Nearly Free Electron

In the tight bonding model, the electron eigenstates are initially assumed to be localized around the atoms, then a hopping term is introduced to allow them to delocalize. In the nearly free electron model, we take the opposite approach. That is, the electron eigenstates are initially assumed to be completely delocalized (plane waves for free electrons), then a periodic potential is turned on to localize them. Periodicity is key.

Periodic Function and Reciprocal Lattice

Consider a lattice $R = \{\vec{R}\}$ and a periodic function with the periodicity of the lattice $f(\vec{x} + \vec{R}) = f(\vec{x})$. Observing this periodicity in Fourier space

$$f(\vec{x} + \vec{R}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G} \cdot (\vec{x} + \vec{R})} = e^{i\vec{G} \cdot \vec{R}} f(\vec{x})$$
(1)

we conclude that $e^{i\vec{G}\cdot\vec{R}}$ must equal 1 for this periodicity to hold, which means the Fourier spectrum of any lattice-periodic function is necessarily discretize and can only have values at *reciprocal lattice points* \vec{G} , constraint by

$$e^{i\vec{G}\cdot\vec{R}} = 1 \tag{2}$$

The collection of all such \vec{G} form the *reciprocal lattice* $G = {\vec{G} | e^{i\vec{G}\cdot\vec{R}} = 1}$

Schrödinger's Equation in Periodic Potential

Recall the Schrödinger's equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3}$$

When $V(\vec{r} + \vec{R}) = V(\vec{r})$, this equation begs to be expanded in Fourier space (against the plane wave basis $\{ |\vec{k}\rangle \} = \{e^{i\vec{k}\cdot\vec{r}}\}$) for two reasons. Firstly, $V(\vec{r})$ is lattice-periodic and therefore has discrete expansion coefficients. Secondly, plane waves are eigenfunctions of ∇^2 . Carrying out the expansion $\psi(\vec{r}) = \sum_{\vec{k}} \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$ and $V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$, where \vec{k} is any momentum vector (for now),

and \vec{G} is any reciprocal lattice vector. Equation (3) becomes

$$\sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \sum_{\vec{k}} \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{k}} (E - \frac{\hbar^2 |\vec{k}|^2}{2m}) \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \Rightarrow$$
$$\sum_{\vec{G}} \sum_{\vec{k}} V_{\vec{G}} \psi_{\vec{k}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} = \sum_{\vec{k}} (E - \frac{\hbar^2 |\vec{k}|^2}{2m}) \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

Shift the summation index on the left $\vec{k} \rightarrow \vec{k} + \vec{G}$

$$\sum_{\vec{G}} \sum_{\vec{k}} V_{\vec{G}} \psi_{\vec{k}-\vec{G}} e^{i\vec{k}\cdot\vec{r}} = \left(E - \frac{\hbar^2 |\vec{k}|^2}{2m}\right) \sum_{\vec{k}} \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \Rightarrow$$

$$\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \left(\sum_{\vec{G}} V_{\vec{G}} \psi_{\vec{k}-\vec{G}} - \left(E - \frac{\hbar^2 |\vec{k}|^2}{2m}\right) \psi_{\vec{k}}\right) = 0 \Rightarrow$$

$$\sum_{\vec{G}} V_{\vec{G}} \psi_{\vec{k}-\vec{G}} - \left(E - \frac{\hbar^2 |\vec{k}|^2}{2m}\right) \psi_{\vec{k}} = 0, \ \forall \vec{k}$$
(4)

Remember, the boxed equation is equivalent to the Schodinger's equation, which means as long as it is satisfied, $\psi(\vec{r}) = \sum_{\vec{k}} \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$ will be an eigenfunction

tion of the Hamiltonian operator. Notice that this equation only couples \vec{k} separated by \vec{G} . Thus, for a given $\vec{k_o}$, if we choose the set of coefficients $K = \{\psi_{\vec{k}} | \vec{k} = \vec{k_o} + \vec{G}; \vec{G} \in G\}$ to satisfy (4), then we have the freedom to set all other coefficients to 0 ($\psi_{\vec{k}} = 0, \forall \vec{k} \in K^C$) and still have $\psi(\vec{r})$ be an eigenfunction of the Hamiltonian. Formally

$$\psi_{(\vec{k_o})}(\vec{r}) = e^{i\vec{k_o}\cdot\vec{r}} \sum_{\vec{G}} \psi_{\vec{k_o}+\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$
(5)

Notice, I have put () around $\vec{k_o}$ to signal that $\psi_{(\vec{k_o})}$ is a *spatial* wave function determined from a choice of $\vec{k_o}$ rather than a coefficient in frequency space. Further notice, $\psi_{(\vec{k_o}+\vec{G'})} \forall \vec{G'} \in G$ are equivalent representation of the same thing (the sum can be shifted). Borrowing the ideas of remainder theorem and equivalent classes from number theory, we can define THE representation for the class of eigenfunctions equivalent to $\psi_{(\vec{k_o})}(\vec{r})$ as

$$\psi_{(\vec{q})}(\vec{r}) = e^{i\vec{q}\cdot\vec{r}}u_{\vec{q}}(\vec{r})$$
(6)

where

$$u_{\vec{q}}(\vec{r}) = \sum_{\vec{G}} \psi_{\vec{q}+\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

$$\tag{7}$$

and

$$\vec{k_o} = Q\vec{G} + \vec{q} \tag{8}$$

with $Q \in \mathbb{N}$ and $\vec{q} < \vec{G} \ \forall \vec{G} \in G$. Notice $u_{\vec{q}}(\vec{r}) = \sum_{\vec{G}} \psi_{\vec{q}+\vec{G}} e^{i\vec{G}\cdot\vec{r}}$ is latticeperiodic. In essence, (6) is the simplest form of an eigenvector in periodic potential. $u_{\vec{q}}(\vec{r})$ is often referred to as the Bloch function and \vec{q} is known as the *crystal momentum*.

Periodic Boundary Condition

Incidentally, the form (6) also naturally arises from a partition of plane waves in a periodic box. Consider a 1D box of length L with period boundary conditions. Any wave function can be expanded as

$$\psi(x) = \sum_{k} \psi_k e^{ikx} \tag{9}$$

where
$$k = \frac{2\pi}{L}M$$
 (10)

If we consider a partition of the box into N smaller boxes of equal size a such that L = Na

$$\psi(x) = \sum_{M} \psi_k e^{i\frac{2\pi}{Na}Mx} \tag{11}$$

by the remainder theorem, $\exists q, r \in \mathbb{N}$ such that

$$M = qN + r \tag{12}$$

then

$$\psi(x) = \sum_{r} \sum_{q} \psi_{q,r} e^{i\frac{2\pi}{Na}(qN+r)x}$$
$$= \sum_{r} e^{i(\frac{2\pi}{L}r)x} \sum_{q} \psi_{q,r} e^{i(\frac{2\pi}{a}q)x}$$
(13)

If we define

$$\psi_r(x) = e^{i(\frac{2\pi}{L}r)x}u_r(x) \tag{14}$$

following the form of (6). Then we see that indeed $u_r(x) = \sum_q \psi_{q,r} e^{i(\frac{2\pi}{a}q)x}$ has period *a*. In essence, with a simple partition

$$\psi(x) = \sum_{k} \psi_{k} e^{i(\frac{2\pi}{L}M)x} = \sum_{r} e^{i(\frac{2\pi}{L}r)x} \sum_{q} \psi_{q,r} e^{i(\frac{2\pi}{a}q)x}$$
(15)

In conclusion, *partitioned plane waves* are the eigenfunctions of a periodic potential.