FoP3B Part I Lecture 2: Energy band gaps

In this lecture we will develop the nearly-free electron model rigorously using quantum mechanical perturbation theory. Introducing the electron-nuclear potential energy (V_{ion}) the Hamiltonian is modified to $H = H_0 + V_{ion}$, where H_0 is the (free electron) unperturbed Hamiltonian, with plane wave solutions, $\exp(i\mathbf{k}\cdot\mathbf{r})/L^{3/2}$, for the electron eigenfunctions (L is the length of the solid cube and $L^{3/2}$ is a normalisation constant). From *non-degenerate* perturbation theory the electron energy is:

$$E(\boldsymbol{k}) = E_0(\boldsymbol{k}) + \langle \boldsymbol{k}|V_{ion}|\boldsymbol{k}\rangle + \sum_{\boldsymbol{k'}\neq\boldsymbol{k}} \frac{|\langle \boldsymbol{k'}|V_{ion}|\boldsymbol{k}\rangle|^2}{E_0(\boldsymbol{k}) - E_0(\boldsymbol{k'})} \quad \ldots (1)$$

Consider the numerator in the second order term. $\langle \mathbf{k}'|V_{\text{ion}}|\mathbf{k}\rangle = \frac{1}{L^3}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} V_{\text{ion}}(\mathbf{r})d\mathbf{r}$, which is simply the Fourier transform of V_{ion} for reciprocal vector $\mathbf{k}$-$\mathbf{k}'$, i.e. $V_{\mathbf{k}-\mathbf{k}'}$. For crystals V_{ion} is periodic and therefore $V_{\mathbf{k}-\mathbf{k}'}$ is only non-zero provided $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, where $\mathbf{G}$ is a reciprocal vector. Furthermore, $\langle \mathbf{k}|V_{\text{ion}}|\mathbf{k}\rangle = V_0$, which we can arbitrarily set to zero, as we did previously in the free electron theory. Therefore, the energy depends only on the second order term.

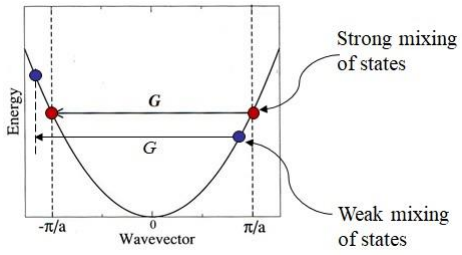

Figure 1

Figure 1 illustrates the mixing of two states with wavevectors separated by $\mathbf{G}$. For states away from the Brillouin zone boundary (e.g. the blue points), the energy difference is large, meaning that the second order correction is small (note that the energy difference appears in the denominator of the second order term). However, states close to the Brillouin zone boundary (red points) have similar energies and therefore show strong mixing.

States at the Brillouin zone boundary have identical energies, so that the second order correction diverges. *Degenerate* perturbation theory is therefore required for these states.

Degenerate Perturbation Theory

Let two states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ be degenerate (i.e. have identical energy). The two states can interact to give a new state $|\psi\rangle$ of energy E: $|\psi\rangle = \alpha|\mathbf{k}\rangle + \beta|\mathbf{k}'\rangle$. The linear coefficients α,β and energy E are related by:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad \ldots (2)$$

where the matrix element $H_{ij} = \langle i|H|j\rangle$, with $|i\rangle$, $|j\rangle$ representing $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ respectively. For the self-terms, $H_{11} = \langle \mathbf{k}|H|\mathbf{k}\rangle = \langle \mathbf{k}|H_0+V_{\text{ion}}|\mathbf{k}\rangle = \langle \mathbf{k}|H_0|\mathbf{k}\rangle = E_0(\mathbf{k})$ and similarly $H_{22} = \langle \mathbf{k}'|H|\mathbf{k}'\rangle = E_0(\mathbf{k}') = E_0(\mathbf{k})$. The cross-term

$$H_{12} = \langle \mathbf{k}|H|\mathbf{k}'\rangle = \langle \mathbf{k}|H_0 + V_{\text{ion}}|\mathbf{k}'\rangle = \langle \mathbf{k}|V_{\text{ion}}|\mathbf{k}'\rangle = V_{\mathbf{k}'-\mathbf{k}}$$

(note that from $H_0|\mathbf{k}'\rangle = E_0(\mathbf{k}')|\mathbf{k}'\rangle$, it follows that $\langle\mathbf{k}|H_0|\mathbf{k}'\rangle = E_0(\mathbf{k}')\langle\mathbf{k}|\mathbf{k}'\rangle = 0$, due to orthonormality of $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$). Since $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, $H_{12} = V_{\mathbf{k}'-\mathbf{k}} = V_{\mathbf{G}}$. Similarly, $H_{21} = \langle \mathbf{k}'|H|\mathbf{k}\rangle = V_{-\mathbf{G}} = V_{\mathbf{G}}$ (since V_{ion} is real the Fourier coefficients must satisfy $V_{-\mathbf{G}} = V_{\mathbf{G}}$).

For non-zero values of α,β:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \qquad \ldots (3)$$

which leads to two solutions for the energy given by $E_{\pm} = E_0(\mathbf{k}) \pm |V_{\mathbf{G}}|$. Substituting in (2) results in $\alpha = \pm\beta$, so that the (normalised) wavefunction $|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\mathbf{k}\rangle \pm |\mathbf{k}'\rangle)$. These results are identical to our qualitative description of the nearly-free electron theory in the previous lecture. In particular, $|\psi_{\pm}\rangle$ has the same form as the wavefunctions constructed through interference of incident and Bragg diffracted waves at the Brillouin zone boundary. Furthermore, $|\psi_{\pm}\rangle$ has different energies $E_{\pm}$, which are separated by a band gap of magnitude $2|V_{\mathbf{G}}|$ (see Figure 2).

Degenerate perturbation theory can also be extended to include $|\mathbf{k}\rangle$, $|\mathbf{k}'\rangle$ states that are close to the Brillouin zone boundaries. Figure 2 depicts the situation for a 1D chain of atoms with periodic spacing a (the Brillouin zone boundary is therefore $|\mathbf{G}/2| = \pm\pi/a$).

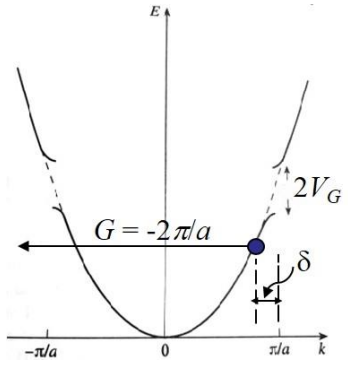

Figure 2

For $k = (\pi/a) - \delta$ and $k' = k + G = -\pi/a - \delta$, it can be shown that for small δ:

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

Close to the Brillouin zone boundary the energy is a quadratic function of δ, as plotted in Figure 2. Note that the gradient is zero at the Brillouin zone boundary, indicating the presence of standing waves with zero group velocity $v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$.

Band filling and Electrical conductivity

We will now examine the link between band filling and electrical conductivity. Consider again a 1D chain of N atoms with periodic spacing a (the length of the chain is therefore $L = Na$). From the boundary conditions the spacing between **k**-points is $2\pi/L$. The number of electronic states within the Brillouin zone of width $(2\pi/a)$ is therefore 2 x $(2\pi/a)/(2\pi/L)$, where the factor of '2' is due to spin degeneracy. But 2 x $(2\pi/a)/(2\pi/L) = 2L/a = 2N$, i.e. there are twice as many electronic states within the Brillouin zone as there are atoms[1]. Therefore, for monovalent atoms the Brillouin zone is only half full, meaning that electrons can move under an electric field, since there are empty, higher energy states to which they can be easily promoted to. This explains why Group I metals, such as sodium and potassium, are good conductors. However, if the atoms are divalent the first Brillouin zone is completely full, and the unoccupied levels

[1] The result holds for 3D solids as well, except for 3D the number of electronic states is twice the number of primitive unit cells.

are separated by a band gap, i.e. there is an activation barrier. Therefore, Group II elements must be insulators, although this is inconsistent with the fact that metals such as calcium and magnesium are, in fact, good electrical conductors.

The reason for the discrepancy is because we have been considering 1D solids. Real materials are 3D, but we can resolve the discrepancy by analysing the simpler 2D case instead. Consider a 2D solid consisting of atoms periodically arranged in a square lattice. The reciprocal lattice points and first, second Brillouin zones are shown in Figure 3a, along with the Fermi surface as predicted by free electron theory (recall that since $E \propto k^2$ for free electrons the Fermi surface is a circle). There are occupied energy levels within both the 1st and 2nd Brillouin zones. Now consider the energy gap at the first Brillouin zone boundary arising from nearly-free electron theory (Figure 3b). If the energy gap $2V_G$ is large it is energetically unfavourable to have electrons in the 2nd Brillouin zone, so that these electrons must be transferred to the 1st Brillouin zone. After transfer the 1st Brillouin zone will be completely full, and since there is a large energy gap separating the occupied and unoccupied states, the material will be insulating. However, if V_G and the band gap is small, only *some* of the electrons in the 2nd Brillouin zone will be transferred to the 1st Brillouin zone (note the energy reduction due to electron transfer must be greater than the energy gain due to occupying states of larger wavenumber k within the 1st Brillouin zone). There are now occupied and unoccupied states within both 1st and 2nd Brillouin zones, meaning that electrical conduction can take place from electrons within both zones. This is consistent with electrical conductivity in divalent metals.

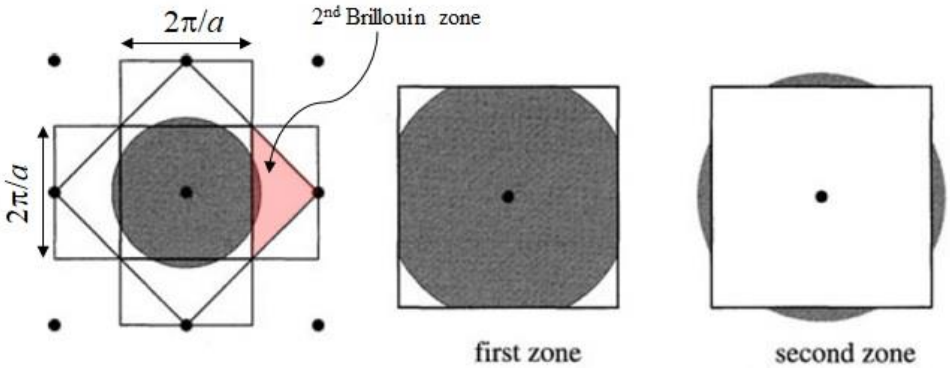

Figure 3a: reciprocal lattice and 1st, 2nd Brillouin zones for a divalent square lattice. The shaded circle represents occupied energy states, as predicted by free electron theory.

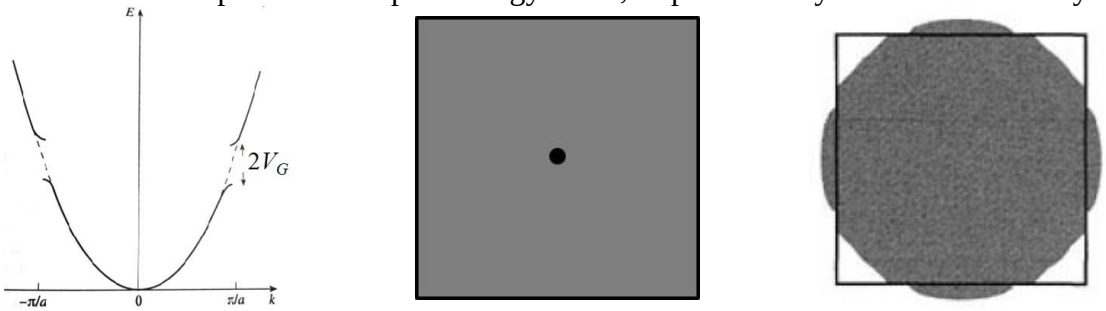

Figure 3b: (left) band gap at the Brillouin zone boundary. If the bad gap is large it is energetically favourable for all electrons to occupy the 1st Brillouin zone causing it to be completely full (middle). For smaller band gaps only part of the electrons will be transferred from 2nd to 1st Brillouin zones (right; compare with Fig 3a).