Lecture 13

Tuesday, February 16, 2010

Two views

Why there seem to be almost always "two something's" wherever we look and whatever problem we consider, e.g. Republicans and Democrats, "good" and "evil," double helix, two genders, day and night, etc..., I don't know, but we have it here in solid state physics, too: two seemingly opposite views, which are in fact two sides of the same coin.

In one view, electrons are viewed as "free" at first. The effect of the crystal potential is the formation of the energy band. In this view, the energy available for electrons become *narrow* as the crystal potential is considered. This is the view that flows naturally from form 3 of Bloch's theorem: $\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_n(\vec{k}+\vec{G}) \exp\left(i(\vec{k}+\vec{G})\cdot\vec{r}\right)$.

In another view, electrons are viewed as "localized" first, each valence electron belonging to a local environment, i.e. atom/ion/molecule in a basis. The crystal potential makes these local states unstable, making it possible for electrons to hop and explore the entire crystal. In this view, the energy available for electrons become *wide* as the total crystal potential is considered. This is the view that flows naturally from form 4 of Bloch's theorem: $\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\, \phi_n(\vec{r}-\vec{R})$.

"localized"

These two views, which may be called the "**itinerant**" view and the "**local**" view, are equivalent within the band theory. They become distinguished more sharply when electron-electron interactions are considered. We will discuss this when we discuss magnetism later.

Bragg scattering and the central equation

Recall from the previous lecture that the matrix element $\langle \vec{k}'|U|\vec{k}\rangle \neq 0$ only when $\vec{k}' = \vec{k}+\vec{G}$, where $|\vec{k}\rangle$ is the Dirac notation for the state corresponding to the (normalized) plane wave function $e^{i\vec{k}\cdot\vec{r}}/\sqrt{V}$ ($V =$ volume). So, for the given periodic potential U, we define

$$U_{\vec{G}} = \langle \vec{k}+\vec{G}|U|\vec{k}\rangle$$

$U_{\vec{G}} = \frac{1}{V}\int d\vec{r} e^{-i\vec{G}\cdot\vec{r}} U(\vec{r})$ is the Fourier component of $U(\vec{r})$. Since $U(\vec{r})$ is a real valued function, $U_{-\vec{G}} = U^*_{\vec{G}}$.

The above form of matrix element means that the potential energy U applied to a plane wave state $|\vec{k}\rangle$ has the effect of generating all possible Bragg scattered waves as in

$$U|\vec{k}\rangle = \sum_{\vec{G}} U_{\vec{G}} |\vec{k} + \vec{G}\rangle$$

On the other hand, the kinetic energy operator $T = \frac{p^2}{2m}$ is already diagonal in the plane wave basis

$$T|\vec{k}\rangle = \lambda_{\vec{k}}|\vec{k}\rangle, \quad \lambda_{\vec{k}} = \frac{\hbar k^2}{2m}$$

Using form 3, we know we can write down the eigenstate of $H = T + U$ as

$$|\psi_{\vec{k},n}\rangle = \sum_{\vec{G}} C_n(\vec{k} + \vec{G})|\vec{k} + \vec{G}\rangle$$
$$H|\psi_{\vec{k},n}\rangle = T|\psi_{\vec{k},n}\rangle + U|\psi_{\vec{k},n}\rangle = \epsilon_{\vec{k},n}|\psi_{\vec{k},n}\rangle$$

In this view, our task is to find the eigen values $\epsilon_{\vec{k},n}$ and the coefficients $C_n(\vec{k} + \vec{G})$ for the eigen vectors. The "band index" n distinguishes each eigen solution for the given crystal momentum $\vec{k}$.

How might one (hope to) solve this problem? Let us take a look. The eigenvalue equation is $(T - \epsilon_{\vec{k},n})|\psi_{\vec{k},n}\rangle + U|\psi_{\vec{k},n}\rangle = 0$.

The first term $= (T - \epsilon_{\vec{k},n})|\psi_{\vec{k},n}\rangle = \sum_{\vec{G}} C_n(\vec{k} + \vec{G})(T - \epsilon_{\vec{k},n})|\vec{k} + \vec{G}\rangle =$
$\sum_{\vec{G}} C_n(\vec{k} + \vec{G})(\lambda_{\underset{\vec{k}+\vec{G}}{\cancel{\vec{k},n}}} - \epsilon_{\vec{k},n})|\vec{k} + \vec{G}\rangle$.
The second term
$= U|\psi_{\vec{k},n}\rangle = \sum_{\vec{G}''} C_n(\vec{k} + \vec{G}'')U|\vec{k} + \vec{G}''\rangle =$
$\sum_{\vec{G}'',\vec{G}'} C_n(\vec{k} + \vec{G}'')U_{\vec{G}'}|\vec{k} + \vec{G}'' + \vec{G}'\rangle = \sum_{\vec{G},\vec{G}'} C_n(\vec{k} + \vec{G} - \vec{G}')U_{\vec{G}'}|\vec{k} + \vec{G}\rangle$

Collecting these two terms and noting that the each coefficient of $|\vec{k} + \vec{G}\rangle$ is zero, we get

$$(\lambda_{\vec{k}} - \epsilon_{\vec{k}})C_n(\vec{k} + \vec{G}) + \sum U_{\vec{G}'}C_n(\vec{k} + \vec{G} - \vec{G}') = 0$$

we get

$$\left(\lambda_{\underset{\vec k+\vec G}{\cancel{\vec k,n}}} - \epsilon_{\vec k,n}\right) C_n\left(\vec k+\vec G\right) + \sum_{\vec G'} U_{\vec G'} C_n\left(\vec k+\vec G-\vec G'\right) = 0$$

This **central equation** is basically the eigenvalue equation written in terms of the "vector" $C_n\left(\vec k+\vec G\right)$, whose vector component index is $\vec G$. The dimension of that vector will determine how many eigen solutions we have, which in this case is infinite.

General behavior of $U_{\vec G}$

By definition $U(\vec r) = \sum_{\vec R} U_b\left(\vec r-\vec R\right)$, where $U_b\left(\vec r-\vec R\right)$ is the sum of all atomic/ionic potentials in a given basis.

$$U_{\vec G} = \frac{1}{V}\int d\vec r\, e^{-i\vec G\cdot\vec r} U(\vec r) = \sum_{\vec R}\frac{1}{V}\int d\vec r\, e^{-i\vec G\cdot\vec r} U_b\left(\vec r-\vec R\right)$$

$\vec r' = \vec r - \vec R$

$$= \sum_{\vec R}\frac{1}{V}\int d\vec r'\, e^{-i\vec G\cdot\vec r'}\, U_b(\vec r') = \underbrace{\frac{N_l}{V}}_{\substack{\text{Number of lattice points}\\ \text{bases}}}\int d\vec r'\, e^{-i\vec G\cdot\vec r'}\, U_b(\vec r')$$

$$= \frac{1}{V_c}\int d\vec r\, e^{-i\vec G\cdot\vec r}\, U_b(\vec r)$$

In other words, in $U_{\vec G} = \frac{1}{V}\int d\vec r\, e^{-i\vec G\cdot\vec r}\, U(\vec r)$, we can simply replace the total volume (V) by the volume of a cell (V_c), and the total potential ($U(\vec r)$) by the potential due to one basis/cell alone ($U_b(\vec r)$).

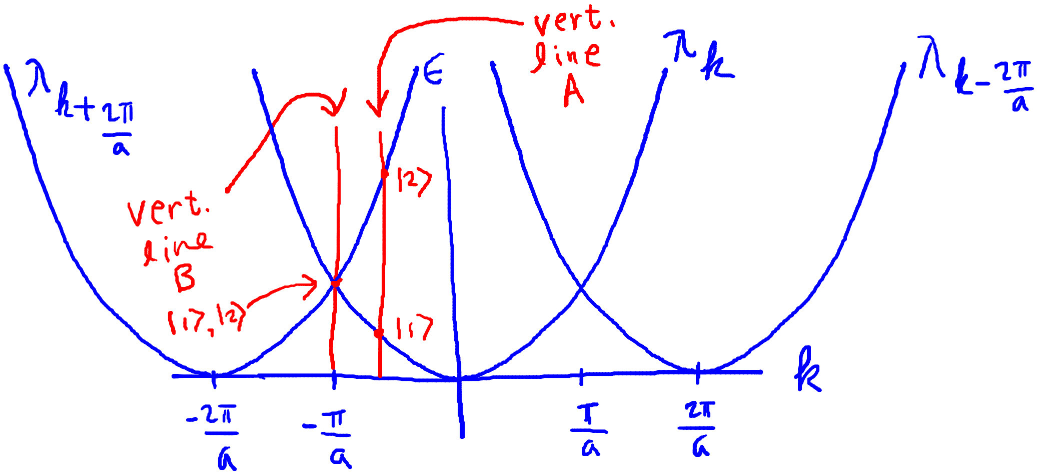
For large $\vec G$, we would expect that $U_{\vec G}$ approach zero as $\vec G$ increases in size. This is similar to the behavior of the atomic form factor: $f\left(\vec G\right) \to 0$ as $G \to \infty$. Note that $U_{\vec G}$ is basically a sum of Coulomb interactions between ions and the electron. For a bare ($U_b \propto 1/r$), or screened (Yukawa-type; $U_b \propto \frac{e^{-br}}{r}$), Coulomb potential, $U_{\vec G} \to \frac{1}{G^2}$ as $G \to \infty$. [Note: For an unrealistic potential, such as a delta function potential (Kronig-Penney model), the value $U_{\vec G}$ can be finite for $G \to \infty$. Such a case is interesting, in that, the model can be exactly solvable despite that. We will not be interested in such models, though.]

In general, the central equation is not solvable. However, a pretty good approximation scheme can be employed, where one keeps as few $U_{\vec G}$'s as possible while describing well the cohesive energy and the band structure.

Nearly free electron model

This is a useful model to consider, not only for pedagogy but also ~~inparas~~ in practice since the real band structure can sometimes be approximated pretty well with this type of model (read the "Pseudopotential Methods" in Kittel, Chapter 9).

The name "nearly free electron" means that the dispersion relation $\epsilon_{\vec{k},n}$ remains almost that of the free electron (folded into the first BZ). ~~For this to be valid,~~ This would come true if the matrix element $U_{\vec{G}}$ is ~~though to be~~ very small. But, how small? Much smaller than any finite energy splitting of the folded-in free electron states away from the BZ boundary.



To be specific, consider a 1D crystal, with the lattice constant a. The infinite dimensional matrix that we need to solve is defined by a vertical line for each crystal momentum $\hbar k$. For a given vertical line, any state that is crossed by the folded-in free electron dispersion and that vertical line defines a state in the basis. As the free electron energy can go to infinite energy (ignoring, until you learn quantum field theory, the fact that the relativistic theory must be used at a large energy), you can see that there will be infinite number of states.

Here, we show only the two lowest states on the left part of the first BZ.

For line A, the two states $|1\rangle = |k\rangle$ and $|2\rangle = \left|k + \frac{2\pi}{a}\right\rangle$ are separated in energy. We require that $U_{\vec{G}}$ be much smaller than the separation energy for these two states. For line B, the two states $|1\rangle = \left|k = -\frac{\pi}{a}\right\rangle$ and $|2\rangle = \left|k = -\frac{\pi}{a} + \frac{2\pi}{a}\right\rangle$ are degenerate in energy. These cases are fundamentally different!

For ~~this part~~ the following discussion, a solid understanding of the time independent perturbation theory of QM is necessary. Please read up on that, if you are not sure about this topic.

Line A: Here the non-degenerate perturbation theory of QM is valid.
$E^{(0)} = \lambda_k$ (unperturbed free electron energy)
$E^{(1)} = \langle 1|U|1\rangle = \langle 2|U|2\rangle = U_0$ (the zero-wave-vector-component of U)
$E^{(2)} = \sum_{n\neq 1} \frac{|\langle n|U|1\rangle|^2}{E_1^{(0)} - E_n^{(0)}}$ (for state 1$= |1\rangle$) and $\sum_{n\neq 2} \frac{|\langle n|U|2\rangle|^2}{E_2^{(0)} - E_n^{(0)}}$ (for state 2$= |2\rangle$)
Thus, up to the 1st order, the energy levels simply experience a uniform shift by U_0 (this is true for all states, as we shall see shortly). Up to the 2nd order, the energy levels for state 1 and state 2 repel each other by the amount $\frac{|\langle 2|U|1\rangle|^2}{\left|E_1^{(0)} - E_2^{(0)}\right|} = \frac{\left|U_{\frac{2\pi}{a}}\right|^2}{\left|E_1^{(0)} - E_2^{(0)}\right|}$, with the state 1 being lowered in energy by this amount and the state 2 being raised in energy by this amount. Consideration of other states $n = 3, 4, \ldots$ will not change the fact that the energy of state 1 is lowered. This is the general behavior. The ground state (state 1) can only be lowered in energy (due to the denominator $E_1^{(0)} - E_n^{(0)}$), while higher lying states (such as state 2) can be pushed up or down, due to the 2nd order perturbation.

Line B: Here, the degenerate perturbation theory should be used. Which just means that we need to diagonalize the Hamiltonian sub-matrix in the subspace spanned by the degenerate basis states. In the current problem, the matrix to diagonalize is using the basis states $|1\rangle = \left|k = -\frac{\pi}{a}\right\rangle$ and $|2\rangle = \left|k = \frac{\pi}{a}\right\rangle$:

$$\begin{pmatrix} \lambda_{-\frac{\pi}{a}} + U_0 & U^*_{\frac{2\pi}{a}} \\ U_{\frac{2\pi}{a}} & \lambda_{\frac{\pi}{a}} + U_0 \end{pmatrix}$$

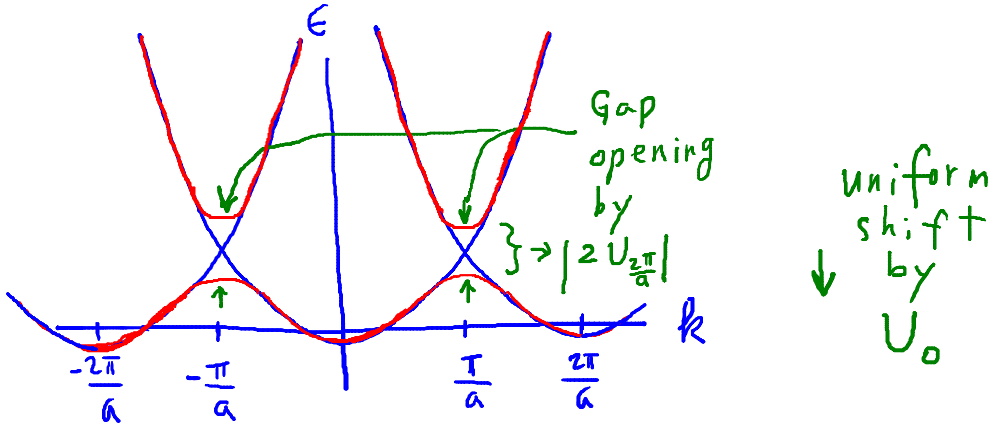
With $E^{(0)} \equiv \lambda_{-\frac{\pi}{a}} = \lambda_{\frac{\pi}{a}}$, the solution of this equation is easy to obtain:
$E^{(0)} + U_0 \pm \left|U_{\frac{2\pi}{a}}\right|$.

Note that this type of degenerate perturbation theory must be used whenever the level spacing between the unperturbed energies of state 1 and state 2 are on the order of or smaller than $U_{\vec{G}}$.

Combining these two results, we get the following result.

red : perturbed band energy

blue : unperturbed energy + U_0



In this diagram, the small 2nd order effect is ignored. So, the red line follows the blue line away from the BZ boundary $k = \pm\frac{\pi}{a}$. The only appreciable effect then occurs near the BZ boundary. Notably, at the BZ boundary, an energy gap of $|2U_{\frac{2\pi}{a}}|$ opens up. I.e. from the top of the lower band and the bottom of the upper band, there is a region where no electron state is allowed! Hooray! Cheers to Quantum Mechanics!