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Density Functional Theory with Quantum Espresso

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Practical Aspects of DFT, Part 1

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Reciprocal Space and Fourier Transform in Crystals

- Fourier transform:

$$\tilde{f}(\vec{q}) = \int e^{-i\vec{q}\cdot\vec{r}} f(\vec{r}) d\vec{r}$$

- In crystals, the Fourier transform of a periodic function is expressed only with reciprocal space vectors:

$$f(\vec{r}) = \sum_{\vec{G}} \tilde{f}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

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Reciprocal Space and Fourier Transform in Crystals

- The **G** vectors satisfy the condition

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

- Here, **R** represents the vectors describing the atoms in the crystal. While $\mathbf{a_1}$, $\mathbf{a_2}$, and $\mathbf{a_3}$ are the lattice vectors of the direct lattice, the shortest lattice vectors of the reciprocal lattice $\mathbf{b_1}$, $\mathbf{b_2}$, and $\mathbf{b_3}$ are defined as

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

- The reciprocal lattice vectors can then be expressed as

$$\vec{G} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3, \quad n_1, n_2, n_3 \in \mathbb{Z}.$$

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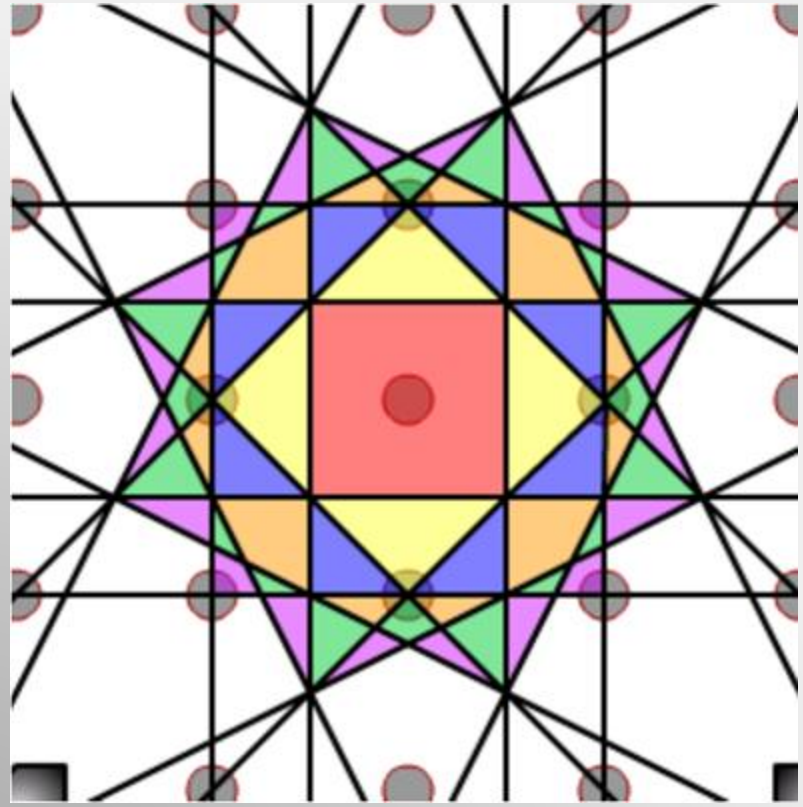

The Brillouin Zone

- The Brillouin zone is defined as the region in the reciprocal lattice that contains all points closer to a given lattice point than to any other.
- The first Brillouin zone is colored red, while the second one in yellow etc.

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Bloch's Theorem

Bloch proposed that the wavefunctions of electrons in a crystal are periodic due to the symmetry of the crystal and can be written as:

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

$\phi_{\vec{k}}(\vec{r})$: Electron wavefunction

$u_{\vec{k}}(\vec{r})$: Periodic function obeying $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$

$\vec{k}$: Wave vector.

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Plane Wave Expansion and Cutoff Energy

- To transform the Kohn-Sham equations into a linear algebraic expression, basis function expansion is used.
- For crystals, due to their periodic structure, plane waves are preferred

$$\phi_{i,\vec{k}}(\vec{r}) = \frac{1}{\Omega}\sum_{\vec{G}} u_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

- where Ω is the volume of the crystal.
- Truncate the sum using a cutoff energy

$$\frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2 \leq E_{\text{cut}}$$

Next: Practicalities, Part 2

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Practical Aspects of DFT, Part 2

Brillouin Zone Sampling and the Monkhorst-Pack k-point Grid

- During DFT calculations, it is necessary to perform certain integrals over the Brillouin zone.

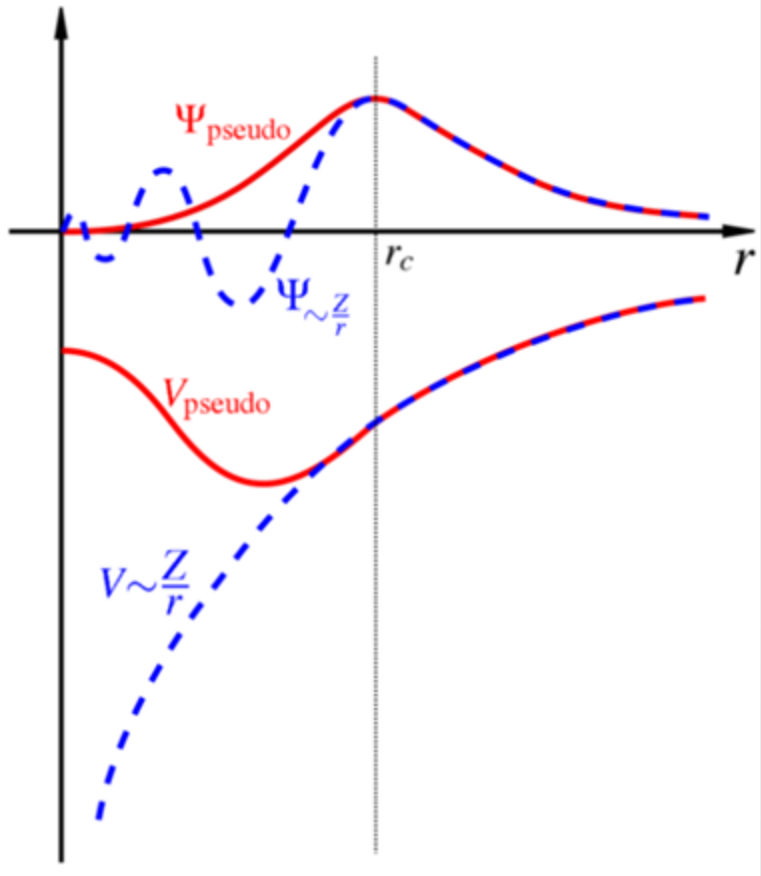
$$\int \epsilon(\vec{k}) d\vec{k} \approx \frac{1}{N_{\vec{k}}} \sum_{\vec{k} \in \mathrm{BZ}} f(\vec{k})$$

- According to the Monkhorst-Pack method, the k-points are defined as

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

Practical Aspects of DFT, Part 2

Pseudopotentials



- A model potential is used in place of the core's infinitely steep potential.
- This removes the rapid oscillations near the core.
- Only valence electrons are explicitly calculated.

$$V_{\text{pseudo}}(r) = \begin{cases} V_{\text{core}}(r) & r \leq r_c, \\ V_{\text{valence}}(r) & r > r_c, \end{cases}$$

where r_c is a cutoff defining the core region.

Practical Aspects of DFT, Part 2

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Steps of Electronic Minimization in DFT

1. An initial density is guessed – usually from a superposition of atomic densities.
2. The Kohn-Sham (KS) equations are solved to compute new wavefunctions and densities.
1. From the new orbitals, a new set of KS equations are written.
2. Iteration continues until the total energy converges, i.e. difference from the previous iteration is negligible.

Practical Aspects of DFT, Part 2

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Geometry Optimization

- Find the atomic positions that minimize the total energy Etotal.

$$\frac{\partial E_{\text{total}}}{\partial \mathrm{R}_I} = 0,$$

  where $\mathbf{R}_I$ is the position vector of atom I .
- An initial atomic geometry is guessed.
- The forces are calculated (via the Hellmann-Feynman theorem)
- Atomic positions are updated according to the forces

$$\vec{R}_I^{(n+1)} = \vec{R}_I^{(n)} + \Delta \vec{R}_I,$$

- Iteration continues until the forces fall below the tolerance.

Next: I/O Structure of QE, Part 1

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