

Chapter 2 Preliminaries and revision

2.1 The electromagnetic spectrum: magnitudes and units

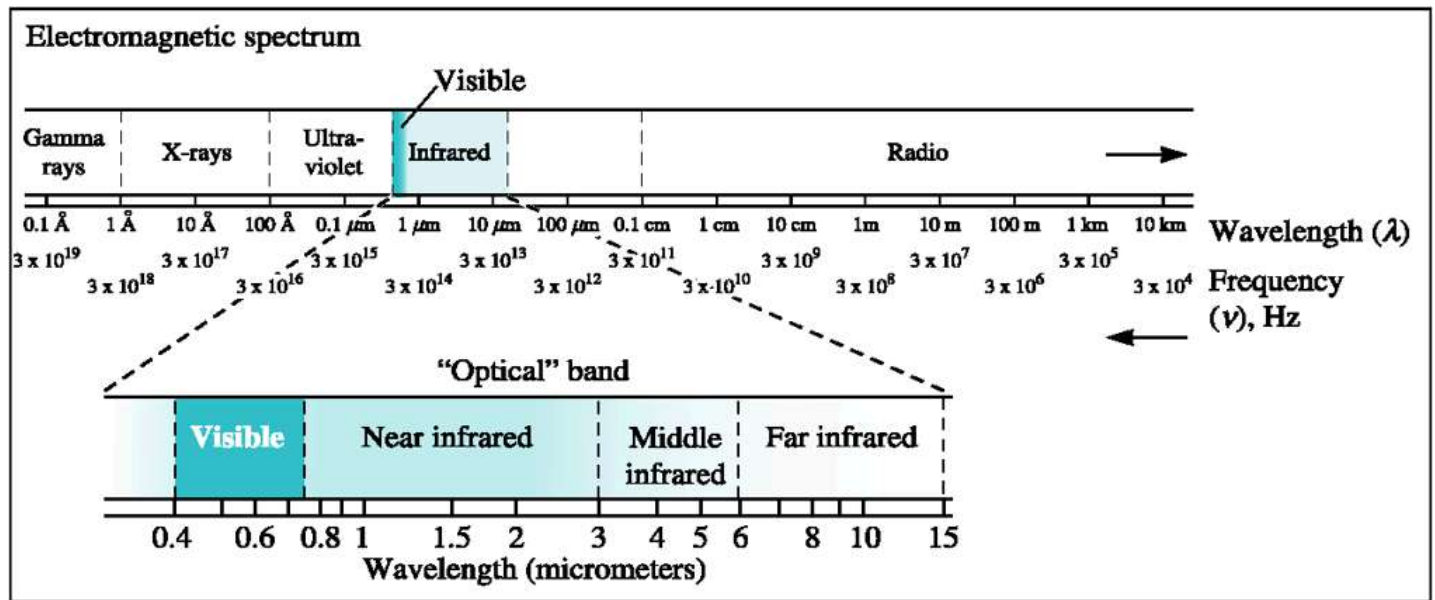


Figure 2.1: The electromagnetic spectrum. ●

Some of this course will use real, published data and one needs to be agile in changing units.

- $1 \text{ eV} = 8065 \text{ cm}^{-1} = 2.418 \times 10^{14} \text{ Hz}$.
- 1 eV corresponds to a wavelength of 1.24 \mu m
- 1 cm^{-1} (one wavenumber) $= 2.998 \times 10^{10} \text{ Hz}$.
- Visible light has energies of around 2 eV , as shown in Fig.2.1.

2.2 Dispersion relations

Dispersion relations (graphs of energy E or frequency ω versus wavevector k) are maps of particle behaviour and also indicate whether and how one type of particle could interact with another, because each point on a curve represents a state with a specific energy and momentum.

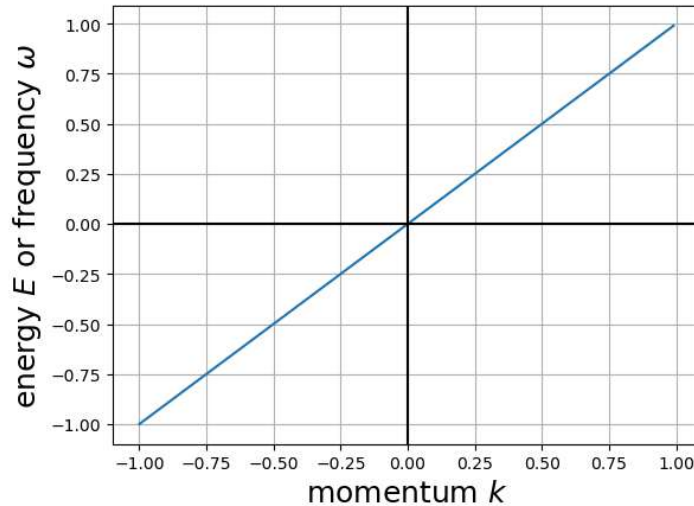


Figure 2.2: Dispersion curve for massless particle

Fig. 2.2 shows the *dispersion relation* for a massless particle such as a photon ($\omega = ck$, so that the slope of the curve ($\partial\omega/\partial k$) is related to the particle (group) velocity).

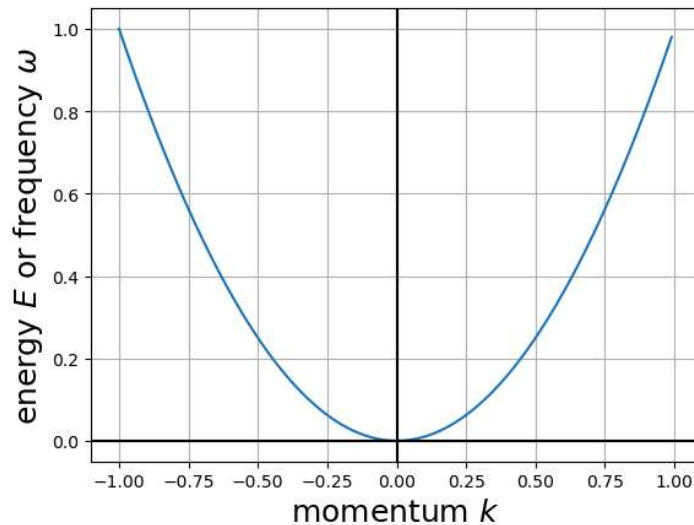


Figure 2.3: Dispersion curve for particle with mass

Fig. 2.3 shows the dispersion relation for a particle with mass. Since $E = \hbar^2 k^2 / 2m$, the curvature ($\partial^2 E / \partial k^2$) is obviously related to the effective mass m^* of the particle (PH22006 Electrons in Periodic Potentials), a result which still has meaning even where the dispersion is not parabolic.

$$1/m^* = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \quad (2.1)$$

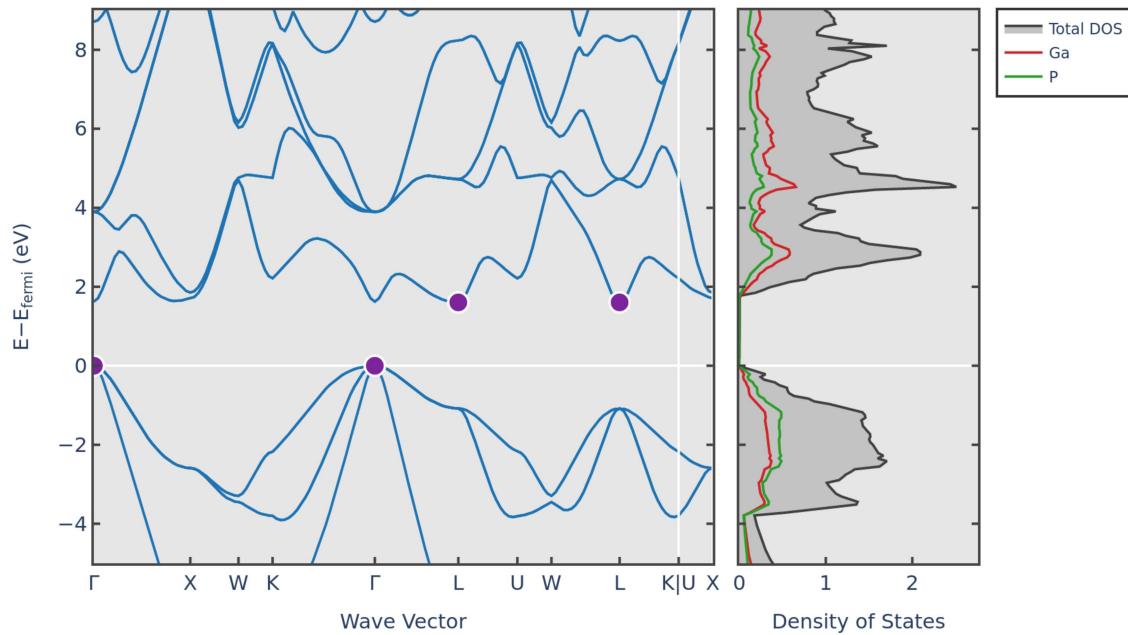


Figure 2.4: Left: electronic band structure; Right: density of electron states in energy for gallium phosphide. ●

Fig. 2.4 shows a calculated dispersion relation (“*band structure*”) for electrons in the cubic crystalline material gallium phosphide (GaP; red LEDs are based on this material). Fig. 2.5 shows a calculated dispersion relation for *phonons* in gallium phosphide.

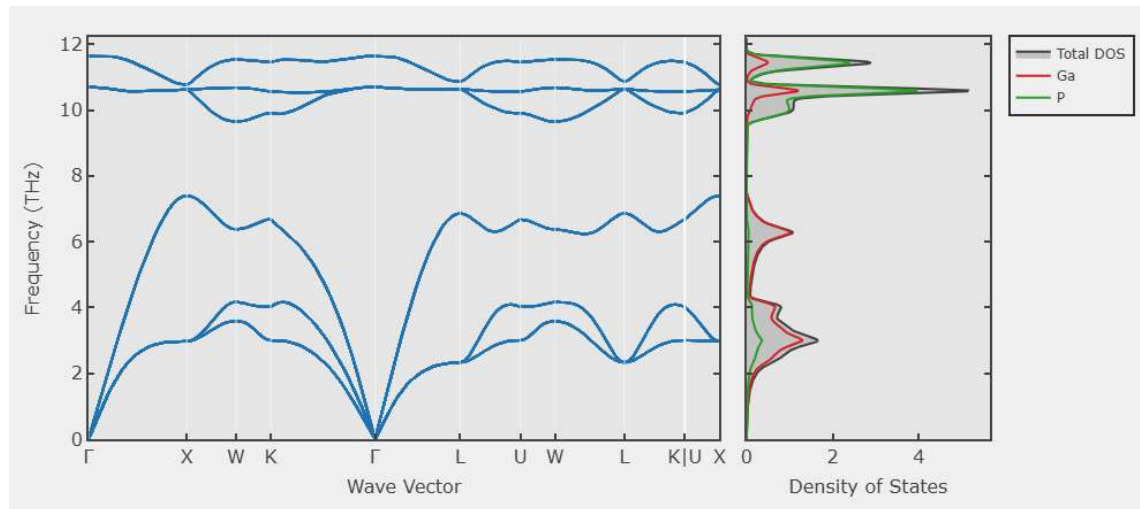


Figure 2.5: Left: phonon band structure; Right: phonon density of states in energy for gallium phosphide. ●

Different regions of these two dispersion curves tell us different things about the material GaP: you should be able to identify that GaP is a semiconductor, deduce its electron and hole effective masses, its speeds of sound, and the lowest photon energy at which it starts to absorb or emit light. One can also infer from Fig. 2.5 that GaP has two atoms per unit cell and that they are different chemical species. These band structure diagrams are clearly more complex than Fig. 2.2 or Fig. 2.3, telling us to expect rich physical phenomena from quantum states in condensed matter (compared to particles in vacuum).

As a demonstration of how new physics can arise, imagine a photon propagating through GaP. Notice from Fig. 2.5 that the LO and TO phonons, which have an electric dipole moment and can interact with light, are close to dispersionless (i.e, near to flat lines) at the Brillouin zone centre (conventionally labelled Γ , meaning $k = 0$). We can represent them near Γ on the following figure, Fig. 2.6 as horizontal red dashed lines (one hidden behind the horizontal black line!). We can represent the photon as a point on the steep dashed red line $\omega = vk$ (slope $v = c/n$). Because the photon and phonon interact, a new set of dispersion curves indicated by the solid black lines is observed where the original curves would have crossed: new *quasiparticles* are formed which are not photons or phonons, but somewhere in between; these are called *polaritons*. Far from the crossing point, light-like and phonon-like behaviour is recovered.

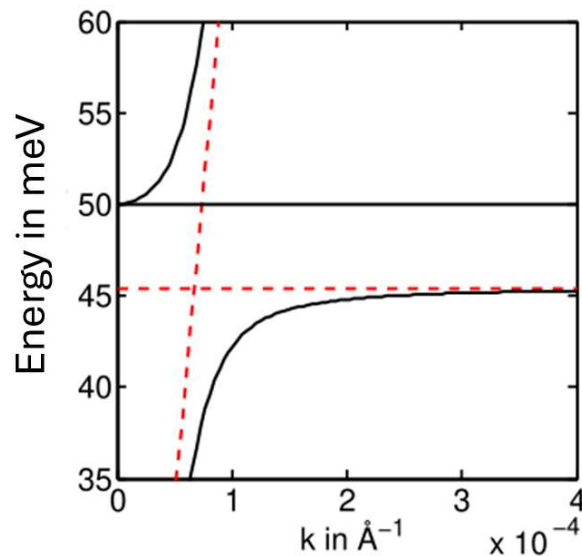


Figure 2.6: From wikipedia: the dispersion curve of polaritons in GaP.

Note that the crossing point of the dispersion curves of two excitations is special because it is the point where an interaction between them conserves energy and momentum. This is generally true, of course, not just in condensed matter physics.

2.3 Band structure: nearly-free electron theory

We start with a reminder of energy band theory in crystalline solids (PH22006 Foundations of Physics: Condensed Matter Physics) as this will be the foundation of our understanding of the electronic and optical properties of matter. Many of the ideas and models we will develop will turn out to be relevant also to molecular materials and to non-crystalline materials (glasses and soft matter). The following quotes directly from the lecture notes for PH22006, but we can now take advantage of a knowledge of quantum mechanics and perturbation theory. The results that we will obtain should be familiar (revision) but the route to them will be more formal than previously.

Diffraction of an electron wave with wavevector k by a periodic crystal results in additional waves each with wavevectors $k + g$, where g is a reciprocal lattice vector and g (in 1D) satisfies the condition $g \cdot a = 2\pi h$ (h is an integer). If the electron experiences a constant potential (which we can define to be zero in the absence of boundaries), the wavefunction $\psi_k^0(r)$ is a plane wave. We'll write the 3D version:

$$\psi_k^0(r) = \frac{1}{\sqrt{\text{vol.}}} e^{ik \cdot r}. \quad (2.2)$$

If a periodic crystal potential $V(r)$ is present, diffraction means that the wavefunction becomes

$$\psi_k(r) = \sum_g c_{k+g} e^{i(k+g) \cdot r}, \quad (2.3)$$

where c_{k+g} are a set of constants that have to be found. This leads directly to the Bloch form for the wavefunction, where $u(r)$ is a function that has the lattice periodicity (i.e, is the same in every unit cell):

$$\psi_k(r) = e^{ik \cdot r} u_k(r). \quad (2.4)$$

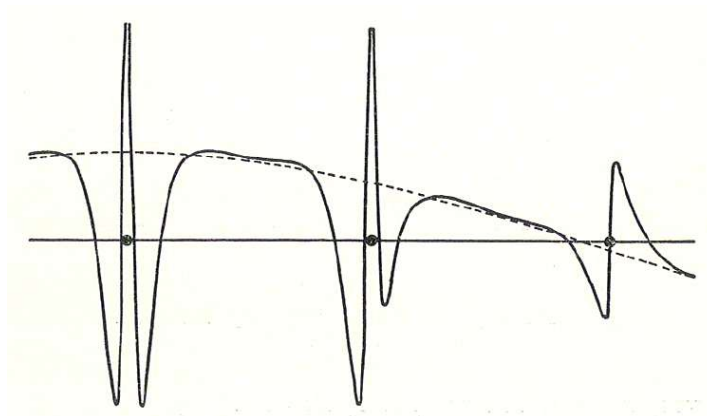


Figure 2.7: Wavefunction (solid line) consisting of a plane wave (dotted line) multiplying a cell-periodic function.

It was proved in PH22006 that $E(k) = E(k + g)$, which implies that the energy bands are periodic in g and energy band diagrams (dispersion relations) only need to be plotted over a limited G range, as was done in Fig. 2.4 for GaP. Of course GaP is a 3D crystal and so bands for a path through reciprocal space covering a set of G vectors in different directions have been plotted; different directions are not equivalent.

2.4 Perturbation theory for the shape of the bands

A plane wave electron state in **free space** with momentum k , energy E_k^0 and wavefunction $\psi_k^0(r) = |0, k\rangle$, is the solution of the Hamiltonian (expressed here in two forms):

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi_k^0(r) &= E_k^0 \psi_k^0(r) \\ H_0 |0, k\rangle &= E_k^0 |0, k\rangle. \end{aligned} \quad (2.5)$$

In the presence of a crystal potential $V(r)$ (often written more generally as a correction H_1 to the Hamiltonian), then the Schrodinger equation is as follows, and has new solutions $\psi_k(r) = |k\rangle$ which will have the form of Eq. (2.4):

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi_k(r) + V(r) \phi_k(r) &= E_k \psi_k(r) \\ (H_0 + V(r)) |k\rangle &= E_k |k\rangle. \end{aligned} \quad (2.6)$$

From standard non-degenerate perturbation theory (PH22006; valid except where the bands meet at the Brillouin zone boundary), we can quote the expression for the new energy E_k to second order:

$$E_k = E_k^0 + \langle 0, k | V(r) | 0, k \rangle + \sum_{k'} \frac{|\langle 0, k | V(r) | 0, k' \rangle|^2}{E_k^0 - E_{k'}^0} \quad (2.7)$$

This general result will be proved if required - the proof is not examinable in this course.

The first term on the right of Eq. (2.7) is the original energy as a function of k and the second term is a constant shift in energy (independent of k ; let's call it V_0), so only the third term gives us the change in the *shape* of the bands. To understand how to calculate $\langle 0, k | V(r) | 0, k' \rangle$, it is

helpful to expand the potential as a Fourier series in g (note that, since $V(r)$ is periodic, we only require a Fourier *series*, and not an FT).

$$V(r) = \sum_g V_g e^{ig \cdot r} \quad (2.8)$$

where

$$V_g = \int V(r) e^{-ig \cdot r} dr^3. \quad (2.9)$$

Then we can write out $\langle 0, k | V(r) | 0, k' \rangle$ in full:

$$\langle 0, k | V(r) | 0, k' \rangle = \frac{1}{vol.} \int e^{-ik \cdot r} \left(\sum_g V_g e^{ig \cdot r} \right) e^{ik' \cdot r} dr^3 \quad (2.10)$$

For each value of g , Eq. (2.10) makes it clear that the integral is non-zero only if $-k + g + k' = 0$ or $k' = k - g$, so that we can simplify the above as

$$E_k = E_k^0 + V_0 + \sum_g \frac{|V_g|^2}{E_k^0 - E_{k-g}^0} \quad (2.11)$$

which shows us that the shape of the bands is determined by the Fourier components of the potential. Notice the sign of the denominator: if $|0, k\rangle$ is the lower energy state, it goes down in energy, and if it is the higher energy state, it goes up. It is common to describe this as bands ‘repelling’ each other and gives an insight into why a gap might open up at $k = g/2$.

However, degenerate perturbation theory is needed to find the size of the band gap (because at the Brillouin zone edge, where $k = g/2$, the denominator of Eq. (2.11) goes to zero). This is straightforward but not in the remit of this course (see Kittel, section 1.1); if just one Fourier component G is taken into account, the band gap would be found to be $E_g = 2V_G$.

2.5 The Fermi energy

Each band can hold $2N$ electrons where N is the number of primitive unit cells. Important electrons are the valence electrons i.e. those in outermost atomic shells that determine chemical properties. Bands are filled up to the Fermi energy, E_F , at low temperature.

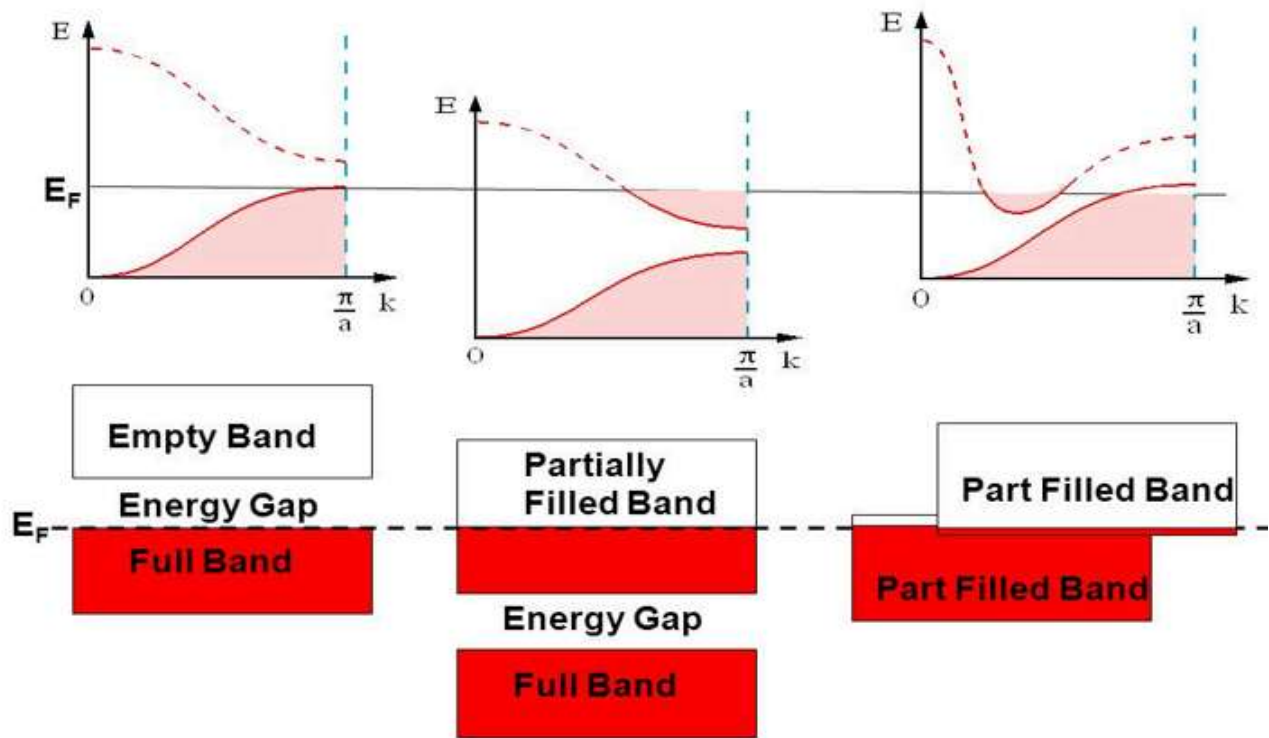


Figure 2.8: Band structure of (left) a semiconductor, (centre) a metal, and (right) a metal with partially-filled bands. •

The position of the Fermi level E_F relative to the band edges determines whether solids are metals or insulators/semiconductors, as shown in Fig. 2.8. If E_F is below top of a band then electrons can easily be excited to empty states above E_F by an electric field – the material will be a good conductor. If E_F is at the top of a filled band then significant energy is needed to excite electrons to the next band– this makes a poor conductor.

Let's revisit a couple of the figures describing this from PH22006:

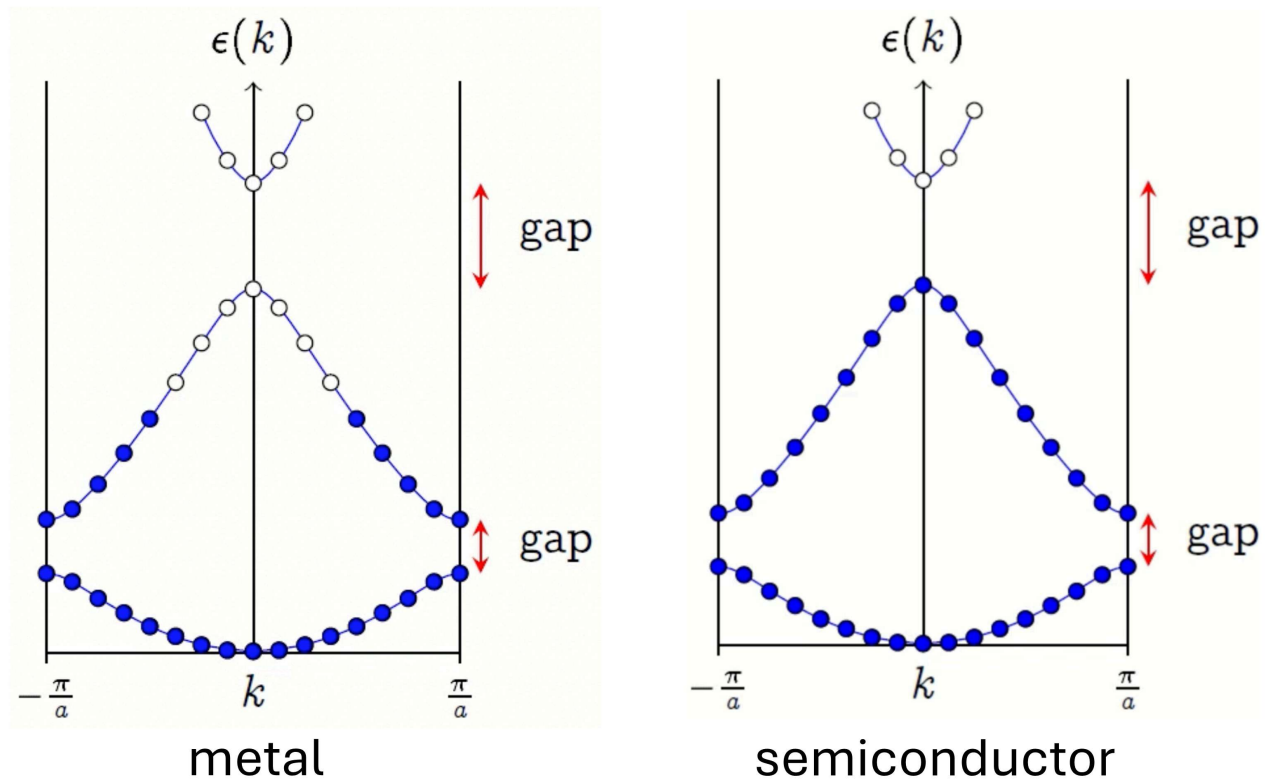


Figure 2.9: Band structure of (left) a metal, and (right) a semiconductor, showing the filling of the bands. •

2.6 Conductivity and mobility

There is nothing really new here, but for completeness we'll include some revision of Drude theory needed later in this unit.

Given an electron dispersion curve (band structure) $E(k)$, we can write the electron velocity v_e as

$$v_e(k) = \frac{1}{\hbar} \nabla_k E(k) \quad (2.12)$$

In the case of parabolic bands with effective mass m^* , for example, this gives $v_e = \hbar k / m^*$.

We can then write an *electron current density* j_e in terms of v_e as $j_e = -nev_e$ where n is the free electron density. In a macroscopic sample of cross-sectional area A normal to j , the current I is given by $I = Aj_e$.

A general equation of motion for an electron with scattering (mean free) time τ is

$$m^* \frac{dv_e}{dt} = -e(\mathcal{E} + v_e \times B) - \frac{m^* v_e}{\tau} \quad (2.13)$$

For a steady current flowing under the action of a constant field \mathcal{E} (so $d/dt \rightarrow 0$) and $B = 0$, we obtain $v_e = -e\mathcal{E}\tau/m^*$. Thus, $j = ne^2\tau/m^* \times \mathcal{E}$ (which is a version of **Ohm's Law**) and we can define the *conductivity* σ as the constant of proportionality between field and current,

$$\sigma = \frac{ne^2\tau}{m^*} = ne\mu, \quad (2.14)$$

where we have also introduced the electron *mobility* $\mu_e = e\tau/m^*$. We will link σ to optical properties later.

If holes and electrons are both present, the total current is additive: $j = j_e + j_h$ and therefore so is the conductivity. In general, holes and electrons will have different masses and scattering rates.