Solid State Physics: Final Exam Review

December 10, 2018

1 LCAO and Tight Binding

1.1 Gentle Introduction: Covalent Bonding of Hydrogen Atoms

Imagine a system in which two Hydrogen atoms are held with fixed-position nuclei ("Born-Oppenheimer Approximation") and a shared electron between them. Goal: calculate the eigenenergies of the system as a funtion of the distance from the fixed nuclei.

The Hamiltonian of the system is given by

$$H = K + V_1 + V_2$$

where

$$K = \frac{\mathbf{p}^2}{2m}$$

and the coulombic potential due to the nucleus fixed at position $\mathbf{R}_i$ is given by

$$V_i = \frac{e^2}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_i|}$$

We can write down a trial solution of the form

$$|\psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle$$

where $|i\rangle$ are the atomic orbitals (or "tight-binding orbitals") representing the ground state solution for that particular isolated nucleus. That explicitly means the following

$$(K + V_1) |1\rangle = \epsilon_0 |1\rangle$$
$$(K + V_2) |2\rangle = \epsilon_0 |2\rangle$$

where ϵ_0 is the ground state energy of a single Hydrogen atom.

In the LCAO/tight-binding method, we make the following approximation: **the atomic orbitals $|i\rangle$ are orthogonal** such that

$$\langle i|j\rangle = \delta_{ij}$$

The Schrodinger equation can be written as

$$H \left| \psi \right\rangle = E \left| \psi \right\rangle$$

or, alternatively, in the $\left| i \right\rangle$ basis:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = E \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$$

By using a variational method where

$$E = \frac{\left\langle \psi \right| H \left| \psi \right\rangle}{\left\langle \psi | \psi \right\rangle}$$

and

$$\frac{\partial E}{\partial \phi_i} = \frac{\partial E}{\partial \phi_i *} = 0$$

We obtain an eigenvalue equation

$$\sum_j H_{ij} \phi_j = E \phi_i$$

where $H_{ij} = \left\langle i \right| H \left| j \right\rangle$. The components of H can be written explicitly as

$$H_{11} = \left\langle 1 \right| H \left| 1 \right\rangle = \left\langle 1 \right| K + V_1 \left| 1 \right\rangle + \left\langle 1 \right| V_2 \left| 1 \right\rangle = \epsilon_0 + V_{cross}$$

$$H_{22} = \left\langle 2 \right| H \left| 2 \right\rangle = \left\langle 2 \right| K + V_2 \left| 2 \right\rangle + \left\langle 2 \right| V_1 \left| 2 \right\rangle = \epsilon_0 + V_{cross}$$

$$H_{12} = \left\langle 1 \right| H \left| 2 \right\rangle = \left\langle 1 \right| K + V_2 \left| 2 \right\rangle + \left\langle 1 \right| V_1 \left| 2 \right\rangle = -t$$

$$H_{21} = \left\langle 2 \right| H \left| 1 \right\rangle = \left\langle 2 \right| K + V_1 \left| 1 \right\rangle + \left\langle 2 \right| V_2 \left| 1 \right\rangle = -t^*$$

We make the following observations:

- The on-site energy is given by

$$\left\langle i \right| K + V_i \left| i \right\rangle = \epsilon_0$$

- The coulombic potential due to site j on site i is given by

$$\left\langle i \right| V_j \left| i \right\rangle = V_{cross}$$

- The *hopping term* is defined by

$$\left\langle j \right| V_j \left| i \right\rangle = \left\langle i \right| V_i \left| j \right\rangle^* = -t$$

The eigenvalue equation then takes on the form of a 2×2 matrix equation

$$\begin{bmatrix} \epsilon_0 + V_{cross} & -t \\ -t^* & \epsilon_0 + V_{cross} \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = E \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$$

Diagonalization yields the eigenenergies

$$E_{\pm} = \epsilon_0 + V_{cross} \pm |t|$$

1.2 Tight-Binding Chain

In this section, we seek to observe that all waves in periodic environments behave similarly. Here we consider electron waves, but we should consider the similarities to vibrational waves (phonons) as well.

The one-dimensional tight binding has the following description.

- There is a single orbital on atom n, denoted $|n\rangle$.

- Periodic boundary conditions are imposed such that $|N\rangle = |0\rangle$.

- Atomic orbital states are orthogonal.

$$\langle n|m\rangle = \delta_{nm}$$

- The general trial wavefunction has the form

$$|\Psi\rangle = \sum_n \phi_n |n\rangle$$

- The effective Schrodinger equation is

$$\sum_m H_{nm}\phi_m = E\phi_n$$

where $H_{nm} = \langle n| H |m\rangle$.

- The Hamiltonian can be written

$$H = K + \sum_j V_j$$

where $K = \mathbf{p}^2/2m$ and $V_j = V(\mathbf{r} - \mathbf{R}_j)$.

Given the description above, we have

$$
\begin{aligned}
H |m\rangle &= (K + V_m) |m\rangle + \sum_{j\neq m} V_j |m\rangle \\
&= \epsilon_{atomic} |m\rangle + \sum_{j\neq m} V_j |m\rangle
\end{aligned}
\tag{1}
$$

Therefore,

$$H_{nm} = \langle n| H |m\rangle = \epsilon_{atomic}\delta_{mn} + \sum_{j\neq m} \langle n| V_j |m\rangle$$

where

$$\sum_{j\neq m} \langle n| V_j |m\rangle = \begin{cases} V_0 & n = m \\ -t & n = m \pm 1 \\ 0 & 0 \end{cases}$$

So,

$$H_{n,m} = (\epsilon_{atomic} + V_0)\delta_{nm} - t(\delta_{n+1,m} + \delta_{n-1,m}) = \epsilon_0\delta_{nm} - t(\delta_{n+1,m} + \delta_{n-1,m})$$

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1.2.1 Solution

We propose an ansatz

$$\phi_n = \frac{e^{-ikna}}{\sqrt{N}}$$

Note the absence of of a frequency component to the exponent, which is due to the fact that we are seeking solutions to the time-independent Schrodinger equation.

- For a system with N sites, and length $L = Na$, there are N possible solutions of the ansatz form.

- Each solution corresponds to $k = 2\pi m/L$, where $m = 0, ..., N - 1$.

Plugging the ansatz into the Schrodinger equation gives

$$\sum_m H_{nm}\phi_m = \epsilon_0 \frac{e^{-ikna}}{\sqrt{N}} - t\left(\frac{e^{-ik(n+1)a}}{\sqrt{N}} + \frac{e^{-ik(n-1)a}}{\sqrt{N}}\right) \tag{2}$$

and we also know that

$$E\phi_n = E\frac{e^{-ikna}}{\sqrt{N}} \tag{3}$$

Equating the previous two equations gives us

$$E = \epsilon_0 - 2t\cos(ka)$$

(Note the correspondance to the phonon spectrum for the 1D monatomic chain). The dispersion curve is shown in Fig. 1.

Some notes about the dispersion relation:

- The periodicity is $k \to k + \frac{2\pi}{a}$ (like phonons).

- Zero group velocity (flat curve) at the Brillouin zone boundary (like phonons).

- Electrons may only have eigenstates within a certain *band*, referring to both the energy range in which the eigenstates exist as well as the individual branches of the dispersion curve itself.

- The *bandwidth* refers to the difference between the maximum and minimum energies in a band. In Fig. 1, the bandwidth is $4t$.

- The bandwidth, $4t$, is dependent on the hopping amplitude and, therefore, on the interatomic spacing between nuclei. This dependence is shown in Fig. 2.

- As seen in Fig. 2, the effect of the hopping is to raise the energy of some eigenstates and lower the energy of others (such that the average is still ϵ_0). If the band is not completely filled, then the average energy dips below ϵ_0 since some higher states are not filled.
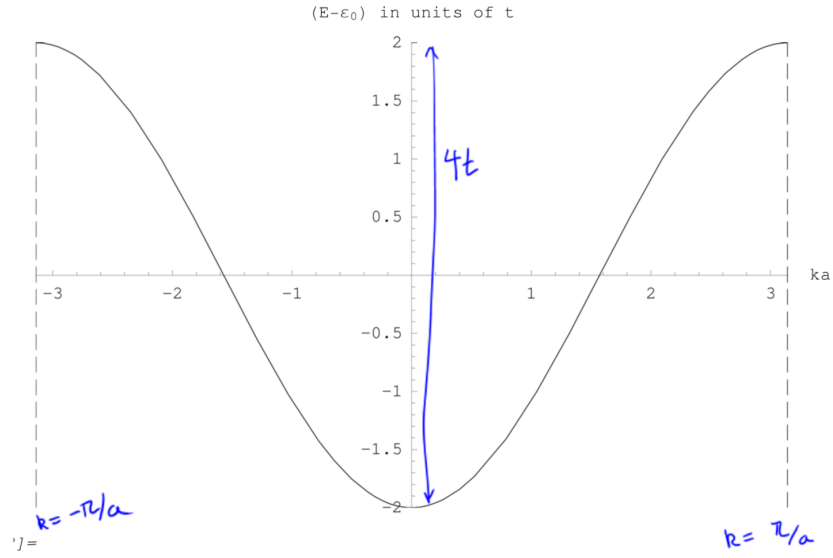
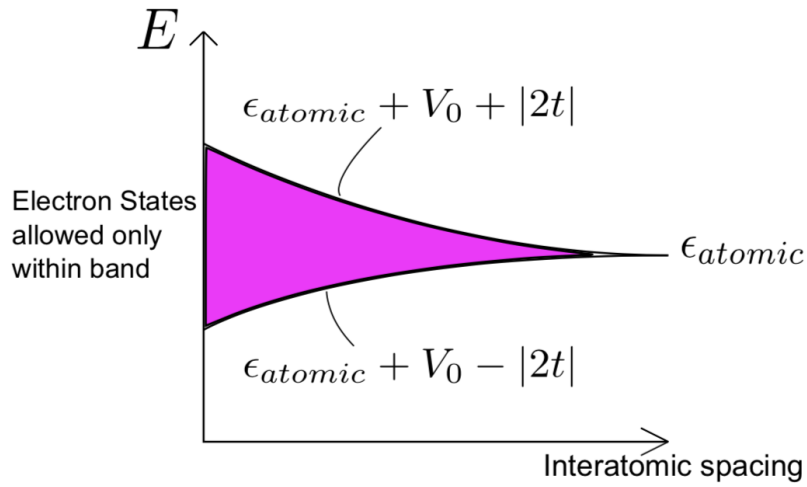Figure 1: Dispersion curve for tight-binding chain.

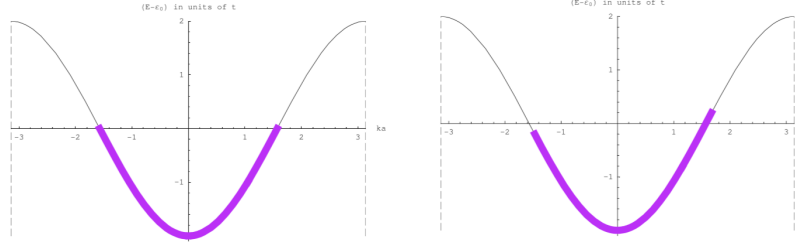Figure 2: Bandwidth dependence on interatomic spacing.

Figure 3: Monovalent Fermi surface and shifted Fermi sea.

Near the bottom of the band in Fig. 1, where k is close to zero, the dispersion is approximately parabolic. For small k, $cos(ka) \approx 1 - k^2a^2/2$, so

$$E(k) \approx Constant + ta^2k^2$$

Note: If the minimum were at the Brillouin zone edge, we would need to expand around $k = \pi/a$ instead. Since the dispersion of the free electron can be written as

$$E_{free}(k) = \frac{\hbar^2k^2}{2m}$$

We can relate the two dispersion relations to calculate an *effective mass* m^* such that the dispersion at the bottom of the band behaves as a free electron of mass m^*.

$$\frac{\hbar^2k^2}{2m^*} = fa^2k^2$$

and the effective mass is then

$$m^* = \frac{\hbar^2}{2ta^2}$$

1.3   Band Filling

1.3.1   Monovalent Case

If every atom in the one-dimensional, single-orbital tight binding model were to "donate" an electron, then we would have a total of N electrons. These electrons occupy the N lowest-energy states in the band, which has N allowed eigenstates, but each eigenstate can be populated by a spin-up and a spin-down electron. The band is therefore only half filled, as seen in the left of Fig. 3.

In Fig. 3, the Fermi surface (the energy level separating occupied and unoccupied states) is ϵ_0. By providing a small bit of energy, the Fermi sea can be shifted slightly such that the electrons take on an average net positive momentum (right side of Fig. 3) and current is able to flow. For this reason, monovalent materials are frequently metals.
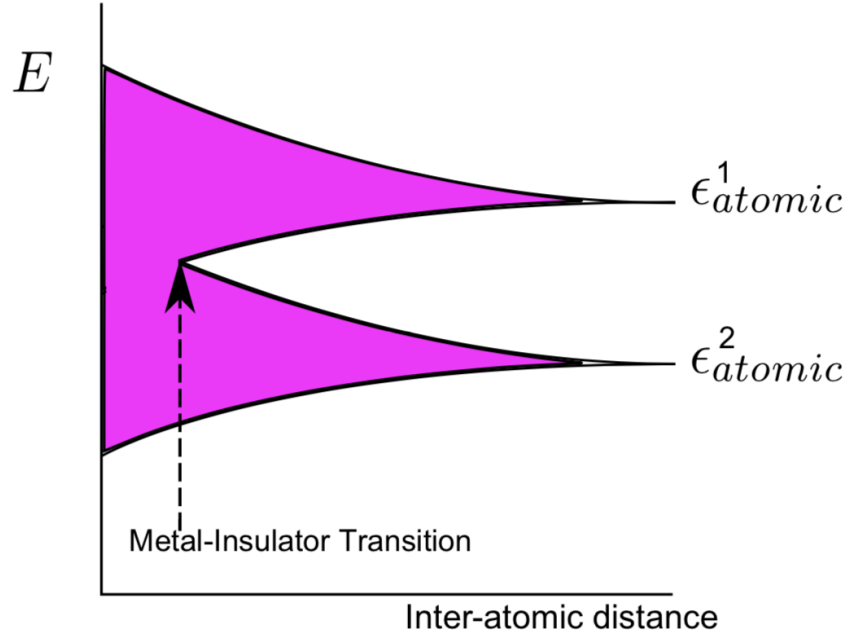
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Figure 4: Energy bandwidth as a function of inter-atomic distance. Two atomic orbitals per site.

1.3.2 Divalent Case

In the divalent case, there are a total of $2N$ atoms, which fill all spin-up and spin-down states of each of the N allowed eigenstates. That is, the band is completely filled. Therefore, there are no free k states to which the Fermi sea could shift to allow a current to be induced. **A filled band carries no current**. This results in a *band insulator*.

1.4 Multiple Bands

In the one-dimensional, single-orbital tight-binding model, there is a single band. However, if we consider multiple orbitals per unit cell, more bands will emerge. We may consider, for example:

- Multi-atom unit cells with one or more orbitals each.

- Single-site unit cells with multiple orbitals per site.

The energy bandwidth as a function of inter-atomic spacing is shown in Fig. 4 for the case where there are two orbitals per single-site. The dispersion relation for the two-site, single orbital case is shown in Fig. 5. Some notes:
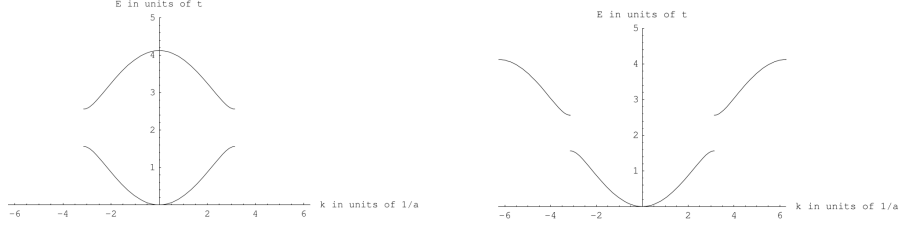
Figure 5: Dispersion relation for tight-binding model with two sites per unit cell, one orbital per site.

- If both species are divalent, then there are already a total of two electrons filled each orbital on every atom - that is, both branches of the dispersion are filled.

- If both species are monovalent, then only the bottom band is filled (i.e. only half the states are filled). So, there are k states available to shift the Fermi sea (around the Fermi surface, which is halfway between the top and bottom bands). However, to shift the sea, we need to apply an electric field strong enough to overcome the energy gap between the bands. **A filled band is an insulator as long as there is a finite gap to any higher-level band**.

- As seen in Fig. 4, as the interatomic distance decreases, the bandwidths of the individual bands come to overlap and there is no longer a gap between the lower- and higher-energy bands. In this limit, the material comes to behave as a metal.

2 Nearly Free Electron Model

The difference between the nearly free electron model and the tight binding model:

- In the nearly free electron model, electrons are considered as free electron waves that are only very weakly perturbed by the periodic potential of the atoms in the solid.

- In the tight binding model, electrons are considered very tightly bound to atoms with a possible weak hopping to other atoms.

The nearly free electron model starts with the free electron case:

- The free electron Hamiltonian is

$$H_0 = \frac{\mathbf{p}^2}{2m}$$

- The eigenstates are the plane waves $|\mathbf{k}\rangle$ with eigenenergies

$$\epsilon_0(\mathbf{k}) = \frac{\hbar^2|\mathbf{k}|^2}{2m}$$

We now introduce a weak periodic potential $V(\mathbf{r})$.

- For any lattice vector $\mathbf{R}$, $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$.

- The matrix elements of $V(\mathbf{r})$ are given by

$$V_{k',k} = \langle \mathbf{k}'|\, V\, |\mathbf{k}\rangle = \frac{1}{L^3} \int d^3r\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\, V(\mathbf{r}) \equiv V_{\mathbf{k}'-\mathbf{k}}$$

- The integral in the previous point will vanish unless the Laue condition is met. Therefore,

$$V_{k',k} = V_{\mathbf{G}}\delta_{\mathbf{G},\mathbf{k}'-\mathbf{k}}$$

In words, this means that a plane-wave state $|\mathbf{k}\rangle$ can only scatter into another plane-wave state $|\mathbf{k}'\rangle$ if $\mathbf{k}$ and $\mathbf{k}'$ are separated by a reciprocal lattice vector $\mathbf{G}$ - this is conservation of crystal momentum.

We now apply perturbation theory. To second order, the shift in the eigenenergies due to the potential $V(\mathbf{r})$ is given by

$$\begin{aligned}
\epsilon(\mathbf{k}) &= \epsilon_0(\mathbf{k}) + \langle \mathbf{k}|\, V\, |\mathbf{k}\rangle + \sum_{\mathbf{k}'=\mathbf{k}+\mathbf{G}} \frac{|\langle \mathbf{k}'|\, V\, |\mathbf{k}\rangle|^2}{\epsilon_0(\mathbf{k}) - \epsilon_0(\mathbf{k'})} \\
&= \epsilon_0(\mathbf{k}) + V_0 + \sum_{\mathbf{k}'=\mathbf{k}+\mathbf{G}} \frac{|\langle \mathbf{k}'|\, V\, |\mathbf{k}\rangle|^2}{\epsilon_0(\mathbf{k}) - \epsilon_0(\mathbf{k'})}
\end{aligned} \tag{4}$$

Some notes about this result:

- We may assume that $V_0 = 0$ for simplicity since this is just a constant shift in the energy spectrum.

- The second-order sum is taken over all $\mathbf{k}'$ for which $\mathbf{G} \neq 0$.

- In the degenerate situation, $\epsilon_0(\mathbf{k})$ and $\epsilon_0(\mathbf{k}')$ are approximately equal and the sum will diverge. The conditions for this case are

$$\epsilon_0(\mathbf{k}) = \epsilon_0(\mathbf{k}')$$

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}$$

- In one dimension, this is satisfied for $k' = -k = \frac{n\pi}{a}$ (i.e. on the Brillouin zone boundary).

2.1   Degenerate Pertubation Theory

When two plane wave states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle = |\mathbf{k} + \mathbf{G}\rangle$ have approximately the same energy (i.e. they are close to the zone boundaries), then we need to diagonalize this subspace. We begin with

$$\langle \mathbf{k}| H |\mathbf{k}\rangle = \epsilon_0(\mathbf{k})$$

$$\langle \mathbf{k}'| H |\mathbf{k}'\rangle = \epsilon_0(\mathbf{k}') = \epsilon_0(\mathbf{k} + \mathbf{G})$$

$$\langle \mathbf{k}| H |\mathbf{k}'\rangle = V_{\mathbf{k}-\mathbf{k}'} = V_{\mathbf{G}}^*$$

$$\langle \mathbf{k}'| H |\mathbf{k}\rangle = V_{\mathbf{k}'-\mathbf{k}} = V_{\mathbf{G}}$$

We now write the diagonalized state as a linear combination of these plane-wave states.

$$|\Psi\rangle = \alpha |\mathbf{k}\rangle + \beta |\mathbf{k}'\rangle = \alpha |\mathbf{k}\rangle + \beta |\mathbf{k} + \mathbf{G}\rangle$$

We obtain the Schrodinger equation

$$\begin{bmatrix} \epsilon_0(\mathbf{k}) & V_{\mathbf{G}}^* \\ V_{\mathbf{G}} & \epsilon_0(\mathbf{k} + \mathbf{G}) \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

which yields the characteristic equation

$$(\epsilon_0(\mathbf{k}) - E)\,(\epsilon_0(\mathbf{k} + \mathbf{G}) - E) - |V_{\mathbf{G}}|^2 = 0$$

Two cases arise:

- *Case 1*: $\mathbf{k}$ exactly at the zone boundary. In this case, $\epsilon_0(\mathbf{k}) = \epsilon_0(\mathbf{k} + \mathbf{G})$ and the characteristic equation reduces to

$$(\epsilon_0(\mathbf{k}) - E)^2 = |V_{\mathbf{G}}|^2$$

  which yields

$$E_{\pm} = \epsilon_0(\mathbf{k}) \pm |V_{\mathbf{G}}|$$

  A gap opens at the zone boundary - where once the energy was $\epsilon_0(\mathbf{k})$, we now see two energies split by $2|V_{\mathbf{G}}|$.

  Consider $V(x) = V \cos(2\pi x/a)$.

   - Brillouin zone boundaries are at $k = \pi/a$ and $k' = -k = -\pi/a$.
   - $k' - k = G = -2\pi/a$
   - $\epsilon_0(k') = \epsilon_0(k)$
   - The diagonalized states corresponding to $E_{\pm}$ are

$$|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|k\rangle \pm |k'\rangle)$$

     where
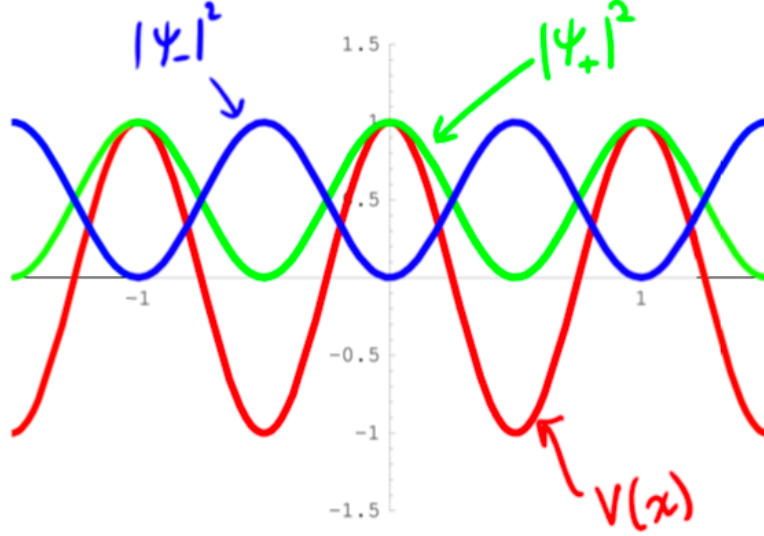
$$|k\rangle = e^{ikx} = e^{ix\pi/a}$$

Figure 6: Probability amplitudes of diagonalized states, plotted with potential in real-space.

$$|k'\rangle = e^{ik'x} = e^{-ix\pi/a}$$

Therefore,

$$|\Psi_+\rangle \propto \cos(x\pi/a)$$
$$|\Psi_-\rangle \propto \sin(x\pi/a)$$

- The periodic potential scatters between the two plane waves $|\mathbf{k}\rangle$ and $|\mathbf{k} + \mathbf{G}\rangle$. If these two plane waves have the same energy, they mix strongly to form two states: one with higher energy (concentrated on the potential maxima) and one with lower energy (concentrated on the potential minima. See Fig. 6.

- *Case 2*: $\mathbf{k}$ near the zone boundary. Consider a plane wave k near the zone boundary such that $k = n\pi/a + \delta$. This wavevector can scatter to $k' = -n\pi/a + \delta$. Plugging these wavevectors into the free-energy solution gives unperturbed energies

$$\epsilon_0(k) = \epsilon_0(n\pi/a + \delta)) = \frac{\hbar^2}{2m}\left[(n\pi/a)^2 + 2n\pi\delta/a + \delta^2\right]$$

$$\epsilon_0(k') = \epsilon_0(-n\pi/a + \delta) = \frac{\hbar^2}{2m}\left[(n\pi/a)^2 - 2n\pi\delta/a + \delta^2\right]$$

Plugging these into the characteristic equation yields

$$\left(\frac{\hbar^2}{2m}\left[(n\pi/a)^2 + \delta^2\right] - E\right)^2 = \left(\frac{\hbar^2}{2m}2n\pi\delta/a\right)^2 + |V_G|^2$$

From which we obtain

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

If δ is small, then

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

The result of both cases is that we conclude that in the presence of some periodic potential, a gap of size $2|V_G|$ opens at the zone boundary and near the zone boundary this gap is quadratic in δ. See Fig. 7. At the Brillouin zone boundaries, the dispersion is parabolic around the extrema of the bands. We can write

$$E_+(G + \delta) = C_+ + \frac{\hbar^2\delta^2}{2m_+^*}$$

$$E_-(G + \delta) = C_- - \frac{\hbar^2\delta^2}{2m_-^*}$$

which gives us the effective masses

$$m_\pm^* = \frac{m}{\left|1 \pm \frac{\hbar^2(n\pi/a)^2}{m}\frac{1}{|V_G|}\right|}$$

2.2   Higher Dimensions

In two and three dimensions, we observe the following about the nearly free electron model:

- Near the Brillouin zone boundary, a gap opens due to scattering by a reciprocal lattice vector. See Fig. 8.

- States of energy slightly higher than the zone boundary are pushed up, while states of energy slightly lower are pushed down.

- In the one-dimensional case, for k on a zone boundary, there was exactly one k' such that $k' = k + G$ and $\epsilon_{0(k)=\epsilon_0(k')}$. In higher dimensions, there may be multiple k' that may need to be mixed to find the degenerate eigenstates. For example, in 2D, $(\pm\pi/a, \pm\pi/a)$ all have the same energy and are separated by reciprocal lattice vectors.
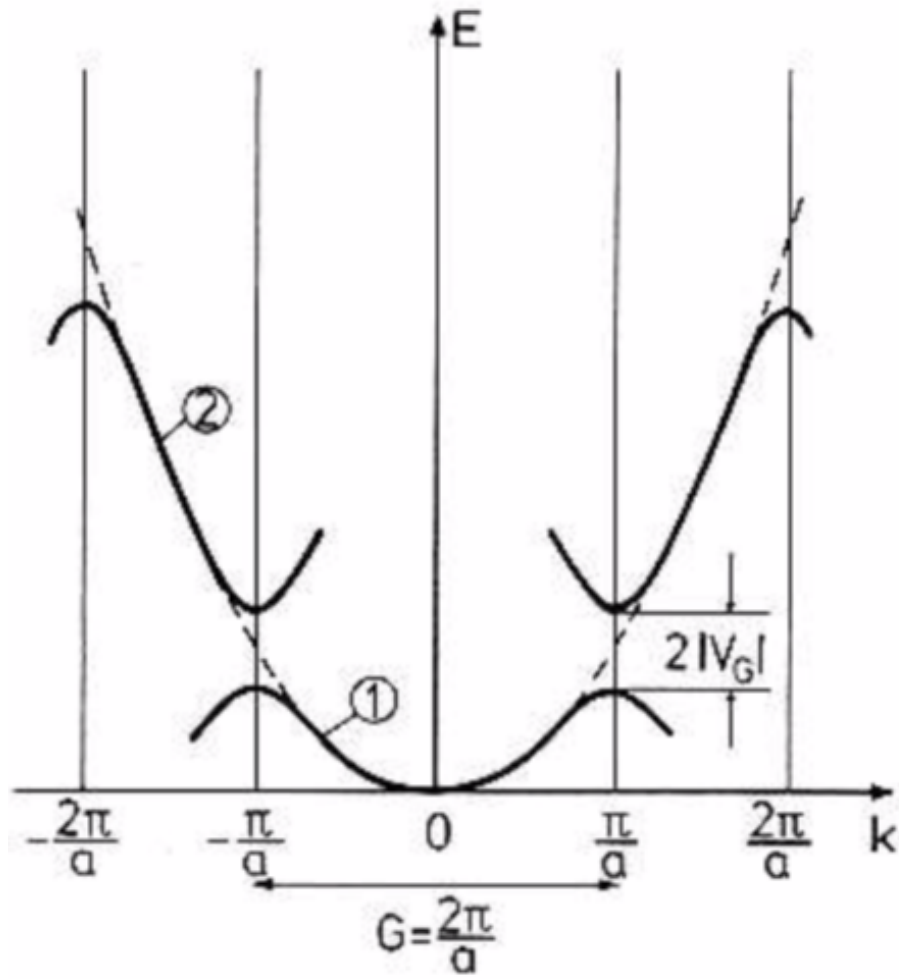
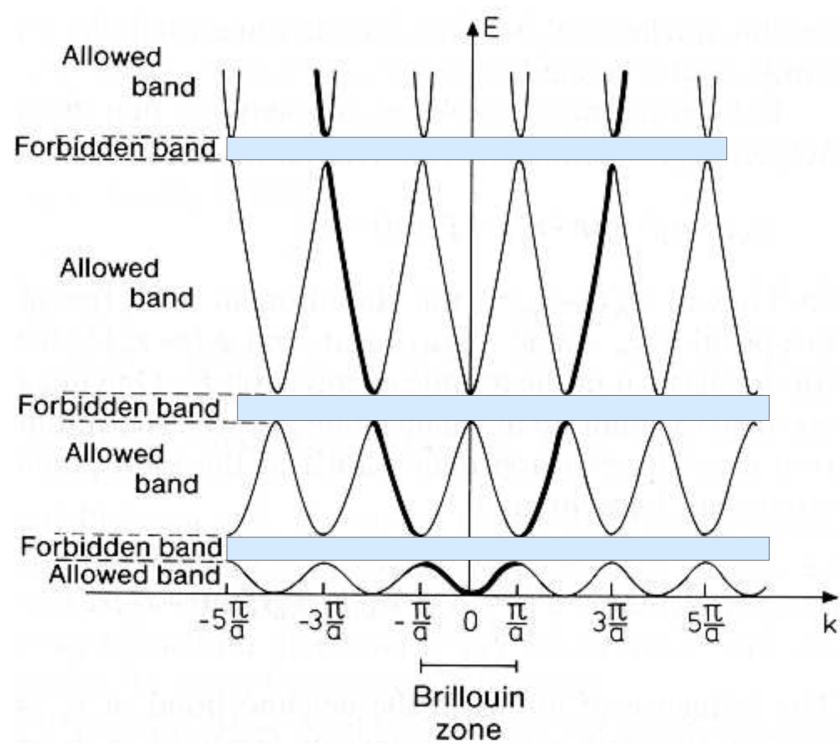Figure 7: Dispersion due to small perturbation in free-electron model.

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Figure 8: Dispersion due to small perturbation in free-electron model.

3 Bloch's Theorem

- How do we know the plane-wave approach to electrons is valid since the periodic potential may be very strong (and therefore, perturbation theory may not be valid)?

- No matter how strong the periodic potential, as long as it is periodic, the crystal momentum is conserved.

- **Bloch's Theorem**: An electron in a periodic potential has eigenstates of the form

$$\Psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}^{\alpha}(\mathbf{r})$$

  where $u_{\mathbf{k}}^{\alpha}$ is periodic in the unit cell and the crystal momentum $\mathbf{k}$ can be chosen within the first Brillouin zone.

- There may be many states at each $\mathbf{k}$ and these are indexed by α.

- The function u is known as the *Bloch function* and Ψ is sometimes called the *modified plane wave*.

- Because u is periodic in the unit cell, we can write

$$u_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{G},\mathbf{k}}^{\alpha}(\mathbf{r})e^{i\mathbf{G}\cdot\mathbf{r}}$$

  which guarantees that $u_{\mathbf{k}}^{\alpha}(\mathbf{r}) = u_{\mathbf{k}}^{\alpha}(\mathbf{r} + \mathbf{R})$.

- The modified plane wave can then be written as

$$\Psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{G},\mathbf{k}}^{\alpha}(\mathbf{r})e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

- The implication: **every eigenstate can be written as a sum of plane waves with differ by reciprocal lattice vectors**.

- The reason for Bloch's theorem is that $\left\langle \mathbf{k}' \middle| V \middle| \mathbf{k} \right\rangle$ is zero unless the Laue condition is fulfilled:

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}$$

- The Schrodinger equation is block-diagonal in $\mathbf{k}$ and only planewaves that differ by $\mathbf{G}$ can be mixed together.

Conclusion: electrons in a periodic potential have eigenstates labeled by the crystal momenta. Even though the potential felt by the electron due to the atomic sites may be very strong, electrons still behave as if they do not see the atoms at all. They almost form plane-wave eigenstates - the only difference if that they are multiplied by a periodic Bloch function u and are functions of the crystal momentum.
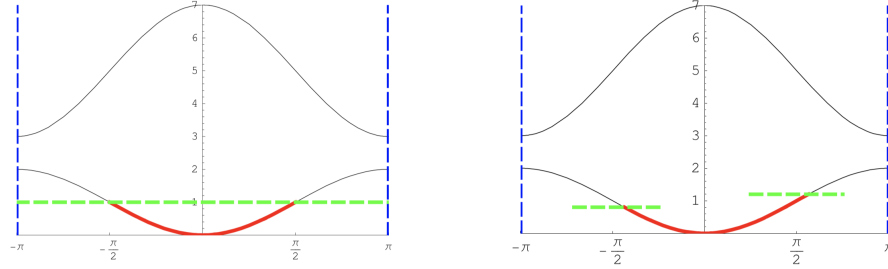
Figure 9: Band diagrams of monovalent 1-D monatomic chain with two orbitals per unit cell. The Fermi surface is shown as a dashed line. When an electric field is applied, the Fermi sea shifts, inducing a current.
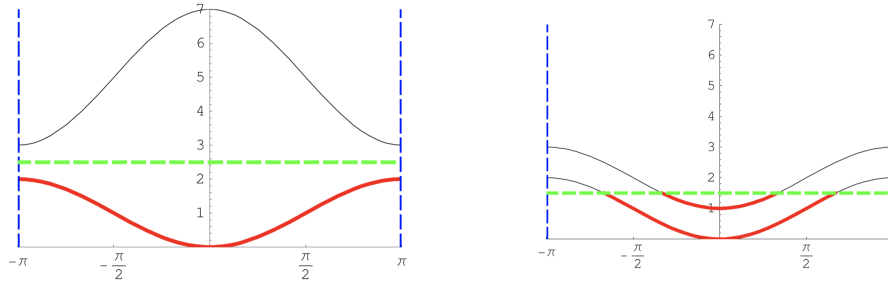

Figure 10: Band diagrams of divalent 1-D monatomic chain with two orbitals per unit cell. The Fermi surface (chemical potential) is shown as a dashed line, within the band gap. On the left, a direct band gap is shown. On the right, a metal is shown - if the higher energy band were to be lifted, an indirect band gap would be obtained.

4   Insulator, Semiconductor, or Metal

4.1   Energy Bands in One Dimension

- The number of permissible k-states in a single Brillouin zone is equal to the number of unit cells (N) in the system.

- One electron per unit cell → 2 electrons fill each of the bottom $N/2$ states, so they band is half full. See Fig. 9.

- If two electrons are donated per unit cell, then the bottom band is completely filled. See Fig. 10.

- The highest occupied band is known as the *valence band*, while the lowest unoccupied band is the *conduction band*.
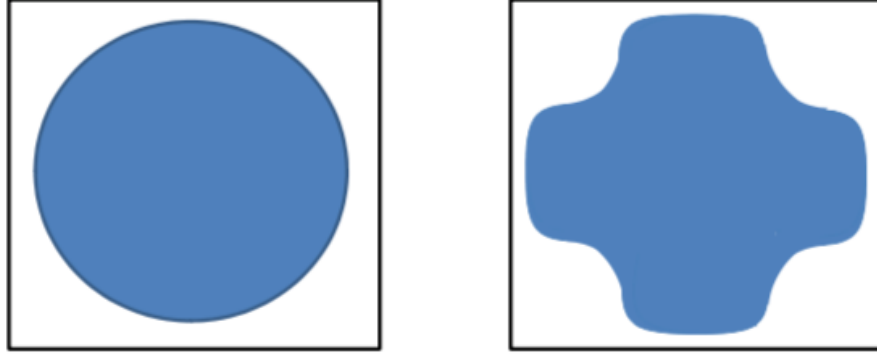
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Figure 11: Two-dimensional Fermi surface of a. free electrons b. weakly periodic potential. The Fermi sea area remains constant.

- In the case of a filled valence band, a sufficiently high electric field is required to excite electrons into the conduction band. Below the required field strength, no movement occurs and the material acts as a *band insulator*.

- If the band gap is $< 4eV$, the material is known as a semiconductor since thermal excitations can push some electrons into the conduction band at room temperature.

- In the case of divalent 1-D monatomic chain, typically we obtain a band insulator, but we may obtain a metal as seen in the right of Fig. 10.

4.2 Energy bands in Two, Three Dimensions

4.2.1 Two Dimensions

Consider a square lattice of monovalent atoms, for which the Brillouin zone is also square.

- One electron per atom $\rightarrow$ half-filled band.

- In the absence of a potential, the free electron have a circular Fermi surface, which will be precisely half the area of the Brillouin zone (Fig. 11 a).

- As a weak periodic potential is added, gaps open at the zone boundaries $\rightarrow$ states close to the boundary decrease in energy. These states become preferential and the Fermi surface deforms as shown in Fig. 11 b.

Consider now a square lattice of divalent atoms, for which the Brillouin zone is also square.
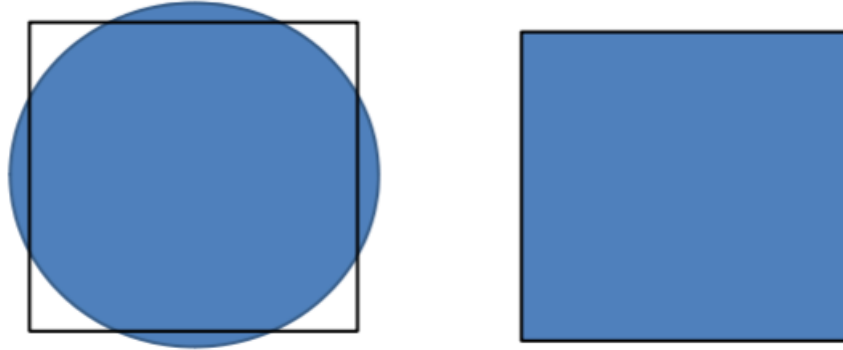
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Figure 12: Two-dimensional Fermi surface of divalent square lattice a. free electron case b. strong periodic potential.

- The free electron fermi surface is still circular, but now the area must be equal to the area of the Brillouin zone (Fig. 12 a).

- As the periodic potential strength is increased, states within the first BZ are lowered in energy and states in the second BZ are raised in energy.

- In the case of a strong periodic potential, the entire lower band becomes filled and the Fermi surface deforms to Fig. 12 b. The behavior is that of an insulator.

- For intermediate strength, some states remain filled in the second band (see Fig 13.). This is equivalent to the 1D case shown in Fig 10b. The behavior is that of a metal.

4.3 Three Dimensions

Consider a 3D material of movalent atoms.

- In the case of a nearly free electron metal (e.g. Potassium), the Fermi surface is almost a perfect sphere of exactly half the volume of the Brillouin zone.

- As the periodic potential gets stronger, the sphere deforms but maintains the same volume.

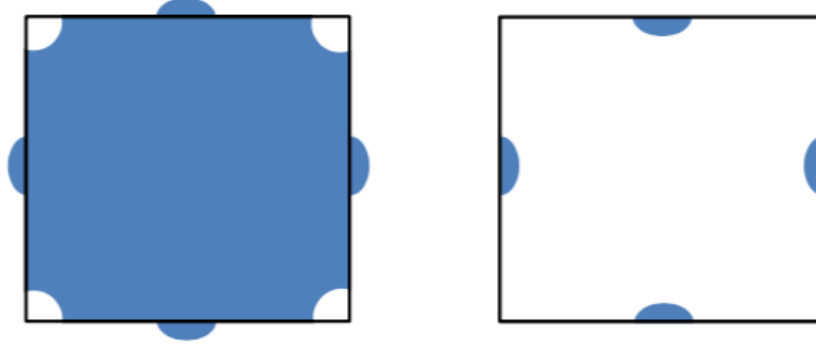- Copper, with a very strong periodic potential, is shown in Fig. 12.

Figure 13: Two-dimensional Fermi surface of divalent square lattice with intermediate periodic potential.

4.4 Tight Binding

- In the tight binding model, we imagine a number of orbitals on each atom (or in a unit cell) and allow them to weakly hop to other orbitals. This spreads the eigen-energies of the atomic orbitals out into bands.

- The one-, two- dimensional Hamiltonians of the tight-binding model are given by

$$H_{nm} = \epsilon_0 \delta_{nm} - t(\delta_{n+1,m} - \delta_{n-1,m}) \tag{5}$$

$$H_{nm} = \epsilon_0 \delta_{n_x m_x} \delta_{n_y m_y} - t(\delta_{n_x+1,m_x} \delta_{n_y m_y} + \delta_{n_x m_x} \delta_{n_y+1,m_y}$$
$$- \delta_{n_x-1,m_x} \delta_{n_y m_y} - \delta_{n_x m_x} \delta_{n_y-1,m_y}) \tag{6}$$

- The 2D solution is

$$E(k) = \epsilon_0 - 2t \cos(k_x a) - 2t \cos(k_y a)$$

- Increasing the number of orbitals increases the accuracy of the solution.

- If the unit cell is divalent, it is important to determine whether bands overlap. If atomic orbitals are sufficiently far apart in energy, small hopping between atoms cannot spread the bands enough to make them overlap.

- In the free electron picture, the gap is proportional to $|V_G|$ - the limit of strong periodic potential guarantees that the bands do not overlap.

4.5 Failures of Band Representation

- We have developed a picture now where the structure and filling of bands determines their properties: insulator, conductor, or semiconductor.
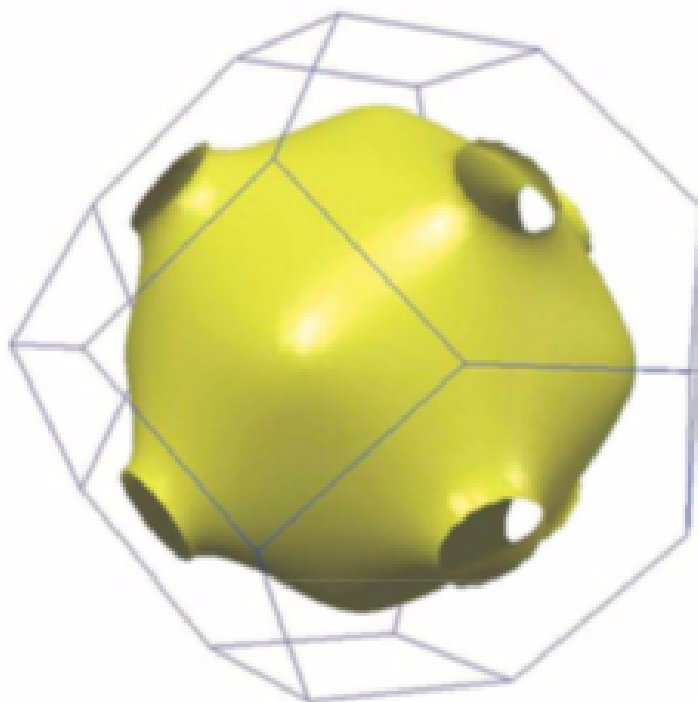
Figure 14: Three-dimensional Fermi surface of monovalent Copper, fcc with a strong periodic potential.

- One important effect has been neglected: Coulomb repulsion between electrons, which can be on the order of several eV.

- It is justifiable to neglect this interaction, but there are cases where the non-interacting picture fails.

- *Magnets*: In ferromagnetism, spins spontaneously align due to interaction effects. Aligning all spins can lower the Coulomb energy between electrons and therefore may be more favorable than filling lowest-energy k-states with both spin states.

- *Mott insulators*: when the coulomb interaction is so strong, that there is a huge penalty to electrons sitting at the same atom site (even if they have different spins). The result is a single electron per site, and the inability for electrons to move from site to site (like a traffic jam).

4.6 Band Structure and Optical Properties

4.6.1 Optical Properties of Insulators and Semiconductors

- Band insulators cannot absorb photons with energies less than the band-gap energy $\rightarrow$ low-energy photons create no excitations, they just pass through. For example, GaAs does not absorb wavelengths > .9 microns ($1.45eV$).

- If an insulator or wide-band-gap semiconductor has a band gap greater than $3.2eV$, it will appear completely transparent since it cannot absorb any wavelength of visible light. See Fig. 15.

- Semiconductors with smaller bandgaps may only absorb higher energy photons. For example, CdS has a bandgap of $2.6eV$ and absorbs violet and blue light. As a result, it looks reddish.

- Semiconductors with very small bandgaps look black since they absorb all visible light frequencies (e.g. GaAs has a bandgap of $1.45eV$).

4.6.2 Direct and Indirect Transitions

- The band gap size determines the *minimum* energy excitation which must be made in an insulator or semiconductor.

- It also matter at which values of **k** these maximum (valence) and minimum (conduction) energies lie.

- **Direct band gap**: Maximum energy of valence band aligns with minimum energy of conduction band. That is, they have the same **k** value. See Fig 10 a.
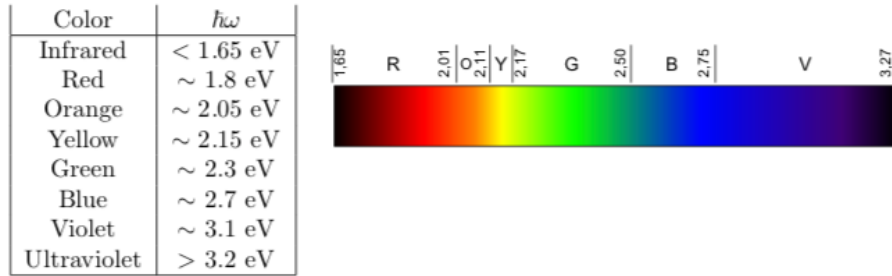
Color	$\hbar\omega$
Infrared	< 1.65 eV
Red	~ 1.8 eV
Orange	~ 2.05 eV
Yellow	~ 2.15 eV
Green	~ 2.3 eV
Blue	~ 2.7 eV
Violet	~ 3.1 eV
Ultraviolet	> 3.2 eV

Figure 15: Energy spectrum of visible light.

- **Indirect band gap**: The values of **k** differ. See Fig 10 b, but imagine that there is a band gap between the bands. In this case, the valence band max is at the zone boundary and the conduction band min is at $k = 0$.

- Both types of gaps can be present. See Fig. 16.

- Indirect band gap transitions are difficult to experience with exposure to light. If a photon is absorbed, both energy and momentum are absorbed. Given an energy E in the eV range, the photon momentum $\hbar|k| = E/c$ is very small.

4.6.3   Optical Properties of Metals

- Since metals are very conductive, photons easily excite electrons which then re-emit light $\rightarrow$ metals look shiny.

- Silver looks brighter than gold or copper because, even though all are monovalent, the energy width of silver's conduction band is greater (i.e. t is large for silver) so higher-energy electronic transitions are much more possible.

- Copper and gold do not absorb blue and violet well (and therefore not re-emitted frequently). For silver, all visible colors and re-emitted well.

4.7   Important Conclusions and Summary
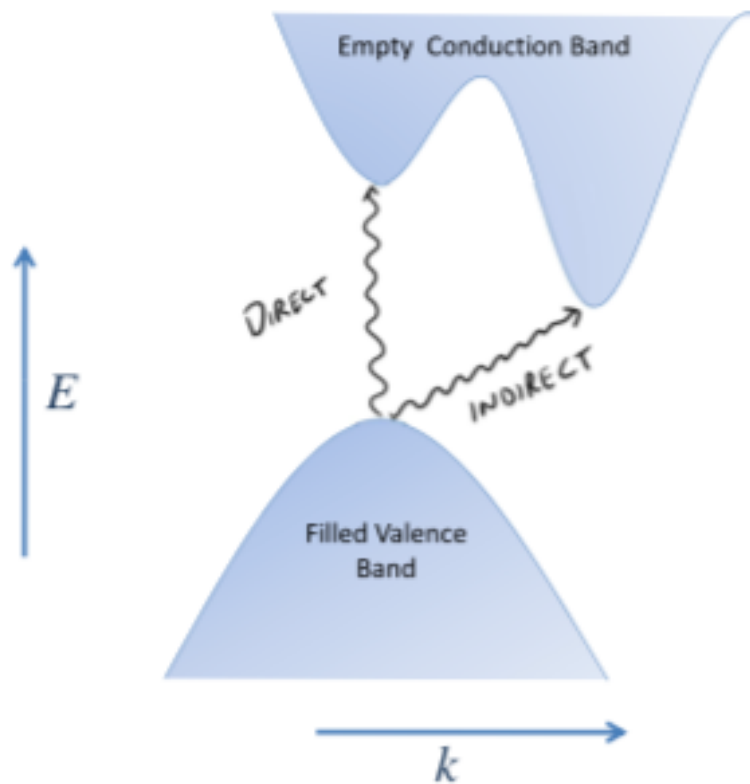
To do: Chapters 16, 23, 17

Figure 16: Direct and indirect band gaps. While the indirect transition is lower energy, it is hard for a photon to excite an electron across an indirect band gap because photons carry very little momentum (since the speed of light, c, is large)