Electrons in a periodic potential

Tight Binding

Tight Binding Model

Within the TBA the atomic potential is quite large and the electron wave function is mostly localized about the atomic core. Let's see how the model can be used to demonstrate the formation of bandgaps in *ε(k)* and hence in electronic density of states.

Let's consider two isolated atoms *A* and *B* and see how the wavefunctions of atoms or ions will interact as we bring them together. Then we can reasonably guess that the trial solution of the Schrödinger equation will be of the form:

$$\psi = \psi_A \pm \psi_B$$

The general form of the Schrödinger equation is:

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

where:

$$H = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2} + H_A + H_B + H_{AB}$$

Where H_A, H_B, and H_{AB} are the hamiltonians of isolated atoms and the one corresponding to interaction between *A* and *B*. The problem of finding energy states is the reduced to evaluating:

$$E = \frac{\int \psi^* H \psi}{\int \psi^* \psi} = \frac{H_A \pm H_{AB}}{1 \pm P}$$

And for large interatomic distance R:

$$E_A = \int \psi_A H \psi_A dr, E_{AB} = \int \psi_A H \psi_B dr, \; and \; P = \int \psi_A \psi_B dr \approx 0,$$

Now, for couple of hydrogen atoms we would have $E_A = E_{1S}$, $E_{AB} = \Delta$. And we can see evidence of a forming band gap.

A more accurate consideration (See Ashcroft and Mermin) using ***Bloch's theorem***:

$$\psi_k(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_n \exp(i\boldsymbol{k}\cdot\boldsymbol{R_n})\, u_k(\boldsymbol{r}-\boldsymbol{R_n})$$

Confirm that this is a Boch's function:

$$\psi_k(\boldsymbol{r}+\boldsymbol{T}) = \frac{1}{\sqrt{N}} \sum_n \exp(i\boldsymbol{k}\cdot\boldsymbol{R_n})\, u_k(\boldsymbol{r}-\boldsymbol{R_n}+\boldsymbol{T})$$
$$= \exp(i\boldsymbol{k}\cdot\boldsymbol{T}) \frac{1}{\sqrt{N}} \sum_n \exp(i\boldsymbol{k}\cdot(\boldsymbol{R_n}-\boldsymbol{T}))\, u_k(\boldsymbol{r}-(\boldsymbol{R_n}-\boldsymbol{T})) = \exp(i\boldsymbol{k}\cdot\boldsymbol{T})\, \psi_k(\boldsymbol{r})$$

since both R_n and R_n-T are lattice vectors. Now let's find expectation values of the Hamiltonian:

$$\langle \psi_k | H | \psi_k \rangle = \frac{1}{N} \sum_m \sum_n \exp(i\boldsymbol{k}\cdot\boldsymbol{R_n}-\boldsymbol{R_m}) \langle u_n | H | u_m \rangle$$

where $u_m=u(r-R_m)$, and $\langle u_n|H|u_m\rangle$ will be large if $n=m$ or n and m are nearest sites and will drop rapidly with the distance. Or:

$$\langle u_n|H|u_n\rangle = -\alpha$$
$$\langle u_n|H|u_m\rangle = -\beta, if\ n\ and\ m\ are\ NN$$
$$\langle u_n|H|u_m\rangle = 0\ otherwise$$

then:

$$\varepsilon_k = \langle \psi_k|H|\psi_k\rangle = -\alpha - \beta\sum_n \exp(i\boldsymbol{k}\cdot\boldsymbol{R_n})$$

where the sum is over nearest neighbours only. For 2D lattice we will have:

$$\varepsilon_k = -\alpha - 2\beta\big(\cos(k_x a) + \cos(k_y a)\big)$$

Near $k=0$ we can expand further:

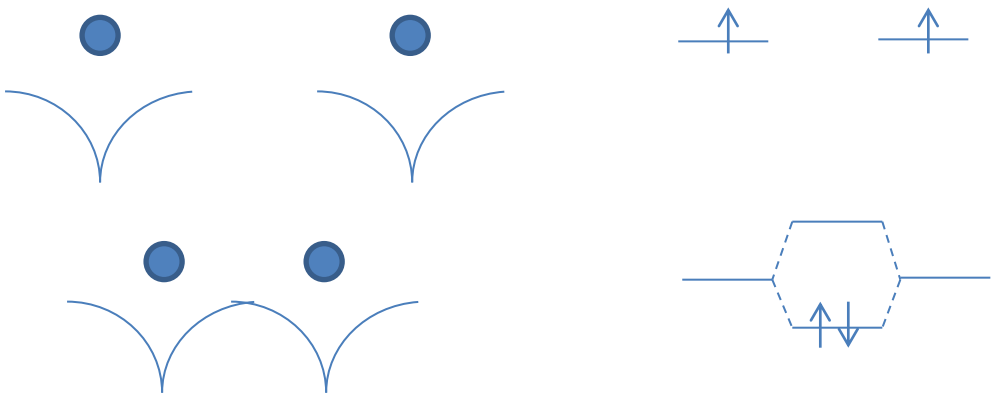
$$cos\phi \approx 1 - \frac{1}{2}\phi^2$$

To obtain:

$$\varepsilon_k \approx -\alpha - 2\beta\left(1 - \frac{1}{2}k_x^2a^2 + 1 - \frac{1}{2}k_y^2a^2\right) = \approx -\alpha - 4\beta - \beta\big(k_x^2 + k_y^2\big)a^2$$

which is a free-electron-like.

Graphically (albeit with a little bit of QM) we can illustrate the above as follows.



And for N atoms we have a band of 2N states: