ELECTRON LEVELS IN A PERIODIC POTENTIAL

(BADOLATO, OCT 2011)

Because the ions in a perfect crystal are arranged in a regular array, we are led to consider the problem of an electron in a potential $V(r)$ with the periodicity of the underlying lattice; i.e.,

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

for all Bravais lattice vectors $\vec{R}$.

We emphasize at the outset that perfect crystals with perfect periodicity is an idealization. Real crystal have

- Impurities (different atoms, missing or misplaced ions)
- Thermal vibrations (phonons).

These imperfections are ultimately responsible for the finite electrical conductivity of metals. In describing crystal disorder (imperfections) progress is best made by using perturbation theory.

We will consider here a perfect periodic lattice and approximate the many-electron problem with a one-electron potential

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

BLOCH FUNCTIONS

The eigenstates ψ of the one-electron Hamiltonian

$$-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}} + V(\vec{r})$$

where $V(\vec{r}) = V(\vec{r}+\vec{R})$, can be chosen to have the form of a plane wave times a function with the periodicity of the lattice

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

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

This is equivalent to write that

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

The Bloch's theorem is stated in both forms.

1^{st} Proof of the Bloch's theorem

The translation operator of a generic lattice vector $\vec{R}$ is

$$T_R\, f(\vec{r}) = f(\vec{r}+\vec{R})$$

$$T_R H = H T_R \quad \text{and} \quad T_R T_{R'} = T_{R'} T_R = T_{R+R'}$$

$\Rightarrow$ T_R and H are commuting operators for any $\vec{R}$

$$[H, T_R] = 0$$

It follows that the eigenstates of H can be chosen to be simultaneous eigenstates of all the T_R

$$H\psi = E\psi$$

$$T_{\vec{R}}\psi = c(\vec{R})\psi$$

It is easy to demonstrate that

$$c(\vec{R}) = e^{ik \cdot R}$$

Therefore

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

$$= e^{ik \cdot R}\psi(\vec{r})$$

PERIODIC BOUNDARY CONDITION

If we impose periodic boundary conditions (Born Von Karman)

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

$$\vec{R} = N_1 \vec{a}_1 + N_2 \vec{a}_2 + N_3 \vec{a}_3 \qquad \vec{a}_i \text{ are the primitive vectors}$$

to the Bloch functions

$$\psi_{n,k}(\vec{r} + N_i \vec{a}_i) = e^{iN_i \vec{k} \cdot \vec{a}_i}\psi_{nk}(\vec{r}) \iff e^{iN_i \vec{k} \cdot \vec{a}_i} = 1$$

The volume $\Delta\vec{k}$ of k-space per allowed value of $\vec{k}$ is

$$\Delta k = \frac{1}{N} \cdot \begin{pmatrix} \text{volume of a reciprocal} \\ \text{lattice primitive cell} \end{pmatrix} = \frac{1}{N} \cdot \left(\frac{(2\pi)^3}{V/N} \right) = \frac{(2\pi)^3}{V}$$

2^{nd} proof of Bloch's Theorem

This approach is notationally more complicated, therefore we restric the system to one-dimension

$$V(x) = V(x+a) \quad \Rightarrow \quad V(x) = \sum_G V_G e^{iGx}$$

which is the fourier series for the potential energy and the expension is over the reciprocal lattice vectors G.

The wave functions can be expanded in plane waves

$$\psi(x) = \sum_k C_k e^{ikx}$$

the sum is over all values of the wavevector permitted by the boundary conditions. $\psi(x+L) = \psi(x) \Rightarrow k = \frac{2\pi}{L} m \quad m \in \mathbb{Z}$.

The wave equation is

$$\left[\frac{p^2}{2m} + \sum_G V_G e^{iGx} \right] \sum_k C_k e^{ikx} = \epsilon \sum_k C_k e^{ikx}$$

The kinetic energy gives

$$\frac{p^2}{2m} \psi(x) = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = \sum_k \frac{\hbar^2 k^2}{2m} C_k e^{ikx}$$

The potential energy

$$V(x)\psi(x) = \left(\sum_G V_G e^{iGx}\right)\left(\sum_k C_k e^{ikx}\right) = \sum_G \sum_k V_G C_k e^{i(G+k)x},$$

which can be rewritten

$$\sum_k \sum_{G'} V_{G'} C_{k-G'} e^{ikx}$$

The wave equation becomes

$$\sum_k e^{ik\cdot r}\left\{\left(\frac{\hbar^2}{2m}k^2 - E\right)c_k + \sum_{G'} V_{G'}\, c_{k-G'}\right\} = 0$$

which means that each separate term must vanish

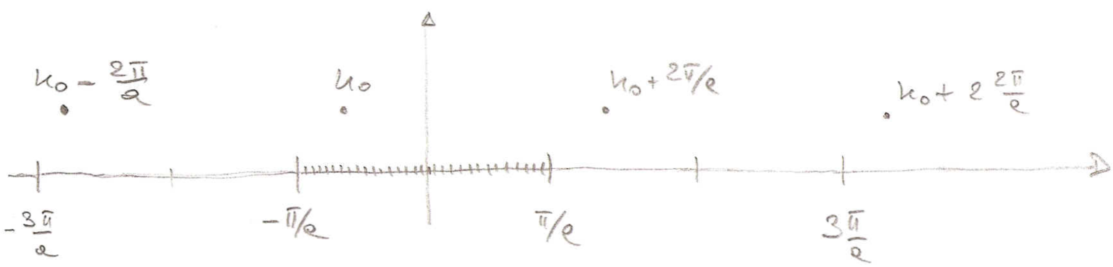
$$\boxed{\left(\frac{\hbar^2}{2m}k^2 - E\right)c_k + \sum_{G'} V_{G'}\, c_{k-G'} = 0}$$

This is nothing but restatement of the original Schrödinger equation in momentum space, simplified by an important fact: the periodicity of the potential, that is, V_G is nonvanishing only when G is a vector of the reciprocal lattice. Thus the original problem has separated into N independent problems, one for each allowed value of $\vec{k}$ in the first Brillouin zone.

Once we determine the C's coefficients from the central equation above, the wave function is given as

$$\psi(x) = \sum_G c(k-G)\, e^{i(k-G)x} = \psi_k(x)$$

that is, it is generated only by a linear combination of functions belonging to the subspace $\left\{k_0 + m\frac{2\pi}{a}\right\}$



If we rearrange $\psi(x)$ as

$$\psi(x) = \psi_k(x) = \left[\sum_G c(k-G)\, e^{-iGx}\right] e^{ikx} = e^{ikx}\, u_k(x)$$

with the definition

$$u_k(x) = \sum_G c(k-G)\, e^{-iGx}$$

Because $u_k(x)$ is a Fourier series over the reciprocal lattice, it is periodic in the direct (real) lattice

$$u_k(x) = u_k(x+R) \qquad R = na$$

* $$u_k(x+R) = \sum_G c(k-G)\, e^{-iGx} \underbrace{e^{-iGR}}_{=1} = u_k(x)$$