Electron Energy Band in Crystals
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The energy structure of electrons in solids is neither like those of electrons in a single atom nor those of free electrons without the potential energies from the nuclei. Instead, the electronic energy level of a single atom splits into multiple ones due to the Pauling exclusion principle. On the other hand, the periodic lattice potential within a solid perturbs the otherwise “free electron”, causing the energy-momentum parabola breaks at the Brillouin zone boundary. This article summarizes the implications of the energy bands.

Bloch’s Theorem

Bloch's theorem states that solutions to the Schrödinger equation for particles in a periodic potential (like crystals) are plane waves modulated by a periodic function, expressed as

$$\psi_{n,k}(r+R) = e^{ikR}\psi_{n,k}(r)$$

where $\psi_{n,k}$ is the wave function of band index n and wave vector k and R the translation vector of the crystal lattice in the real space as opposed to the reciprocal space. The Bloch's Theorem states that the wave function is a product of a plane wave (e^{ikR}) and a function that has the same periodicity as the crystal lattice, which applies specifically to systems where the potential energy is periodic reflecting the symmetry of a lattice. For one dimensional lattice, this plane wave term becomes e^{ikna} where a is the lattice constant.

Tight Binding Approximation

The tight binding approximation proposes that the electronic state vector (wave function) of a crystal lattice is a linear combination of the electronic state vectors of the atoms that located on the lattice:

$$|\psi\rangle = \sum_n \phi_n |n\rangle$$

where $|\psi\rangle$ is the lattice electronic state vector, $|n\rangle$ the ***n-th*** atomic electronic state vector, and ϕ_n the coefficient of the linear combination. The atomic electronic state vectors form an orthonormal basis:

$$\langle m|n\rangle = \delta_{m,n}$$

The lattice Hamiltonian is:

$$H = K + \sum_j V(r - R_j)$$

Therefore, the average electronic energy over the atomic states is:

$$\langle n|H|m\rangle = \langle n|(K + V_m)|m\rangle + \sum_{j\neq m} \langle n|V_j|m\rangle$$

The first term is the average electronic energy of the atom (nucleus plus electron(s)) because the orthogonality of the atomic electronic states. The second term is the interaction between the

electrons from all the lattice atoms. It is conceivable that only the electrons from immediate adjacent atoms have the strongest interactions. Therefore,

$$\sum_{j\neq m}\langle n|V_j|m\rangle = \begin{cases} V_0 & n=m \\ -t & n=m\pm 1 \\ 0 & otherwise \end{cases}$$

and

$$\langle n|H|m\rangle = E_0\delta_{n,m} - t\left[\delta_{n+1,m} + \delta_{n-1,m}\right]$$

where

$$E_0 = V_0 + E_{atomic}$$

is the electronic energy of the atom under the "average influence" (V_0) of all the electronics from other lattice sites. The average electronic energy over the lattice states can be evaluated using the time independent Schrodinger's equation:

$$H|\psi\rangle = E|\psi\rangle$$

$$\sum_m \phi_m H|m\rangle = E\sum_m \phi_m|m\rangle$$

The inner product of above equation with $\langle n|$ is

$$\sum_m \phi_m\langle n|H|m\rangle = E\sum_m\langle n|\phi_m|m\rangle = E\phi_n$$

$$E\phi_n = \sum_m \phi_m\left\{E_0\delta_{n,m} - t\delta_{n+1,m} - t\delta_{n-1,m}\right\}$$

Based on the Bloch Theorem, the one dimensional ϕ_n must take the form $e^{ikna}\varphi_n(x)$:

$$Ee^{ikna}\varphi_n(x) = E_0e^{ikna}\varphi_n(x) - te^{ik(n+1)a}\varphi_n(x) - te^{ik(n-1)a}\varphi_n(x)$$

Collecting the likely terms:

$$E = E_0 – 2t\cos(ka)$$

The electronic energy in a crystal lattice is no longer a single value, but the allowable energy level varies with the wave vector k in the lattice reciprocal space with a periodicity of $2\pi/a$. This forms an energy band of a width of $\pm 2t$. The energy is lowest at the center of the first Brillouin zone and highest at the boundary of the Brillouin zone. Figure 1 depicts the electronic energy within the first Brillouin zone. Again, E_0 is the electronic energy of a single atom also under the influence of all the other atoms on the lattice. It has many levels for the given eigenstate of atomic structure, e.g., $1s$, $1p_x$, $1p_y$, $1p_z$, ***etc***. On a crystal lattice, however, with many more atoms, these levels expands into energy bands, and each band has theoretically N permissible states where N is the number of atoms in the 1D lattice.

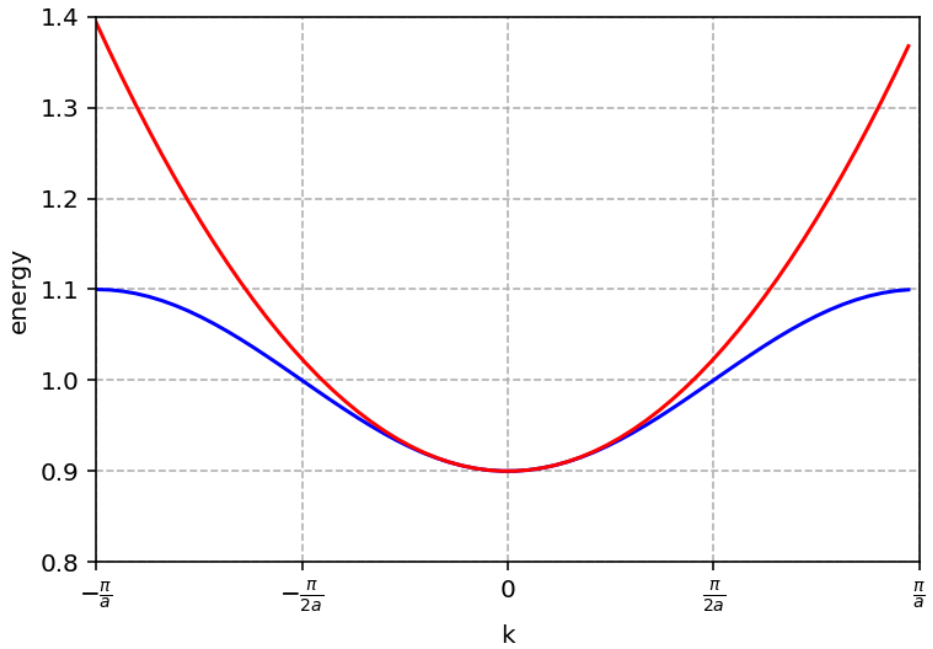

Figure 1. Electronic Energy in 1D Lattice (blue) and the Free Electron Approximation (red)

Between the energy bands are band gaps within which the energy levels are not permitted the same way as the gaps between Hamiltonian eigenvalues. In Figure 1, a red curve shows the free electron approximation as:

$$E_{free} = \frac{\hbar^2 k^2}{2m}$$

At small k, close to the center of the Brillouin zone, the Taylor expansion of $\cos(ka)$ becomes:

$$\cos(ka) = 1 - \frac{k^2 a^2}{2!}$$

Let E_{free} be equal to E of electrons in 1D lattice, we have the effective mass of the electrons at the bottom of the energy band:

$$m^* = \frac{\hbar^2}{2ta^2}$$

The distance between the red curve and the blue curve at the Brillouin boundaries is approximately half of the band gap between the energy state shown and the next state.

Metals, Insulators and Semiconductors

When the energy band is partially filled, the electron distribution among the permissible states within the band can change under an electric field, leading to electricity flow. The top level energy band of a metal is partially filled.

One the other hand, if the energy band is fully filled, the electron in the band has no available states to redistribute. Further, if the band gap is large, the electrons from the lower energy band do not have sufficient energy to be excited and move to the next higher energy band. There is no electricity flow. The electron energy bands of an insulator are fully filled and the band gaps between these bands are generally quite large.

Semiconductors have some interesting properties because their energy bands (valence bands) are fully filled but the band gaps are small enough to allow small amount of electrons to be energized and jump to the next higher energy band (conduction band) leaving positively charged “holes” in the valence band. One may also purposely add electrons in the conduction band and holes in the valence band by a process called “doping”. The excitation can be caused either by lights (photovoltaic cells) or heat.

The electron distribution follows the Fermi-Dirac distribution. However, at room temperature, the band gaps of most semiconductor ($\approx$ 1eV) are sufficiently greater than the heat excitation (0.026 eV). Therefore, it is convenient to use Boltzmann distribution instead of Fermi-Dirac distribution. The density of electrons in the conduction band becomes:

$$n = \frac{1}{4}\left(\frac{2m_e^* k_B T}{\pi\hbar^2}\right)^{3/2} exp\left(-\frac{E_c - E_F}{k_B T}\right)$$

The density of holes in the valence band is:

$$p = \frac{1}{4}\left(\frac{2m_h^* k_B T}{\pi\hbar^2}\right)^{3/2} exp\left(-\frac{E_F - E_v}{k_B T}\right)$$

where m_h^* is the effective mass of the holes, E_c energy at the bottom of the conduction band, E_F Fermi energy, and E_v energy at the top of the valence band. E_c–E_v is the band gap. The so-called mass action relation analogous to a chemical reaction is expressed as:

$$np = \frac{1}{2}\left(\frac{k_B T}{\pi\hbar^2}\right)^3 (m_e^* m_h^*)^{3/2} exp\left(-\frac{E_{gap}}{k_B T}\right)$$

The electron density in an un-doped semiconductor conduction band equals exactly the hole density in the valence band. Therefore, the Fermi energy can be found as:

$$E_F = \frac{1}{2}(E_c + E_v) + \frac{3}{4}k_B T \ln\left(\frac{m_h^*}{m_e^*}\right)$$

It is worth noting that at absolute zero temperature, the Fermi energy is located at the middle of the band gap. Otherwise, the fermi energy is slightly above the middle of the band gap because of the excitation of a small number of electrons from the valence band to the conduction band.