Electrons in a periodic potential

Nearly free electron approximation and tight binding: band theory of solids

Nearly free electron approximation

We observed at the end of previous lecture that free electron approximation cannot adequately describe some of the properties of solids (e.g. semiconductors, insulators, etc.). The origin of that is clearly in assumptions that have been made and in particular in neglecting the potential energy term in the Hamiltonian of the system. Now we shall bring the potential term back into play using two distinct approaches***: Nearly free electron approximation*** and ***Tight Binding***. The former approach takes advantage of the potential energy term being a small addition to the overall Hamiltonian of an infinite lattice – we start with free electrons and look at scattering by the crystal potential. The latter starts from the electronic structure of an atom - we start from isolated atoms and look at the interaction as wavefunctions overlap. The general form of the Schrödinger equation is:

$$\boldsymbol{H}\psi = E\psi$$

where:

$$\hat{H} = \hat{T} + \hat{V}$$

And the new Schrödinger equation in 1D is:

$$\boldsymbol{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial \boldsymbol{r}^2} + V(\boldsymbol{r})\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

The problem is in solving this second order differential equation. Ideally, we would like avoid complications by reducing this equation to something simple – e.g. a system of independent linear equations. It turns out that this can be done with the aid of ***Bloch's theorem*** and periodicity of the potential.

Let's use an electron travelling wave in the form of e^{ikx} (kinetic energy of $\hbar^2k^2/2m$) and assume that this wave is *Bragg scattered* by the wavevector $G = 2\pi/a$, where *a* is a lattice constant (see notes on crystallography). Clearly the crystal potential is periodic in real space, hence we expect it to be periodic in a reciprocal space.

The next step in understanding microscopic behaviour of the system would be to solve the above equation to obtain eigenstates and eigenvalues of an infinite crystal Hamiltonian. In order to simplify the task we shall introduce and prove the ***Bloch's theorem*** which is based on translational invariance of the system.

Bloch's theorem:

For any periodic potential $V(\boldsymbol{r}) = V(\boldsymbol{r} + \boldsymbol{T})$ the solutions of the Schrödinger equation above can be written in the form:

$$\psi_k(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r})\, u_k(\boldsymbol{r})$$

where ***k*** is any allowed wave vector that is obtained for *constant* potential and $u_k(\boldsymbol{r})$ are arbitrary functions that satisfy:

$$u_k(\boldsymbol{r}) = u_k(\boldsymbol{r} + \boldsymbol{T})$$

Any wavefunction that meets this requirement we shall call a ***Bloch wave***. The importance of this theorem is in the observation that it imposes a specific condition on the solutions of the Schrödinger equation for *any* periodic potential.
A different way to write the ***Bloch's theorem***: The eigenstates of a periodic Hamiltonian can be written as a product of a periodic function with a plane wave of momentum k restricted to be in the first Brillouin zone:

$$\psi_k(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r})\, u_k(\boldsymbol{r})$$

furthermore:

$$\psi_k(\boldsymbol{r}+\boldsymbol{T}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{T})\, \psi_k(\boldsymbol{r})$$

Proof of Bloch's theorem
Substituting $\boldsymbol{r} = \boldsymbol{r}' + \boldsymbol{T}$ into the Schrödinger equation gives:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2} + V(\boldsymbol{r}'+\boldsymbol{T})\right]\psi(\boldsymbol{r}'+\boldsymbol{T}) = \varepsilon_k \psi_k(\boldsymbol{r}'+\boldsymbol{T})$$

but since $V(\boldsymbol{r}') = V(\boldsymbol{r}'+\boldsymbol{T})$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2} + V(\boldsymbol{r}')\right]\psi(\boldsymbol{r}'+\boldsymbol{T}) = \varepsilon_k \psi_k(\boldsymbol{r}'+\boldsymbol{T})$$

Therefore $\psi_k(\boldsymbol{r}')$ and $\psi_k(\boldsymbol{r}'+\boldsymbol{T})$ represent the solution with the same energy and thus can only differ by a phase factor $\delta\phi = \boldsymbol{k}\cdot\boldsymbol{T}$, $\psi_k(\boldsymbol{r}'+\boldsymbol{T}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{T})\psi_k(\boldsymbol{r}')$. This will be satisfied:

$\psi_k(\boldsymbol{r}') = \exp(i\boldsymbol{k}\cdot\boldsymbol{r}')\, u_k(\boldsymbol{r}')$,

where $u_k(\boldsymbol{r}') = u_k(\boldsymbol{r}'+\boldsymbol{T})$ and hence

$\psi_k(\boldsymbol{r}'+\boldsymbol{T}) = \exp(i\boldsymbol{k}\cdot(\boldsymbol{r}+\boldsymbol{T}))\, u_k(\boldsymbol{r}'+\boldsymbol{T}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{T})\, \psi_k(\boldsymbol{r}')$ QED

Now let's use Bloch's theorem to solve the Schrödinger equation.

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = \varepsilon_k \psi_k(\boldsymbol{r})$$

The potential is periodic in real space $V(\boldsymbol{r}) = V(\boldsymbol{r}+\boldsymbol{T})$ and hence it is also periodic in reciprocal space and we can write:

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \hat{V}_{\boldsymbol{G}}\, e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

with $\hat{V}_{\boldsymbol{G}} = \frac{1}{\Omega}\int_{cell} V(\boldsymbol{r}) e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} d\boldsymbol{r}$ and $\boldsymbol{G}\cdot\boldsymbol{T} = 2n\pi$, and Ω is a unit cell volume. Now we can substitute expression for *V(r)* and for $\psi_k(\boldsymbol{r})$ taking into account the boundary conditions $\psi_k(\boldsymbol{r}+\boldsymbol{T}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{T})\, \psi_k(\boldsymbol{r})\ and\ \psi_k(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r})\, u_k(\boldsymbol{r})$ (according to the Bloch's theorem, where $u_k(\boldsymbol{r})$ is a periodic function, we can also see that $\psi_k(\boldsymbol{r})$ is not periodic) into the Schrödinger equation. For a linear chain of atoms in 1D we can write $\psi_k(x) = \sum_k C_k\, e^{ikx}$:
Formally, the equation:

$$\boldsymbol{H}\psi = E\psi$$

leads to:

$$\sum_k \frac{\hbar^2 k^2}{2m} C_k\, e^{ikx} + \sum_k \sum_G C_k V_G e^{i(k+G)x} = \varepsilon \sum_k C_k\, e^{ikx}$$

and moving the last term to the left-hand side we get:

$$\left(\frac{\hbar^2 k^2}{2m} - \varepsilon\right) C_k + \sum_G C_{k-G} V_G = 0$$

or

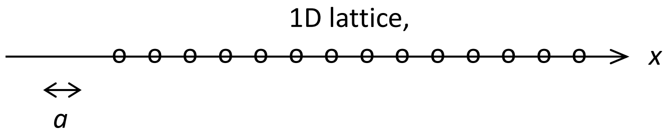
$$(\lambda_k - \varepsilon) C_k + \sum_G C_{k-G} V_G = 0$$

Now we need to solve

$$\begin{vmatrix} \lambda_{k-G} - \varepsilon & V & 0 \\ V & \lambda_k - \varepsilon & V \\ 0 & V & \lambda_{k+G} - \varepsilon \end{vmatrix} = 0$$

to get the energy spectrum.

However, near the Brillouin zone boundary (where the behaviour is very much unlike free-electron approximation) we can obtain the following solutions.



Now, if we include an interaction between an electron and a lattice site containing an atom than the new wavefunctions must include two parts - transmitted and scattered:

$$\psi = A_k e^{ikx} + B_{k\prime} e^{ik\prime x}$$

Considering $k' = k - G$, we shall have:

$$H\psi = \frac{\hbar^2 k^2}{2m} A_k e^{ikx} + \frac{\hbar^2 k'^2}{2m} B_{k\prime} e^{ik\prime x} + V_G\left[A_k e^{i(k\pm G)x} + B_{k\prime} e^{i(k\prime \pm G)x}\right] = \varepsilon(A_k e^{ikx} + B_{k\prime} e^{ik\prime x})$$

Now we multiply both parts by e^{-ikx} *and* $e^{-ik\prime x}$ and integrate over the size of the system using

$$\frac{1}{L}\int_0^L e^{iqx} dx = 1 \; for\; q = 0 \;\; and \;\; \frac{1}{L}\int_0^L e^{iqx} dx = 0 \; for\; q \neq 0$$

we obtain:

$$\varepsilon A_k = \frac{\hbar^2 k^2}{2m} A_k + V_G B_{k\prime}$$

$$\varepsilon B_{k\prime} = V_G A_k + \frac{\hbar^2 (k-G)^2}{2m} B_{k\prime}$$

and solve the following determinant to obtain unique solutions at the Brillouin Zone boundary where $G = \frac{2\pi}{a}$, $|k'| = |k - G| = \frac{\pi}{a}$:

$$\begin{vmatrix} \frac{\hbar^2 (\pi/a)^2}{2m} - \varepsilon & V_G \\ V_G & \frac{\hbar^2 (\pi/a)^2}{2m} - \varepsilon \end{vmatrix} = 0$$

Giving two solutions:

$$\lambda = \frac{\hbar^2 (\pi/a)^2}{2m} \pm V_G$$

With eigenstates: $\psi = \frac{1}{\sqrt{L}} e^{i\left(\frac{\pi}{a}\right)x} + \frac{1}{\sqrt{L}} e^{-i\left(\frac{\pi}{a}\right)x}$ - standing waves.

Around $k = \frac{\pi}{a} \pm \delta$ solutions are:

$$\varepsilon(\pm) = \frac{\hbar^2(\pi/a)^2}{2m} \pm V_G + \frac{\hbar^2\delta^2}{2m}\left(1 \pm \frac{\hbar^2(\pi/a)^2}{2m}\right)$$

Hence we can observe formation of the energy gap with a value of $2V_G$.

Summary

We assumed the following in order to solve Schrödinger equation with a non-zero potential:

1. Validity of Bloch's theorem for a periodic system of atoms
2. Periodicity of the potential in reciprocal space $V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \hat{V}_{\boldsymbol{G}}\, e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$

These assumptions allowed us to reduce a second order differential equation to a system of linear equations whose solutions yielded $\varepsilon(k)$ with an evidence of band gap of the value $2V_G$ forming at the Brillouin zone boundaries.

Few remarks on the behaviour of $\varepsilon(k)$ near the zone boundary. The group velocity of a wave packet (remember $\varepsilon = \hbar\omega$) is given by:

$$v_{\mathbf{k}} = \nabla_{\mathbf{k}}\omega = \frac{1}{\hbar}\frac{\partial\varepsilon_{\mathbf{k}}}{\partial\mathbf{k}} = \frac{1}{\hbar}\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}$$

In 1D, $v_{\mathbf{k}} = \frac{1}{\hbar}\frac{\partial\varepsilon_{\mathbf{k}}}{\partial\mathbf{k}}$