

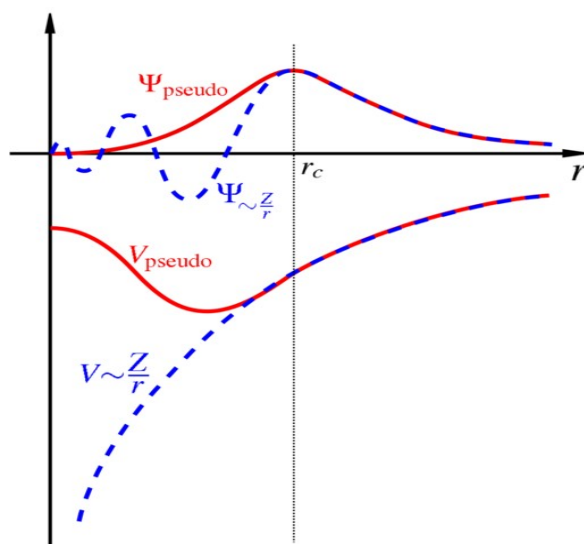
Quantum Mechanical Methods for Extended Systems

In this lecture, we shall consider some advanced quantum mechanics techniques used for extended (periodic) systems.

1. Pseudopotentials

The pseudopotential approximation is an attempt to replace the complicated effects of the motion of the core (i.e. non-valence) electrons of an atom and its nucleus with an effective potential, or pseudopotential. (The pseudopotential approximation was first introduced by Hans Hellmann in the 1930s.)

- The Schrödinger equation contains a modified effective potential term. (Frozen-core approximation)
- The valence wavefunction generated is also guaranteed to be orthogonal to all the core states.
- The nuclear Coulomb interaction screened by the core electrons, Pauli repulsion and exchange and correlation between core and valence electrons are accounted for by angular momentum dependent pseudopotentials.
- The valence electrons are described by pseudo-orbitals (avoid the nodal structure near the nuclei and they can even be nodeless in some types of pseudopotentials).



1.1 Advantages of pseudopotentials.

- They lead to a reduction of the number of electrons in the system, and allow for faster calculation of bigger systems.
- A considerable reduction of basis set size. (valence states are smoother than core states)
- Most relativistic effects are connected to core electrons. These effects can be incorporated in pseudopotentials.

1.2 Norm-Conserving Pseudopotentials

The atomic Schrödinger equation has the form

$$[\hat{T} + V_{AE}] \Psi_l = \epsilon_l \Psi_l \quad (1)$$

where \hat{T} is the kinetic energy operator, and V_{AE} the all-electron potential derived from Kohn-Sham theory. (DFT)

This equation is replaced by a valence electron only equation of the same form

$$[\hat{T} + V_{val}] \Phi_l = \hat{\epsilon}_l \Phi_l \quad (2)$$

Hamann, Schlüter and Chiang proposed a set of requirements for the pseudo wavefunction and pseudopotentials.

The pseudopotential should have the following four conditions.

1. Real and pseudo valence eigenvalues agree for a chosen atomic configuration: $\epsilon = \hat{\epsilon}$
2. Real and pseudo wavefunctions agree beyond a chosen core radius R_c : $\Psi_l(r) = \Phi_l(r)$
3. The integrals from 0 to R ($R \geq Rc$) of the real and pseudo charge densities agree for each valence state. (norm conservation). $\int_0^R r^2 |\psi|(r)^2 dr$
4. The logarithmic derivatives of the real and pseudo wavefunction and their energy derivatives agree for $R > R_c$ (scattering phase-shift agrees).

There are several versions of norm-conserving pseudopotentials:

- Bachelet-Hamman-Schlüter form (BHS)
- Kerker Pseudopotentials
- Trouiller-Martins Pseudopotentials (TM)

1.2 Other types of pseudopotentials

Ultra-soft pseudopotentials (US)

Many modern pseudopotential calculations use a form known as "ultrasoft" pseudopotentials, which were developed by Vanderbilt in the early 1990s.

As the name suggests, ultrasoft pseudopotentials attain much smoother (softer) pseudo-wavefunctions so use considerably fewer plane-waves for calculations of the same accuracy.

This is achieved by relaxing the norm-conservation constraint, which offers greater flexibility in the construction of the pseudo-wavefunctions. In this scheme the total valence density is partitioned into so-called hard and soft contributions.

- Norm-conservation is relaxed.
- Add augmentation charge inside the cut-off sphere to correct charge
- Fewer planewaves needed (one-third less than norm-conserving pseudopotentials).

Projector-augmented waves (PAW)

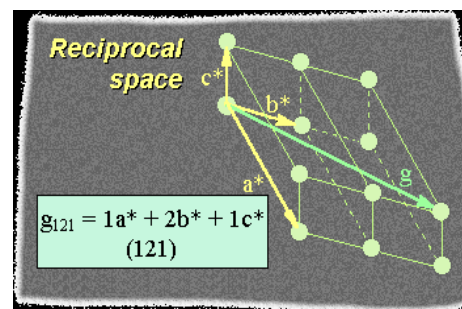
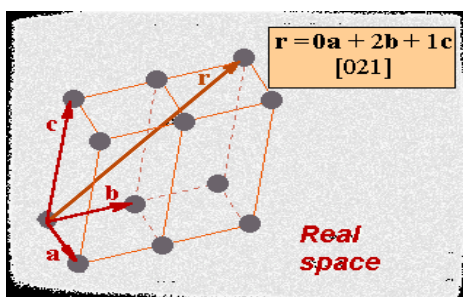
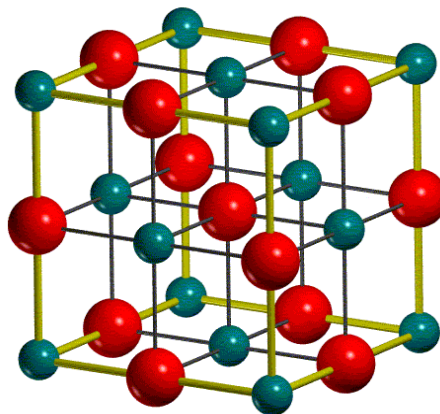
- Pseudonization as for ultra-soft pseudopotentials
- Reconstruct exact wavefunctions in the core region
- The PAW method combines the accuracy of all-electron methods with the efficiency of pseudopotentials

2. Quantum Mechanical methods for Studying the Periodic Systems

In the study of bulk crystals, the system is infinite but periodic, and so it is necessary to be able to reduce this problem to the study of a finite system.

This approach turns out to have several advantages so that it is often easiest to study even aperiodic systems by imposing some false periodicity.

The system is contained within a supercell which is then replicated periodically throughout space.



The unit cell is parallelepiped in shape and is characterized by three lattice vectors $\vec{a}, \vec{b}, \vec{c}$.

Any vector \vec{r} (including atom coordinates in the systems) can be written in terms of these basis vectors.

$$\vec{r} = (\alpha \vec{a}, \beta \vec{b}, \gamma \vec{c}) \quad (3)$$

Reciprocal Lattice

The reciprocal lattice is defined by three vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$ in which \vec{a}^* is perpendicular to \vec{b}^* and \vec{c}^* , and then is scaled so that the scalar product of \vec{a}^* and \vec{a} is 1.

$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \quad \vec{b}^* = \frac{\vec{c} \times \vec{a}}{\vec{b} \cdot \vec{c} \times \vec{a}}, \quad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{\vec{c} \cdot \vec{a} \times \vec{b}} \quad (4)$$

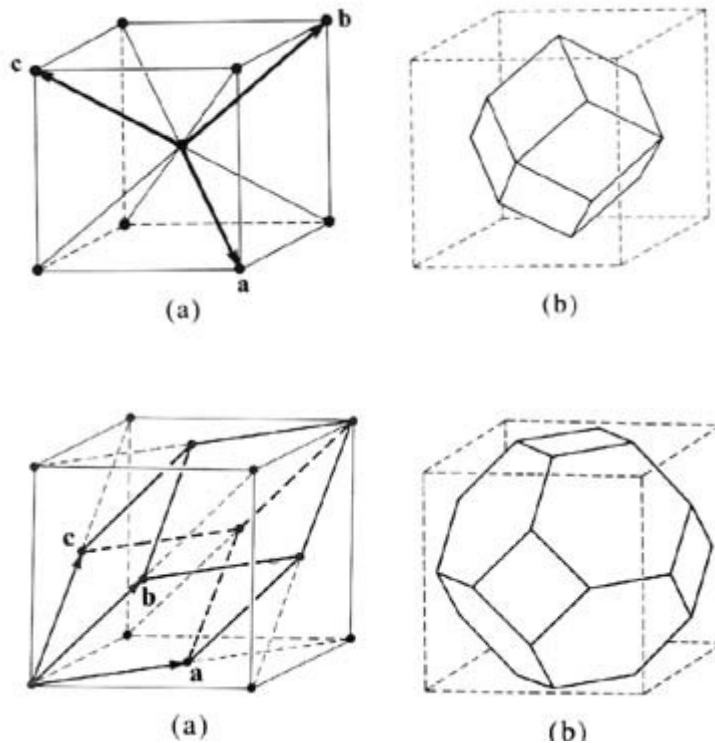
It is convenient to use another set of vectors in computation to represent reciprocal lattice $\vec{a}^s, \vec{b}^s, \vec{c}^s$. The scalar product of \vec{a} and \vec{a}^s is 2π .

The reciprocal lattice vectors are defined by

$$\vec{G} = n\vec{a}^s + m\vec{b}^s + o\vec{c}^s \quad (5)$$

Where n, m, o are integers.

First Brillouin zone

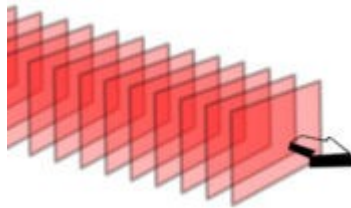


Every BZ has the same volume: $\Omega_{BZ} = \frac{(2\pi)^3}{\Omega_{UC}}$ (proof skipped)

Planewaves

$$e^{i\vec{G}\vec{r}} \quad (6)$$

(explain what is called a planewave)



Bloch's Theorem

Bloch's theorem states that the wavefunction of an electron $\psi(\vec{r})$ can be written as the product of a lattice periodic part $u(\vec{r})$ and a wavelike part $e^{i\vec{k}\vec{r}}$, (ψ and u are related to k which is confined in the BZ):

$$\psi_k(\vec{r}) = u_k(r) e^{i\vec{k}\vec{r}} \quad (7)$$

(proof here).

The lattice periodic part must have the periodicity of the lattice \vec{L} , therefore, it can be written in terms of the reciprocal lattice

$$u_k(\vec{r}) = \sum_{\vec{G}} c_{\vec{G},k} e^{i\vec{G}\vec{r}} \quad (8)$$

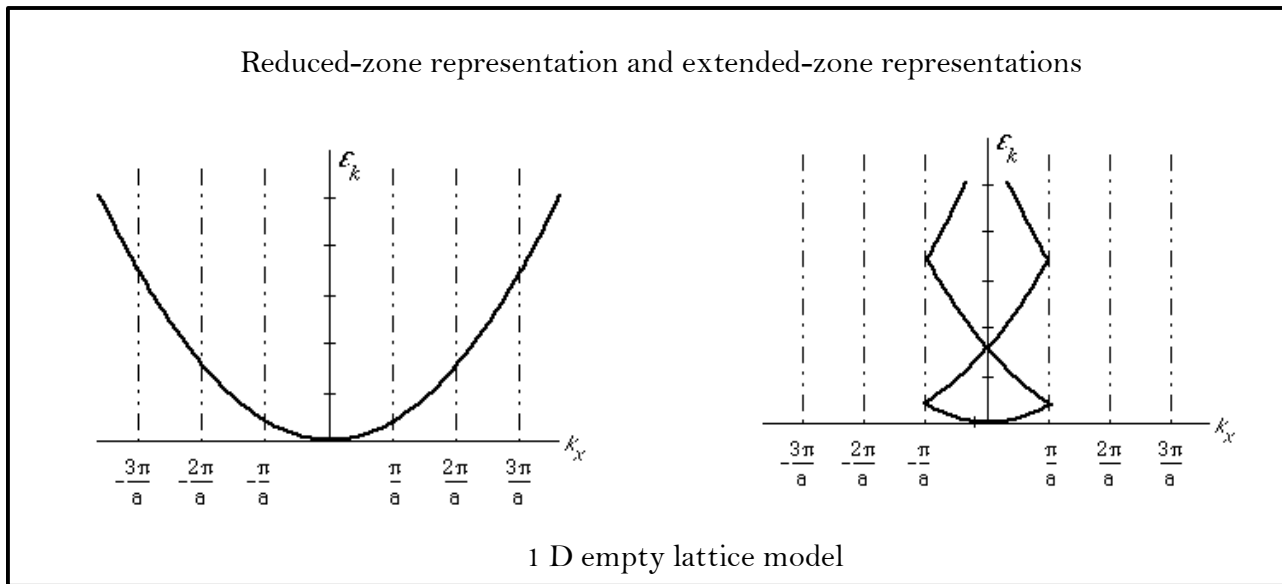
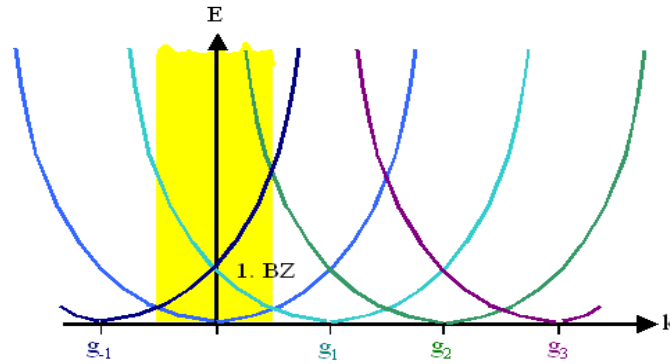
The external potential due to the nuclei is periodic in the lattice and it too can be written as a Fourier expansion of exponential functions of the reciprocal lattice

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\vec{r}} \quad (9)$$

$U_{\vec{G}}$ is the Fourier coefficient. When this is incorporated into the Schrödinger equation, the following form can be derived

$$\left(\frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m} - E \right) c_{\vec{G},k} + \sum_{\vec{G}'} U_{\vec{G}' - \vec{G}} c_{\vec{G}',k} = 0 \quad (10)$$

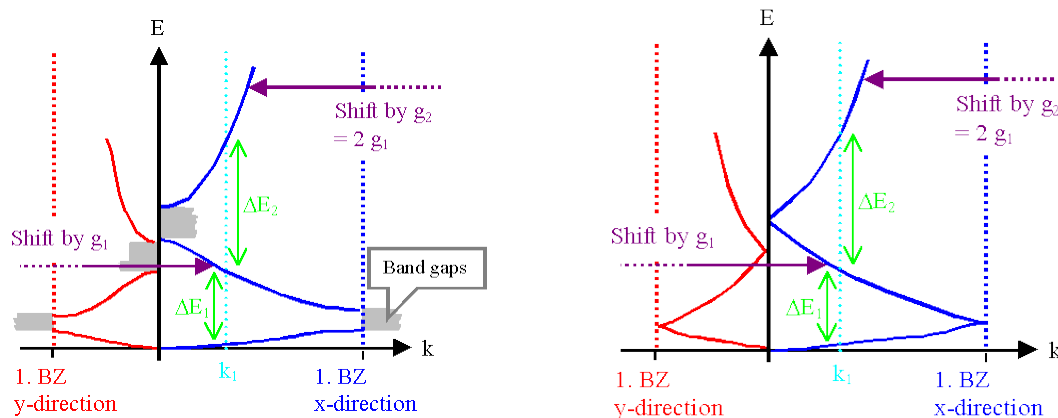
If without perturbation energy $U_{\vec{G}', \vec{G}} = 0$: $E = \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m}$ which is in fact the same for a free particle (free electron).



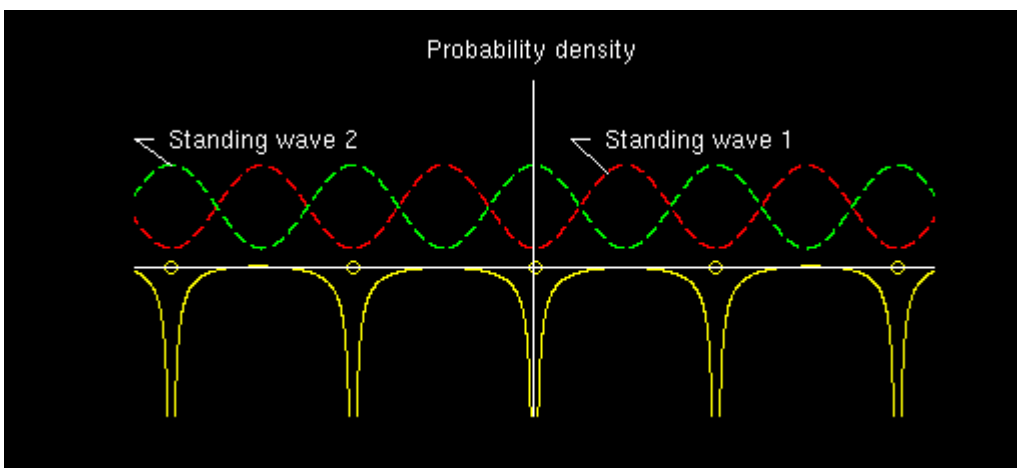
The origin of energy gaps:

$$E_k = \frac{\hbar k^2}{2m} \pm |U_G| \tag{11}$$

when $(\vec{k} + \vec{G})^2 = \vec{k}^2$.

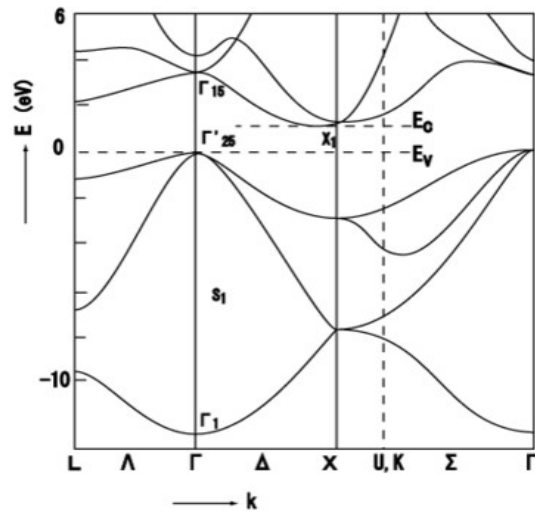
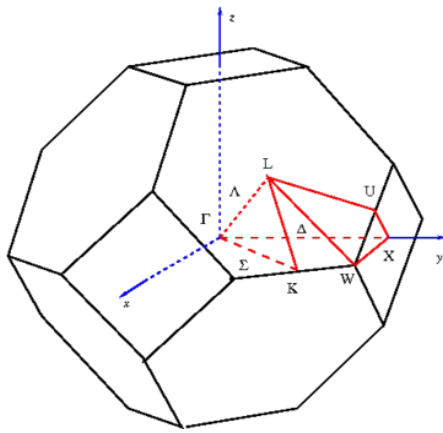


Standing waves that causes energy gaps. (Bragg reflection)



(If time permits, we shall discuss energy gaps (1-D) by the perturbation theory within the nearly free-electron approximation)

The summations are over all reciprocal lattice vectors \vec{G} . As can be seen, for a given value of \vec{k} there are as many forms of this equation as there are reciprocal lattice vectors in the system. Each of these equations for different values of \vec{G} vector gives rise to a solution which is labeled with the band index n .



Density Functional Methods for Studying the Solid State

Each orbital wavefunction is expressed as a linear combination of plane waves which differ by reciprocal lattice vectors

$$\psi_i^{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{i, \vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\vec{r}} \tag{12}$$

The Kohn-Sham equations of the density functional theory then take on the following form

$$\sum_{\vec{G}'} \left(\frac{\hbar^2}{2m} |\vec{k} + \vec{G}| \delta_{\vec{G}, \vec{G}'} + V_{ion}(\vec{G} - \vec{G}') + V_{elec}(\vec{G} - \vec{G}') + V_{xc}(\vec{G} - \vec{G}') \right) c_{i, \vec{k}+\vec{G}'} = \epsilon c_{i, \vec{k}+\vec{G}} \tag{13}$$

Two problems:

- (a) The summation (a Fourier series) over \vec{G}' is in theory over an infinite number of reciprocal lattice vectors.
- (b) There are infinite number of k points.

Practical ways to solve the problem.

Only plane waves with a kinetic energy ($\frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2$) less than some cutoff are included in the calculation. The number of planewaves is roughly

$$N_{PW} = \frac{1}{2\pi^2} \Omega E_{cut}^{3/2} \tag{14}$$

The density can be expressed

$$\begin{aligned} \rho(\vec{r}) &= \frac{1}{\Omega} \sum_i \int d\vec{k} f_i(\vec{k}) \sum_{\vec{G}} \sum_{\vec{G}'} c_{i, \vec{G}'+\vec{k}}^* c_{i, \vec{G}+\vec{k}} e^{i(\vec{G}+\vec{k})\vec{r}} \\ &= \sum_{\vec{G}} \rho(\vec{G}) e^{i\vec{G}\vec{r}} \end{aligned} \tag{15}$$