Swimming in the Fermi sea II

- The Fermi-Dirac distribution function $f_{\mathrm{FD}}(E)$ tells us how we populate *available* states. To get the actual energy distribution of electrons, we must consider the availability of states $g(E)$ as well, because $n(E) = g(E)f(E)$.
- Let's consider just those electrons that are free to move around: the valence electrons.
- If we consider quantum states up to some limit in the principal quantum number n, the number of states N can be found from a sphere of states with $n < n_{\mathrm{max}}$ in (n_x, n_y, n_z) space as we've done before:

$$
\begin{aligned}
N &= (\text{\# spins}) \cdot (\text{octant of sphere with } n > 0) \cdot (\text{sphere of } n \text{ with } E < E_F) \\
&= 2 \cdot \frac{1}{8} \cdot \frac{4}{3}\pi n_{\mathrm{max}}^3 = \frac{\pi}{3} n_{\mathrm{max}}^3 .
\end{aligned}
$$

Swimming in the Fermi sea III

- Again, the total number of states N is related to the maximum state index $n_{\rm max}$ according to $N = \frac{\pi}{3} n_{\rm max}^3$.
- Consider a metal cube of volume L^3, which has particle-in-a-box energies $E_n = n_{\rm max}^2 h^2/(8mL^2)$. If we fill all the states up to a certain value of $n_{\rm max}$, we see that this gives us the Fermi energy E_F (Serway Eq. 10.44):

$$E_F = \frac{h^2}{8mL^2} n_{\rm max}^2 = \frac{h^2}{8m}\frac{(3N/\pi)^{2/3}}{V^{2/3}}$$
$$= \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \quad (1)$$
$$= (3.646 \times 10^{-19}\ \text{eV} \cdot \text{m}^2)\left(\frac{N}{V}\right)^{2/3}$$

where we have used $V = L^3$ to give the volume.

- At low temperature, copper has a valence (free-to-move) electron every 0.23 nm or so (that is, about one per atom), or a free electron density of $N/V = 8.5 \times 10^{28}\ \text{m}^{-3}$ from which one obtains a Fermi energy of $E_F = 7.0$ eV.

Swimming in the Fermi sea IV

- Let's rearrange the Fermi energy expression into an expression for the number of occupied states:

$$E_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad \rightarrow \qquad N = \frac{\pi V}{3}\left(\frac{8mE_F}{h^2}\right)^{3/2}$$

- The rate at which states become available as energy is added to the system is just the derivative of the inverse of the Fermi energy expression of Eq. 1 (like Krane Eq. 10.35, or Serway 10.39):

$$\begin{aligned} g(E) &= \frac{dN}{dE} = \frac{\pi V}{2}\left(\frac{8m}{h^2}\right)^{3/2} E^{1/2} \\ &= \frac{N}{\frac{\pi V}{3}\left(\frac{8mE_F}{h^2}\right)^{3/2}} \frac{\pi V}{2}\left(\frac{8m}{h^2}\right)^{3/2} E^{1/2} \\ &= \frac{3}{2}\frac{N}{E_F^{3/2}}\sqrt{E} \end{aligned}$$

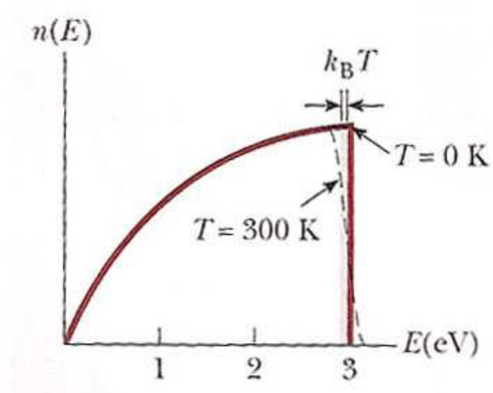
Swimming in the Fermi sea V

Putting the density of available states $g(E)$ together with the probability of occupying available states $f_{\mathrm{FD}}(E)$, we have the Fermi-Dirac distribution function for electron occupancy $n(E)$ (compare with Krane Eq. 10.36, or Serway Eq. 10.41):

$$
\begin{aligned}
n(E) &= \frac{\pi V}{2}\left(\frac{8m}{h^2}\right)^{3/2} \frac{\sqrt{E}}{\exp[(E-E_F)/(k_B T)]+1} \\
&= \frac{3}{2}\frac{N}{E_F^{3/2}} \frac{\sqrt{E}}{\exp[(E-E_F)/(k_B T)]+1}.
\end{aligned}
$$

This function is plotted in Serway Fig. 10-12. It reaches a maximum near the point when $E = E_F$, in which case $n(E) \rightarrow (3N)/(2E_{F0})$.

Figure 10.12 The number of electrons per unit volume with energy between E and $E + dE$. Note that $n(E) = g(E) f_{\mathrm{FD}}(E)$.



Average energy of an electron?

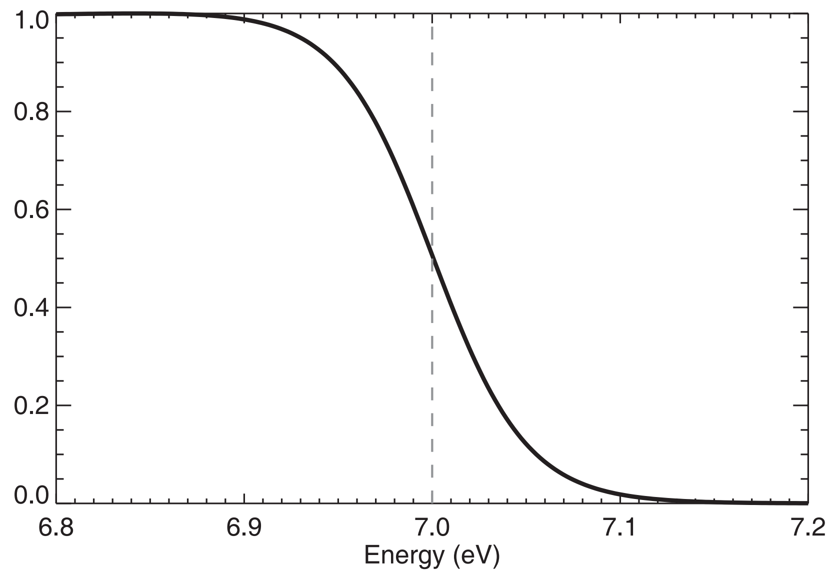
What's the average energy of an electron? We can use our usual approach to find it:

$$\langle E \rangle = \frac{1}{N} \int_0^\infty E\, n(E)\, dE$$

from which it can be found that $\langle E \rangle = \frac{3}{5} E_F$. That is, even as we approach a temperature of absolute zero the conduction electrons have significant energy!

Floating above the Fermi sea

- In fact the Fermi-Dirac distribution does not make a sudden transition from 1 to 0 at E_F, especially at higher temperatures. Here's a normalized plot of $f_{\mathrm{FD}}(E)$ with $E_F = 7.0$ eV at room temperature:



  What fraction of electrons are above the surface of the Fermi sea?

- Approximate the curve as having a triangular region above the Fermi energy. Height of the triangle h is half the peak height, or $h = \frac{3}{4}\frac{N}{E_F}$.

Floating II

To get the width, we should look at the slope:

$$m = \frac{d}{dE}|_{E=E_F}\, n(E) = \frac{d}{dE}|_{E=E_F}\, \frac{3}{2}\frac{N}{E_F^{3/2}}\, \frac{\sqrt{E}}{\exp[(E-E_F)/(k_BT)]+1}$$

Use Maple: `f[x]:=a*sqrt(x)/(exp((x-x_0)/k)+1);`

```
g[x]:=simplify(diff(f[x],x));    eval(g[x],x=x_0);
```

This gives a slope m of

$$m = -\frac{3}{2}\frac{N}{E_F^{3/2}}\,\frac{E_F - k_BT}{4k_BT\sqrt{E_F}}$$

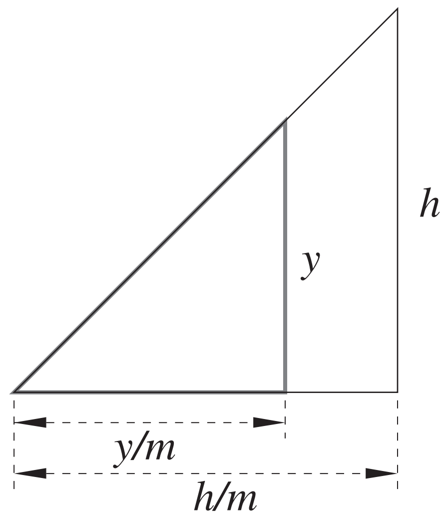
but since $E_F = 7.0$ eV and $k_BT = 1/40$ eV, we can drop the $-k_BT$ in the numerator and write the slope as

$$m \simeq -\frac{3N}{8E_Fk_BT}$$

Floating III

- Now we go from h to 0 with the above slope $-|m|$, which is the same as going from 0 to h with a slope $+|m|$, which happens at an energy $E = h/m$. The area of the triangle is therefore

$$\frac{1}{2}\,h\,\frac{h}{m} = \frac{1}{2}\,\frac{h^2}{m}$$



- We therefore have an approximate result for the number of electrons above the Fermi sea of

$$N_{E>E_F} = \frac{1}{2}\,\frac{h^2}{m} = \frac{1}{2}\,\frac{9}{16}\,\frac{N^2}{E_F^2}\,\frac{8E_F k_B T}{3N} = \frac{3}{4}\,\frac{N k_B T}{E_F}$$

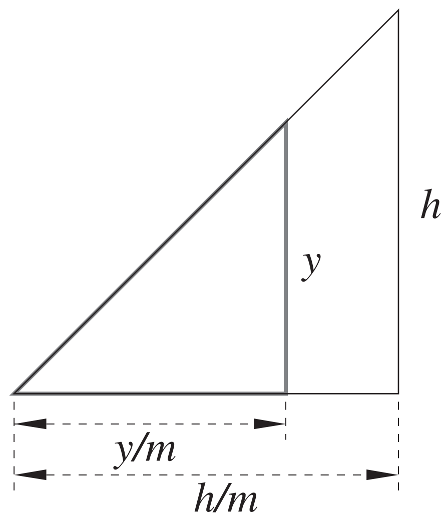
Realize that this is an underestimate.

Floating IV

- Now that we know how many electrons fit in the triangle above the Fermi sea, we need to ask how far we moved them.
- Consider triangles with slopes m. The height of the first one is h, and the height of the second triangle is y. The second triangle has half the area of the first one:

$$\frac{1}{2}\cdot\frac{1}{2}\frac{h^2}{m}=\frac{1}{2}\frac{y^2}{m}\qquad\longrightarrow\qquad h^2=2y^2$$

giving $y=h/\sqrt{2}$.



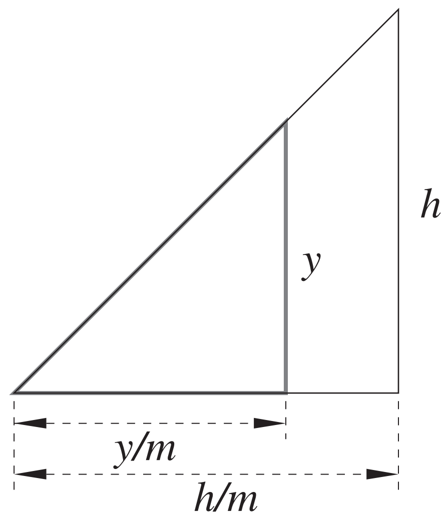
- Now that we know the height of the smaller triangle, we can find its width x from $m=y/x$ or $x=\dfrac{y}{m}=\dfrac{h}{\sqrt{2}m}$

Floating V

- This is the width over from the vertex to the edge of the little triangle. What we really want is the width difference

$$\frac{h}{m} - \frac{h}{\sqrt{2}m} = \frac{h}{m}(1 - 1/\sqrt{2}) = 0.29\frac{h}{m}$$

  which we'll approximate as $h/(3m)$.



- Therefore we have to move electrons from $-h/(3m)$ on the left to $+h/(3m)$ on the right or about $(2/3)(h/m)$ or an energy distance

$$\frac{2}{3}\frac{h}{m} = \frac{2}{3}\frac{\frac{3}{4}\frac{N}{E_F}}{\frac{3N}{8E_F k_B T}} = \frac{4}{3}k_B T$$

Floating VI

- OK, where are we at? We know that the number of electrons swapping triangles is

$$N_{E>E_F} = \frac{3}{4}\frac{Nk_BT}{E_F}$$

- We know that a typical energy change is $\frac{4}{3}k_BT$
- We can then estimate that the heat capacity of the free-electron gas is given by the derivative of number of electrons that change sides, multipled by their energy, or

$$C = \frac{dU}{dT} = \frac{d}{dT}\frac{4}{3}k_BT\frac{3}{4}\frac{Nk_BT}{E_F} = \frac{d}{dT}\frac{Nk_B^2}{E_F}T^2 = 2\frac{Nk_B^2}{E_F}T$$

- The surprising part of this result is that the heat capacity of the valence electrons in a metal goes to zero as the temperature goes to zero!

Final comments

- Again, $C \propto T$ for electrons, so the heat capacity goes to zero as the temperature goes to zero.
- In other words, when we add energy into the system, we very quickly knock some electrons out from the Fermi sea, and once they're out there are a large number of states available to them.
- Since temperature is the inverse of the log of the number of states made available per energy added, we cannot add much heat into the system without quickly affecting its temperature.
- This has consequences for phenomena including superconductivity.

More than one atom

What happens when you bring two atoms near to each other? It depends on the sign of ψ (see Serway Fig. 11.7, 12.17; these figures are from Krane):

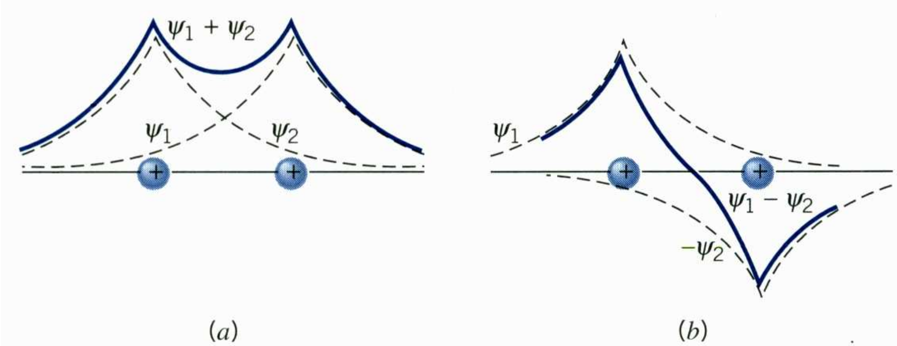


FIGURE 9.2 The overlap of two hydrogenic wave functions. In (*a*), the two wave functions have the same sign, while in (*b*) they have opposite signs.

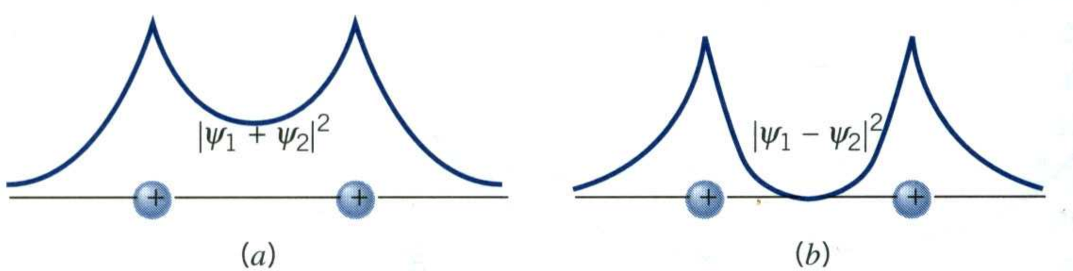


FIGURE 9.3 The probability densities corresponding to the two wave functions of Figure 9.2.

Energy potential for H_2

Energy terms (see Serway Fig. 11.16; thisi figure is from Krane):

- U_P for Coulomb potential between nuclei
- E_+ for $\psi_1 + \psi_2$. In this case the strongest binding is when the two atoms overlap and we have

$$E = -13.6 \text{ eV} \frac{(Z=2)^2}{(n=1)^2} \text{ or -54.4 eV}$$

- E_- for $\psi_1 - \psi_2$. In this case the wavefunction has a zero at small r, which is more like a $2p$ state than a $1s$ state. Therefore the energy goes more like

$$E = -13.6 \text{ eV} \frac{(Z=2)^2}{(n=2)^2} \text{ or -13.6 eV}$$

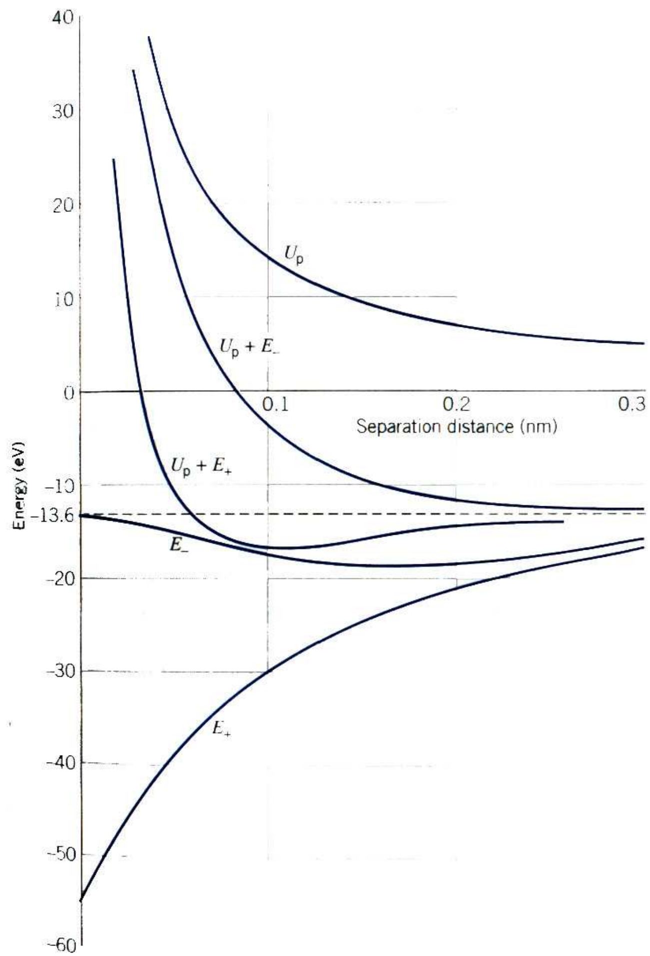


FIGURE 9.4 Dependence of energy on separation distance for H_2.

More than 2 atoms

Go from 2 to 5 to many atoms in close proximity (see Serway Fig. 11.19, 12.16; these figures are from Krane):

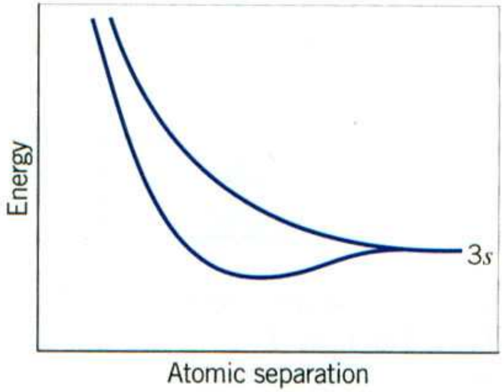


FIGURE 11.13 Splitting of 3*s* levels when two atoms are brought together.

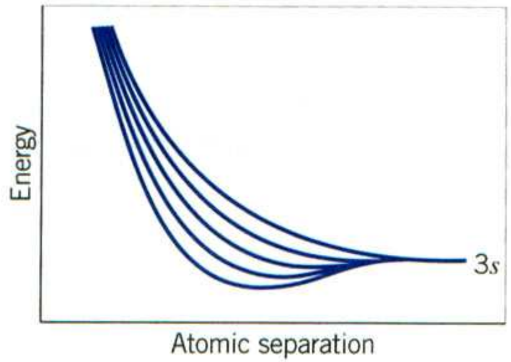


FIGURE 11.14 Splitting of 3*s* levels when five atoms are brought together.

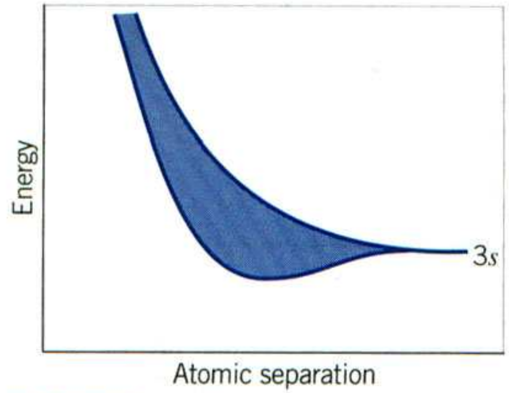


FIGURE 11.15 Formation of 3*s* band by a large number of atoms.

Conclusion: with atoms in a solid we go from energy states to energy bands.

Another way to understand banding

Consider electrons travelling along in a lattice. The relationship between their kinetic energy and wavenumber k is given by

$$E = \frac{p^2}{2m} = \left(\frac{h}{\lambda}\right)^2 \frac{1}{2m} = \left(\frac{h}{2\pi}\frac{2\pi}{\lambda}\right)^2 \frac{1}{2m} = \frac{\left(\hbar k\right)^2}{2m}$$

or $k = \dfrac{\sqrt{2mE}}{\hbar}$ (see Serway Fig. 12.23; this figure is from Krane).

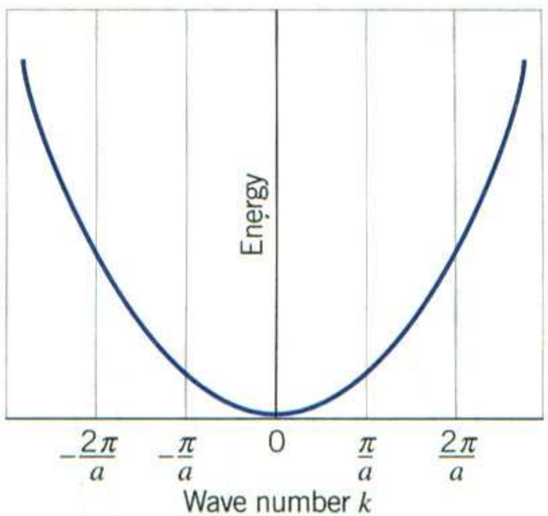


FIGURE 11.25 The parabolic relationship between energy and wave number for a free particle.

Another way to understand banding II

However, at certain values of k we will have strong reflection (and thus no propagation) as given by Bragg's law (see Serway Fig. 12.24):

$$2d\sin\theta = n\lambda \qquad \rightarrow \qquad 2a\sin 90^\circ = n\lambda \qquad \rightarrow \qquad k \equiv \frac{2\pi}{\lambda} = \pi\frac{n}{a}$$

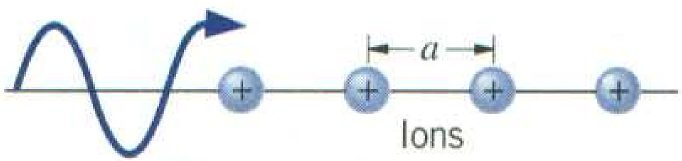


FIGURE 11.24 One-dimensional Bragg scattering. The only possible scattering is a reflection back along the original direction.

Another way to understand banding III

We therefore end up with banding in available energies, where particular values of $k = \pi \frac{n}{a}$ are excluded from the plot of $k = \frac{\sqrt{2mE}}{\hbar}$ (see Serway Fig. 12.25).

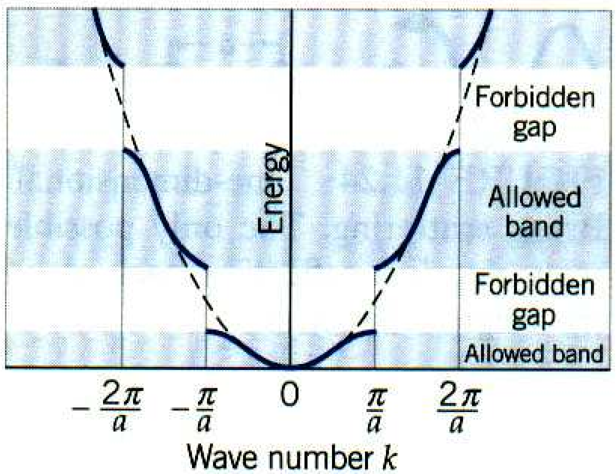


FIGURE 11.27 The relationship between energy and wave number for a one-dimensional lattice. The dashed curve is the free-particle parabola. The solid curves represent waves scattered by the lattice.

Bands and occupancy: a metal

Consider sodium, which is a metal. We fill up states till we reach the Fermi energy (surface of the Fermi sea):

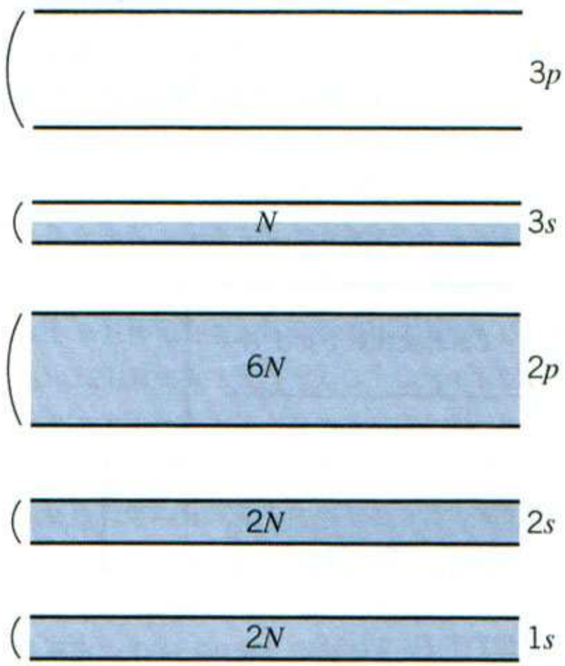


FIGURE 11.16 Energy bands in sodium metal.

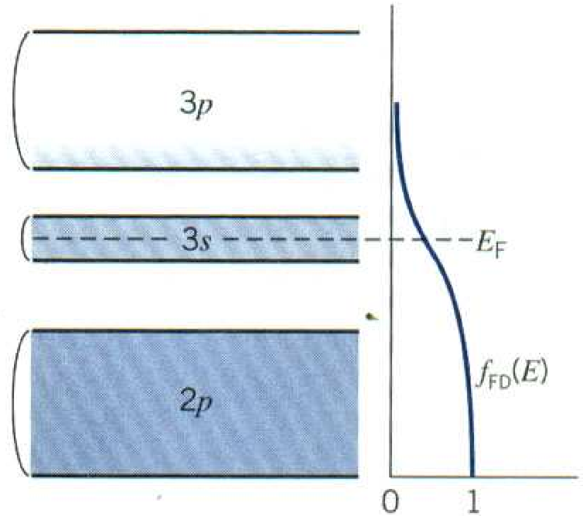


FIGURE 11.18 Population of energy bands in sodium at $T > 0$. The 2p band is no longer completely full and the 3p band is no longer completely empty.

Insulators

Insulators at zero temperature and at finite temperature:

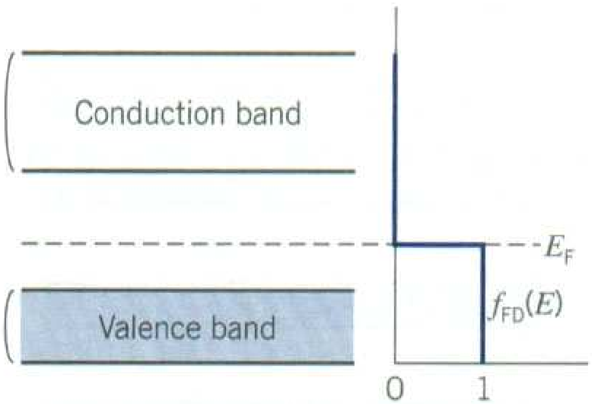


FIGURE 11.19 Band structure in which E_F lies in the gap between bands.

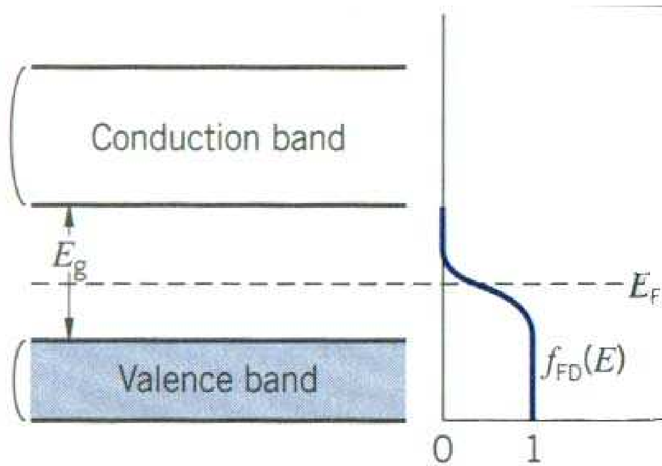


FIGURE 11.20 When $E_g \gg kT$, the conduction band is still unpopulated. This situation is characteristic of an insulator.

When we finally overcome the large energy gap E_g we get electrical breakdown of the material.