Pseudopotentials

• The pseudopotential and the wave function
• Real potential and wave function are shown in blue

• Pseudopotential and pseudo wave function in red

• Outside the cutoff region (vertical black line) the two are identical
Pseudopotentials

- Electrons in the inner shells do not contribute to bonding
- Core electrons are effectively frozen
- Replace Coulomb potential between electrons and nuclei with effective potential, the pseudopotential

\[
egin{align*}
\begin{array}{c}
\text{valence } \psi
\end{array} & \left\{ \begin{array}{c}
3p \quad \psi = -2.7 \text{ eV} \\
3s \quad \psi = -7.8 \text{ eV}
\end{array} \right. \\
\begin{array}{c}
\text{core } \psi
\end{array} & \left\{ \begin{array}{c}
2p \quad \psi = -69.8 \text{ eV} \\
2s \quad \psi = -108 \text{ eV} \\
1s \quad \psi = -1512 \text{ eV}
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
[ -\frac{1}{2} \nabla^2 + V_{\text{eff}} ] \psi_i &= \epsilon_i \psi_i \\
[ -\frac{1}{2} \nabla^2 + V_{\text{pseudo}} ] \psi_{i}^{\text{pseudo}} &= \epsilon_i \psi_{i}^{\text{pseudo}}
\end{align*}
\]
Solids: Real and reciprocal lattices

- we assume: all atoms sit on equilibrium positions
- simplification: infinite and periodic lattice of atoms
- fundamental concept to describe this: Bravais lattice

- Bravais lattice: all the points that can be reached by:

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

- here: \( n_1, n_2, n_3 \) are integer numbers
- vectors \( \mathbf{a} \) are called “primitive vectors”, choice is not unique
Solids: Real and reciprocal lattices

• Bravais lattice: all the points that can be achieved by:

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

• at each of these \( \mathbf{R} \) there can be either one atom (or multiple - see next slide):

• but it is the same object for all \( \mathbf{R} \)
Solids: Real and reciprocal lattices

• Bravais lattice: all the points that can be achieved by:

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

• at each of these \( \mathbf{R} \) there can be either one atom, or many atoms, molecules, …; this is called “atomic basis”
• Basis is the same object for all points \( \mathbf{R} \) of the lattice

(c) physics.stackexchange.com
Solids: Real and reciprocal lattices

- primitive (unit) cell: the volume that can, if repeated infinitely many times, fill the entire space without gaps and without overlap
- choice of the \( \mathbf{a} \) vectors not unique, primitive cell is not unique

(c) http://users-phys.au.dk/philip/pictures/solid_crystalstructures/unitcells.gif
Solids: Real and reciprocal lattices

- recipe to construct primitive cell: Wigner-Seitz construction
- find all the volume that is closer to a given lattice point than to any other lattice point

• 2D:

• 3D:
Towards a Band Theory of Solids: Reciprocal Lattice

- a specific reciprocal lattice refers to a specific real-space lattice
- example: fcc <-> bcc, cubic <-> cubic, …
  - fcc and bcc are reciprocal to each other
  - reciprocal lattice of cubic lattice is cubic
- if direct lattice vectors are known, reciprocal lattice vectors follow from:

\[
b_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

\[
b_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

\[
b_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]
Towards a Band Theory of Solids: Reciprocal Lattice

• Wigner-Seitz cell of reciprocal lattice: Brillouin zone
Bloch theorem for solids

- we assume: all atoms sit on equilibrium positions
- this leads to a periodic lattice of atoms (potential for electrons)
- Bloch theorem:
  - if the potential is periodic, i.e., \( V(r) = V(r + \mathbf{R}) \)
  then wave function is of the form:

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

\[
u_{n,k}(r) = u_{n,k}(r + \mathbf{R})
\]

- this is true for all periodic potentials

\[
E = \frac{\hbar^2 k^2}{2m} = \left(\frac{k\text{reduced} + K}{2m}\right)^2
\]
Band structure in solids

- solution of the free-electron gas:

\[ E(k) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k_{\text{reduced}} + K)^2}{2m} \]
Band structure in solids

- solution of the free-electron gas:

\[ E(k) = \hbar^2 \frac{k^2}{2m} = \hbar^2 \left( \frac{k_{\text{reduced}} + K}{2m} \right)^2 \]

(c) http://users-phys.au.dk/philip/pictures/physicsfigures/node8.html
Band structure in solids: Empty lattice approximation

- lattice is periodic, but no atoms are present
- plot solutions for different lattice types: don’t show periodicity

\[ E(\mathbf{k}) = \hbar^2 \frac{\mathbf{k}^2}{2m} \]

\[ = \hbar^2 \frac{(\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m} \]

(c) [http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php](http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php)
Band Structure and DOS for a real material

Basis Sets

Basis set choices:

• For molecules: use atomic orbitals, or localized functions like Gaussians
• For solids, periodic functions such as sines and cosines (i.e., plane waves)
• Use Bloch Theorem for periodic solids:

\[ [\mathcal{H}, \mathcal{T}_R] = 0 \Rightarrow \varphi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}) \exp(ik \cdot \mathbf{r}) \]

- Hamiltonian and translation operator commute
- Wavefunction of electron \( n \) at wavevector \( k \) in Brillouin Zone (Wigner-Seitz cell in reciprocal space)
- Arbitrary phase factor
- Point \( k \) in Brillouin Zone

\[ u_{nk}(\mathbf{r}) = \sum c_{mn}(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}) \quad |\mathbf{G}| < G_{\text{max}} \]
Basis Sets: Plane waves

Superposition of plane waves to represent orbitals:

\[ u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq G_{\text{max}}} c_{nk}(\mathbf{G}) \exp(i \mathbf{G} \cdot \mathbf{r}) \]
Basis Sets

Superposition of plane waves to represent orbitals:

\[ u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq G_{\text{max}}} c_{nk}(\mathbf{G}) \exp(i \mathbf{G} \cdot \mathbf{r}) \]

A particular plane wave:

\[ f_i(\mathbf{r}) = c_{i,k+G} e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \]

Its kinetic energy:

\[ E_{\text{kin}} = f_i(\mathbf{r}) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right] f_i(\mathbf{r}) = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \]

• Low KE plane waves typically contribute more than higher KE
  => we can truncate the approximation to \( u_{nk}(\mathbf{r}) \) at \( E_{\text{cut}} \)
Quantum Espresso: Plane-wave cutoff convergence

![Energy vs Plane-wave Cutoff](image)

Energy [Ryd] vs. $E_{cut}$ [Ryd]
The wavefunction (and energy) of each electron depends on both its quantum number $n$ and its position $k$ within the Brillouin Zone:

$$\hat{h}_k \psi_{n,k}(\mathbf{r}) = \varepsilon_{n,k} \psi_{n,k}(\mathbf{r})$$

Real-space quantities are computed by a discrete sum over $n$ and integration over $k$ within the Brillouin Zone (approximated over a grid at finite $k$-points):

$$n(\mathbf{r}) = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{1\text{BZ}} \left( \sum_{n=1}^{N_{\text{el}}} |\psi_{n,k}(\mathbf{r})|^2 \right) dk$$

E.g. density, $n(\mathbf{r})$. 

Plane waves: Real-space quantities
Quantum Espresso: k-point convergence