Electron levels in a periodic potential

We consider the problem of an electron in a periodic potential $U(\vec{r}+\vec{R}) = U(\vec{r})$

We will now discuss general properties that depend only on periodicity of the potential

Scale of periodicity $\sim 10^{-8}$ cm $\sim$ de Broglie wavelength

$\Rightarrow$ we need to use quantum mechanics

The problem of electrons in a solid is a many-electron problem. We assume an independent electron approximation where inter-electron interactions are represented by an effective one-electron potential

$U(r)$ is the total potential (ions + eff els) that also has periodicity of the Br. lat

$$H\psi = \left(-\frac{1}{2m}\nabla^2 + U(r)\right)\psi = \varepsilon\psi \qquad (*)$$

Bloch's theorem: The eigenvalues of the one-electron Hamiltonian $(*)$ with $U(r+R)=U(r)$ can be chosen to have the form of a plane wave times a function with periodicity of the Bravais lattice

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_{n\vec{k}}(\vec{r}) \qquad (**)$$

$$u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{nk}(\vec{r})$$

Note, that $(**)$ implies

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

Proof: for every Br lat vector $\vec{R}$ we define a translation operator T_R

$$T_R\, f(r) = f(r+R)$$

From the periodicity of the Hamiltonian for $\forall\, \psi$:

$$T_R H \psi = H(r+R)\,\psi(r+R) = H(r)\,\psi(r+R) = H\, T_R \psi$$

Hence

$$T_R H = H T_R$$

In addition

$$T_R T_{R'} \psi(r) = T_{R'} T_R \psi(r) = \psi(r+R+R')$$

therefore $T_R T_{R'} = T_{R'} T_R = T_{R+R'}$

So, all T_R and H form a set of commuting variables and can be diagonalized simultan

$$H\psi = \varepsilon \psi$$

$$T_R \psi = C(R)\,\psi$$

The eigenvalues $C(R)$ are related

$$T_{R'} T_R \psi = C(R)\, T_{R'} \psi = C(R)\, C(R')\, \psi$$

$$= T_{R+R'} \psi = C(R+R')\, \psi$$

Hence $C(R+R') = C(R)\, C(R')$

Let $\vec{a}_i$ be primitive vectors

$$c(\vec{a}_i) = e^{2\pi i x_i}$$

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$c(\vec{R}) = [c(a_1)]^{n_1}\,[c(a_2)]^{n_2}\,[c(a_3)]^{n_3}$$

$$= e^{i\vec{k}\vec{R}}$$

where $\vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3$

$(\vec{b}_i\vec{a}_j = 2\pi\delta_{ij})$

Hence we showed $T_R\psi = \psi(r+R) = c(R)\psi = e^{ikr}\psi(r)$

Boundary condition

Usually $\psi(r+L_i) = \psi(r)$ but we use bound cond commens. with the unit cell

$$\psi(\vec{r}+N_i\vec{a}_i) = \psi(\vec{r}) \qquad i = 1,2,3$$

$N = N_1 N_2 N_3$ = total # of the prim cells

$$\psi_{nk}(r+N_i a_i) = e^{iN_i\vec{k}_i\vec{a}_i}\,\psi_{nk}(r)$$

$$e^{iN_i\vec{k}\vec{a}_i} = 1$$

$$\vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3$$

$$e^{2\pi i N_i x_i} = 1$$

$$N_i x_i = m_i$$

$$x_i = \frac{m_i}{N_i}$$

$$\vec{k} = \sum_{i=1}^{m} \frac{m_i}{N_i} \vec{b_i}$$

The volume $\Delta \vec{k}$ of $\vec{k}$ - space per allowed value of $\vec{k}$ is the volume of the little parallelepiped with edges $\vec{b}_i / N_i$

$$\Delta k = \frac{\vec{b_1}}{N_1} \cdot \left(\frac{\vec{b_2}}{N_2} \times \frac{\vec{b_3}}{N_3} \right) = \frac{1}{N} \underbrace{\vec{b_1} \cdot \vec{b_2} \times \vec{b_3}}_{\text{volume of the prim. cell in recip. space} = (2\pi)^3/v}$$

v = prim cell in direct space = V/N

$$\Delta k = \frac{(2\pi)^3}{V}$$

Usually

$$e^{i k_i L_i} = 1 \qquad k_i L_i = 2\pi n_i$$

$$\Delta_i k_i = \frac{2\pi}{L_i}$$

$$\Delta k = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V}$$