Lecture 13

Tuesday, February 21, 2012

Bloch Theorem (Waves in crystal IV)

This is the fundamental theorem for waves in crystal, namely particles in crystal. The good news is that we already mentioned it, in "Waves in Crystal I" (Lecture 06). For a formal discussion, please read Appendix B. In the context of electrons, the following statement is more suitable.

Bloch Theorem, Form 1: The Hamiltonian eigen-state for a particle in a crystal can be written as $\psi_{n\vec{k}}(\vec{r}) = \exp(i\vec{k}\cdot\vec{r})\, u_{n\vec{k}}(\vec{r})$

where $u_{n\vec{k}}(\vec{r})$ is a lattice periodic function i.e. $u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$.

Bloch Theorem, Form 2: The Hamiltonian eigen-state for a particle in a crystal can be chosen so that

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

Bloch Theorem, Form 3: (NFE)
The Hamiltonian eigen-state for a particle in a crystal can be chosen so that

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_n(\vec{k}+\vec{G})\exp(i(\vec{k}+\vec{G})\cdot\vec{r})$$

Bloch Theorem, Form 4: (TB)

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\,\phi_n(\vec{r}-\vec{R})$$

$$\phi_n(\vec{r}-\vec{R}) = \frac{1}{V_{BZ}}\int_{BZ} d\vec{k}\, e^{-i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r}) \quad \text{(Wannier orbital)}$$

Here, n = branch index or band index (polarization, optical or acoustical for phonons; band/symmetry index for electrons). In the case of phonons, for a

given $\vec{k}$, there are a finite number of branches. In the case of electrons, there are infinite number of branches.

Note on Form 4: This is the Fourier expansion of $\psi_{n\vec{k}}$ as a periodic function of $\vec{k}$. The Wannier orbital is just the coefficient of the Fourier series. Use $\int_{V_c} d\vec{r} e^{i\vec{G}\cdot\vec{r}} = V_c \delta_{\vec{G},0}$ (Lecture 06), with $\vec{G} \to \vec{R}$ and $\vec{r} \to \vec{k}$! Since $\frac{1}{V_{BZ}} \int_{BZ} d\vec{k} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r})$ is invariant under $\vec{r} \to \vec{r} + \vec{R}'$ and $\vec{R} \to \vec{R} + \vec{R}'$, ϕ_n is a function of $\vec{r} - \vec{R}$.

All of these forms are equivalent. It is quite easy to go from Form 1 to Form 2, or from Form 4 to Form 1. It is also very easy to go from Form 3 to Form 4. Going from Form 2 to Form 3 is not that difficult either. Here, we will do that here, thus proving Bloch's theorem and the equivalence of all four forms.

What does Form 2 mean? When you have a function $f(\vec{r})$, the function $f(\vec{r} - \vec{R})$ is a result of translating that function by $\vec{R}$. Let us call this operation $T_{\vec{R}}$. Form 2 means that $T_{\vec{R}} \psi_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r})$, that is $\psi_{nk}(\vec{r})$ is an eigenstate of the translation operator $T_{\vec{R}}$. As we learn in QM, if two operators commute and if both operators can be diagonalized, then the two operators can be simultaneously diagonalized. Bloch states are those simultaneous eigenstates for the Hamiltonian and $T_{\vec{R}}$. This is the statement of Form 2.

What is the most general form of $T_{\vec{R}}$ eigenstates? Start with $e^{i\vec{k}\cdot\vec{r}}$. Since, however, we are considering a lattice translation, any $\vec{k} + \vec{\mathrm{G}}$ will be equivalent. Thus, $\sum_{\vec{G}} C_{n\vec{k}}(\vec{G}) \exp\left(i\left(\vec{k} + \vec{G}\right) \cdot \vec{r}\right)$ is the most general form. This is how we go from Form 2 to Form 3, at the same time identifying the eigenvalue of $T_{\vec{R}}$.

Crystal momentum

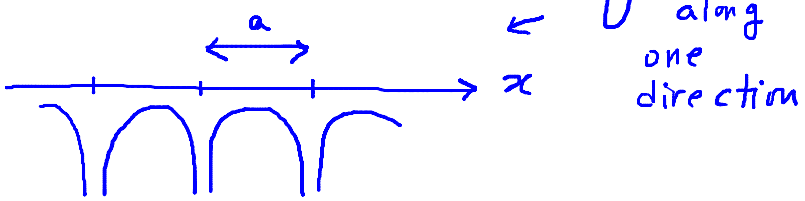
In QM, the translational operator is $e^{-\frac{ip\Delta x}{\hbar}}$, the rotational operator (translation in angle) is $e^{-\frac{iL_z\Delta\phi}{\hbar}}$, and the time evolution operator (translation in time) is $e^{-\frac{iH\Delta t}{\hbar}}$. So, the fact that the eigenvalue of $T_{\vec{R}}$ is given by $e^{-i\vec{k}\cdot\vec{R}}$ is not surprising at all. In this case, $\hbar\vec{k}$ not the momentum, but the crystal momentum, a conserved quantity for a *discrete* translational symmetry. $\vec{k}$ is arbitrary up to $\vec{G}$. I.e., $\vec{k}$ is unique only within a unit cell (e.g. the first BZ).

The dynamical origin of the Bloch theorem

The total Hamiltonian of the system is

$$H = T + U = \frac{p^2}{2m} + U$$

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



For plane wave basis $|\vec{k}\rangle$, the matrix element $\langle \vec{k}'|U|\vec{k}\rangle = 0$ unless $\vec{k}' = \vec{k} + \vec{G}$. This is easy to see

$|\vec{k}\rangle \rightarrow \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$ normalization factor

$$\langle \vec{k}'|U|\vec{k}\rangle = \frac{1}{V}\int d\vec{r}\, e^{-i\vec{k}'\cdot\vec{r}}\, U(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$$

$\vec{r} = \vec{r}' + \vec{R}$

$$= \frac{1}{V} e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}} \int d\vec{r}'\, e^{-i\vec{k}'\cdot\vec{r}'}\, U(\vec{r}')\, e^{i\vec{k}\cdot\vec{r}'}$$

$$= e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}} \langle \vec{k}'|U|\vec{k}\rangle$$

$\therefore \langle \vec{k}'|U|\vec{k}\rangle = 0$ unless $e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}} = 1$

$\vec{k}' - \vec{k} = \vec{G}$

What is this condition? $\vec{k}' - \vec{k} = \vec{G}$ is the Bragg diffraction condition or the crystal momentum conservation condition for a scattering! In general, we can call this condition a **Bragg scattering/reflection** condition as diffraction means elastic, while in general scattering includes inelastic processes.

So, what does this mean? First, note that $|\vec{k}\rangle$ diagonalizes the kinetic energy operator T. Second, U is block-diagonal in the plane wave basis where each block is given by the basis states $\{\vec{k} + \vec{G}\}$. What one knows for sure is then that the eigenstate of the Hamiltonian can be written as $\sum_{\vec{G}} C_{n\vec{k}}(\vec{G}) \exp(i(\vec{k} + \vec{G}) \cdot \vec{r})$

(Form 3). By the way, in this picture, it is easy to understand that there will be an infinite number of states given by different n's, as the number of basis states in the block, $\{\vec{k}+\vec{G}\}$, is as many as the number of plane waves $\exp\left(i\left(\vec{k}+\vec{G}\right)\cdot\vec{r}\right)$.

In general, one can see that this problem is unsolvable, since each block is an infinite dimensional matrix. Amazingly, the Kronig-Penney Model is an exactly solvable model, which is thus interesting. However, it is not very important for a conceptual understanding. And so, it is left for your reading.

Bragg scattering and Bragg diffraction

So, the electrons (or any particles) go through a Bragg scattering $\vec{k}'-\vec{k}=\vec{G}$ due to the crystal potential. What is the condition for the Bragg diffraction? It is that $\left|\vec{k}'\right|=\left|\vec{k}\right|$. This means $\left|\vec{k}+\vec{G}\right|=\left|\vec{k}\right|$. For what $\vec{k}$ values does this condition satisfied? For $\vec{k}$ on Brillouin zone boundaries! (Not just the 1st BZ, but the 2nd BZ, and the 3rd, and on and on.) So, elastic scatterings can happen at the BZ boundaries, while inelastic scatterings happen at other places in the $\vec{k}$ space.

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: $\psi_{n\vec{k}}(\vec{r})=\sum_{\vec{G}}C_n\left(\vec{k}+\vec{G}\right)\exp\left(i\left(\vec{k}+\vec{G}\right)\cdot\vec{r}\right)$.

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: $\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\,\phi_n(\vec{r}-\vec{R})$.

These two views, which may be called the "**itinerant**" view and the "**localized**" 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 $= (T-\epsilon_{\vec{k},n})|\psi_{\vec{k},n}\rangle = \sum_{\vec{G}} C_n(\vec{k}+\vec{G})(T-\epsilon_{\vec{k},n})|\vec{k}+\vec{G}\rangle =$
$\sum_{\vec{G}} C_n(\vec{k}+\vec{G})(\lambda_{\vec{k}+\vec{G},n}-\epsilon_{\vec{k},n})|\vec{k}+\vec{G}\rangle$.
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

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

This **central equation** is basically the eigenvalue equation written in terms of the "vector" $C_n(\vec{k}+\vec{G})$, 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 $U(\vec{r}) = \sum_{\vec{R}} U_b(\vec{r}-\vec{R})$, where $U_b(\vec{r}-\vec{R})$ is the sum of all

atomic/ionic potentials in a given basis.

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

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

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

$\vec{r}\,' = \vec{r} - \vec{R}$

Number of lattice points = bases

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 ($U_b(\vec{r})$).

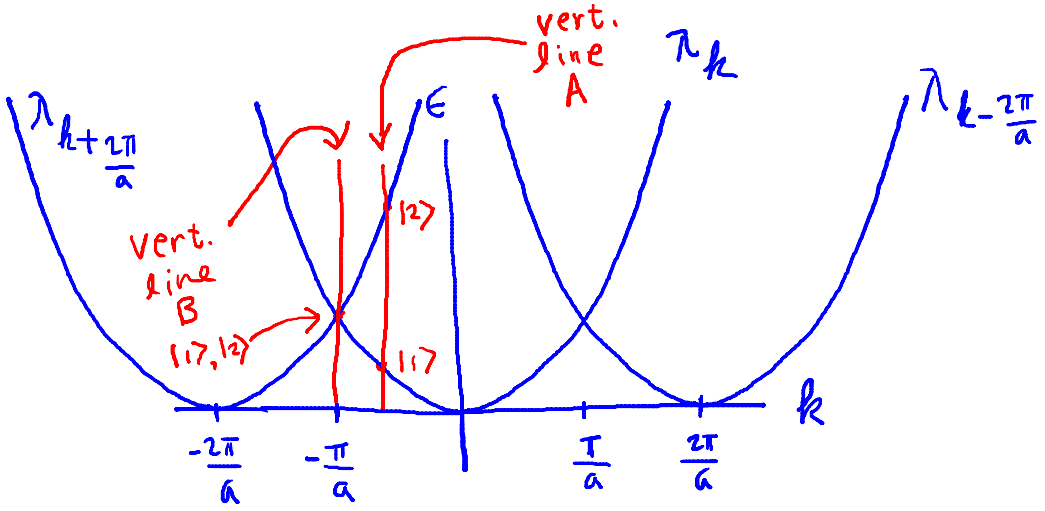
For large $\vec{G}$, we would expect that $U_{\vec{G}}$ approach zero as $\vec{G}$ increases in size. This is similar to the behavior of the atomic form factor: $f(\vec{G}) \to 0$ as $G \to \infty$. Note that $U_{\vec{G}}$ is basically a sum of Coulomb interactions between ions and the electron. For 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 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). This would come true if the matrix element $U_{\vec{G}}$ is 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 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 $|2\rangle = \left|k = \frac{\pi}{a}\right\rangle$:

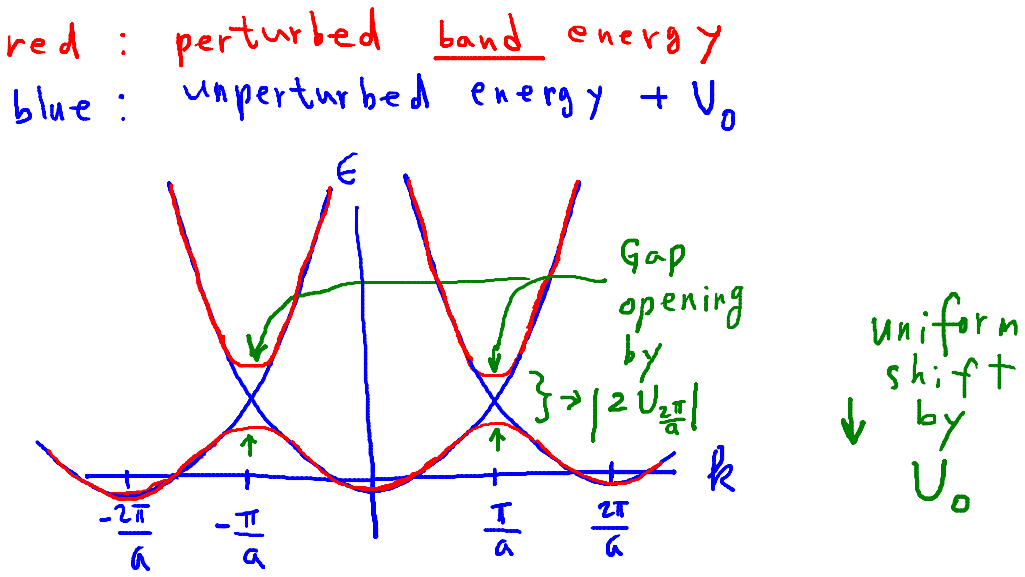
$$\begin{pmatrix} \lambda_{-\frac{\pi}{a}} + U_0 & U^*_{\frac{2\pi}{a}} \\ U_{\frac{2\pi}{a}} & \lambda_{\frac{\pi}{a}} + U_0 \end{pmatrix}$$

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.



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!