank You