PHYSICS 231
Electrons in a Weak Periodic Potential

1 One Dimension

Consider electrons in a weak periodic potential in one-dimension. A state $|k\rangle$ is mixed with states $|k+G\rangle$, where $G = 2\pi n/a$ is reciprocal lattice vector. Here n is an integer and a is the periodicity of the potential, which we take to be unity in what follows. Fig. 1 shows the results of a calculation of the energy in units where $\hbar^2/2m = 1$, so the unperturbed energy is k^2. The first Brillouin zone is $-\pi < k \leq \pi$. For each value of k, we assume that the periodic potential gives a non-zero matrix element (with fixed value 2) between the five states $k, k \pm 2\pi$ and $k \pm 4\pi$. The 5×5 matrix is diagonalized and the eigenvalue closest to the unperturbed value of k^2 is plotted. Fig. 1 is in the extended zone, and the dotted line shows the unperturbed energy. The actual energy follows this quite closely except for gaps at the edges of the Brillouin zones, indicated by the dashed vertical lines in Fig. 1.

Figures 2 and 3 present the same data in the reduced and repeated Brillouin zones. Since the wave vectors k and $k + 2\pi n$ are equivalent, the information in Figures 1 to 3 is the same.

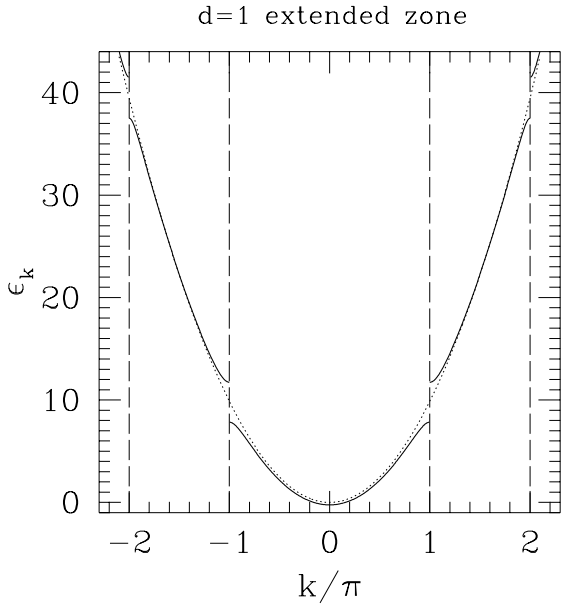

Figure 1: The band structure of a one-dimensional model in the extended zone scheme. The dotted line is the unperturbed energy, $\epsilon_k^0 = k^2$. There are gaps in at the boundaries of the Brillouin zones, $k = \pm n\pi$, in units where the lattice spacing is $a = 1$.

Notice that in this one dimensional model, there is always a gap at the Brillouin zone boundaries, even for an arbitrarily weak potential. As we shall see below, this is not the case in higher dimension where the Brillouin zone boundary is a line (in 2-d) or a surface (in 3-d), rather than just two points as here. (Whether or not an energy gap appears in two or three dimensions depends on the strength of the periodic potential compared with the width of the unperturbed band.)

If Na is the length of the system, then there are N k-values in each band, and hence each band can accommodate $2N$ electrons, the factor of 2 coming from the spin degree of freedom. Since a filled band is inert, this one-dimensional model would always be an *insulator* for two electrons per cell.

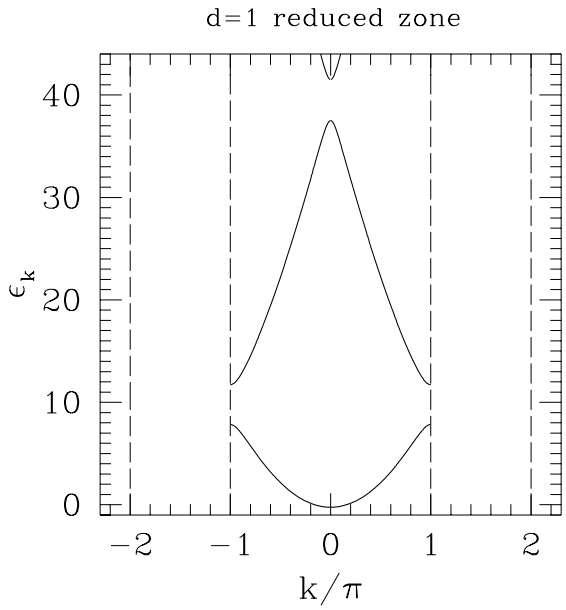

Figure 2: Same as Fig. 1 but in the reduced zone.

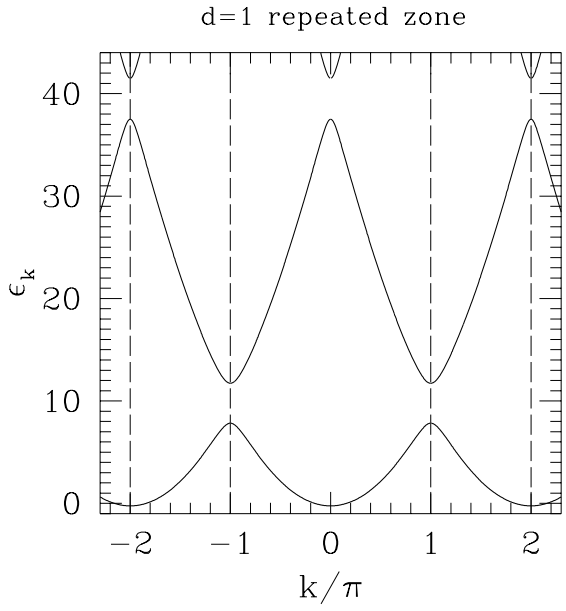

Figure 3: Same as Fig. 1 but in the repeated zone.

2 Two Dimensions

The dispersion relation for a similar calculation on a two-dimensional square lattice is shown in Figs. 4 and 5. In the data for Figure 4, which is along the $\langle 10 \rangle$ direction, the nine states, (k_x, k_y) with $k_x = k, k + 2\pi, k - 2\pi$ and $k_y = 0, 2\pi, -2\pi$, are assumed mixed (by a fixed matrix element of size 1). The unperturbed energy is $\epsilon^0_{\mathbf{k}} = k^2$. In the data for Figure 5, which is along the $\langle 11 \rangle$ direction, the nine states, (k_x, k_y) with $k_x = k, k + 2\pi, k - 2\pi$ and $k_y = k, k + 2\pi, k - 2\pi$, are mixed (again by a matrix element of size 1). The unperturbed energy is $\epsilon^0_{\mathbf{k}} = 2k^2$. In both cases the 9×9 matrix is diagonalized and the energy closest to the unperturbed value is plotted.

One sees that, for the parameters used here, the bottom of the upper band in the $\langle 10 \rangle$ direction lies above the top of the lower band in the $\langle 11 \rangle$ direction. Hence, for two electrons per site, some states at the top of the lower band would be unoccupied, while some states at the bottom of the upper band would be occupied. Hence the system would be a metal. Similar considerations apply in 3-*d*.

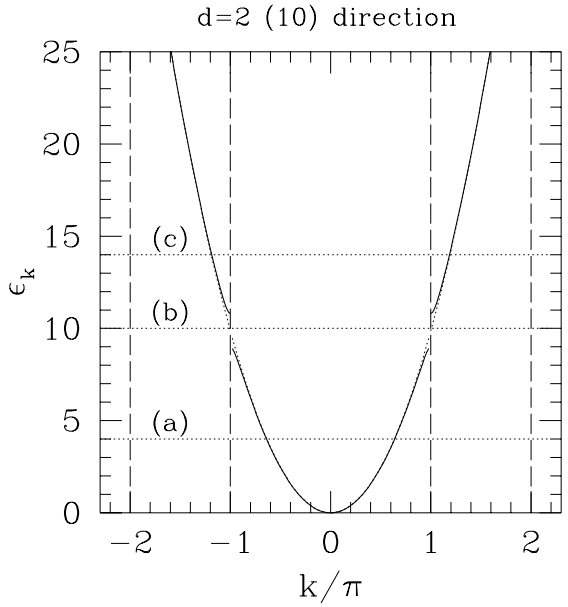

Figure 4: The dispersion relation along the $\langle 10 \rangle$ direction, in the extended zone scheme, for a two-dimensional square lattice with lattice spacing, a, set to unity. A model with a weak periodic potential has been assumed as discussed in the text. The unperturbed energy is $\epsilon^0_{\mathbf{k}} = k^2$. There is a gap at the edge of the Brillouin zone. The lines marked $(a), (b)$ and (c) correspond to the Fermi energies of Figs. 6-8 respectively.

The occupied states and the Fermi surface are shown schematically in Figs. 6-8 for different fillings. Note that with one electron per cell the area of occupied states is half that of the first Brillouin zone, while for two electrons per cell the area of occupied states is equal to that of the Brillouin zone.

In Fig. 6, we assume that the filling is less than unity so all the occupied states have k small compared with the edge of the Brillouin zone and the Fermi surface is roughly circular. The corresponding Fermi energy is indicated by line (a) in Figs. 4 and 5.

For a greater occupancy (a bit less than 2) the Fermi energy (shown by the line (b) in Figs. 4 and 5) lies in the gap for the dispersion relation along the $\langle 10 \rangle$ direction and so the Fermi surface has "necks" which reach out to touch the boundary of the Brillouin zone, see Fig. 7.

For even greater occupancy, the Fermi energy (shown by the line (c) in Figs. 4 and 5 for occupancy

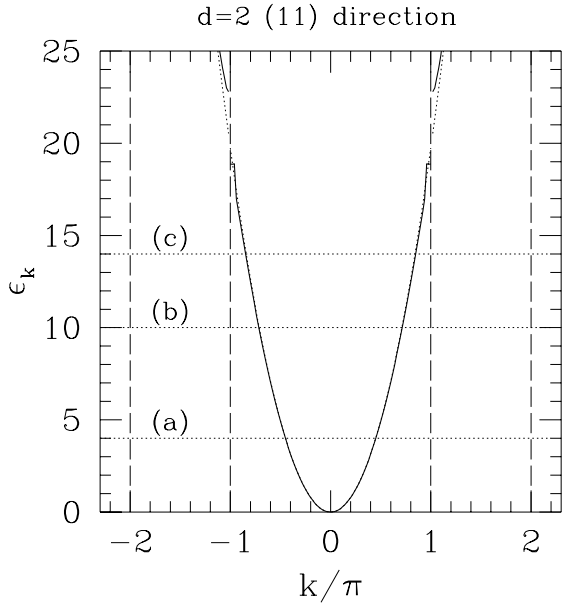

Figure 5: The same as for Fig. 4 but along the $\langle 11 \rangle$ direction. The unperturbed energy is $\epsilon^0_{\mathbf{k}} = 2k^2$. Notice that the top of the lower band here lies *above* the bottom of the upper band in Fig. 4.

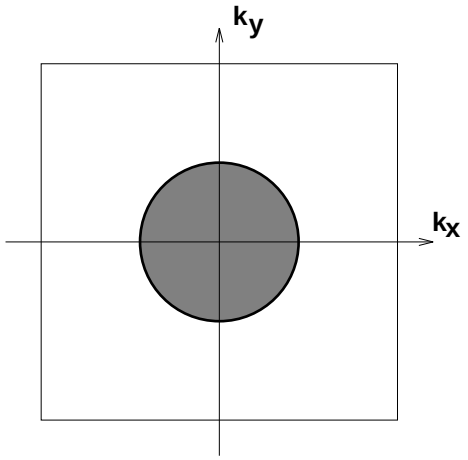

Figure 6: A sketch of the occupied states (shaded region) and Fermi surface for a model of electrons in a weak periodic potential for a two dimensional square lattice. The box indicates the boundary of the first Brillouin zone. The occupancy in this case is less than one electron per cell and the Fermi surface is roughly spherical. The Fermi energy corresponds roughly to that indicated by line (a) in Figs. 4-5.

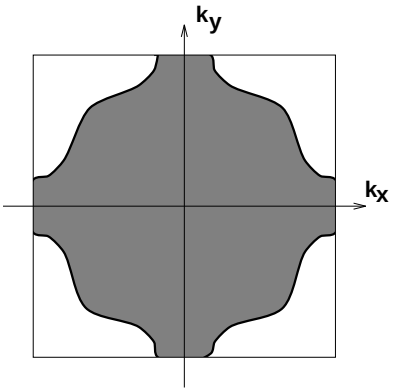

Figure 7: Same as Fig. 6 but for a filling a little less than 2 electrons per site where the Fermi surface forms "necks" which touch the edges of the Brillouin zone. The Fermi energy corresponds to line (b) in Figs. 4-5, *i.e.* it occurs at a gap in the $\langle 10 \rangle$ direction.

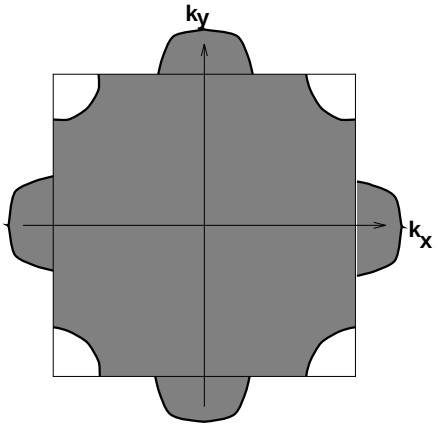

Figure 8: Same as Fig. 7 but for a filling of 2 electrons per site. In addition to some unocuppied states in the first band (near the corners of the zone), there are also some occupied states in the second branch (shown here in the extended zone) near the zone boundary along the $\langle 10 \rangle$ direction. The Fermi energy corresponds to line (c) in Figs. 4-5, *i.e.* it lies in the lower band along the $\langle 11 \rangle$ direction but in the upper band in the $\langle 10 \rangle$ direction.

of 2) is in the lower part of the second band along the $\langle 10 \rangle$ direction but still in the first band along the $\langle 11 \rangle$ direction. Hence the Fermi surface is as shown in Fig. 8.

3 Conclusions

To conclude, we have seen that in two and higher dimensions, a *weak* periodic potential does not necessarily open up an energy gap in general, unlike the situation in one-dimension, though it will open up an energy gap if the periodic potential is big enough. Each band can hold two electrons per cell (the factor of two coming from the spin) so materials with an even number of electrons outside closed shells per unit cell may be either metallic or insulating. For example the elements, Be, Mg, Sr in the second column of the periodic table have one atom per cell (and hence two electrons outside closed shells per unit cell) and are metals. On the other hand, solid hydrogen, which forms a molecular solid H_2 and so has two electrons per cell, is an insulator. It is, however, speculated that solid hydrogen becomes metallic under high pressure (and it is further argued that metallic hydrogen occurs in the core of Jupiter).

By contrast, any material which has an *odd* number of electrons per cell outside closed shells *must*, according to the independent electron approximation, be metallic.[1] For example, the elements, Li, Na, K, Rb and Cs in the first column of the periodic table all have one atom per unit cell (and hence one electron outside closed shells per unit cell) and are metallic. Elements in column 7, *i.e.* F, Cl, Br and I, have an odd number of electrons per atom, but form molecular solids with two atoms per unit cell, and so they have an even number of electrons per cell. Thus it is permissible for them to be insulators as observed.

[1] However, there can be exceptions due to strong Coulomb interactions between electrons which are neglected in the independent electron approximation. These materials, which are called *Mott insulators*, have an odd number of electrons per unit cell and yet are insulators because of strong Coulomb interactions. An example is MnO, for which has one formula unit per unit cell, the Mn has 5 d-electrons and the number of s and p electrons per unit cell is even. Strong correlations among the d-electrons make MnO an insulator and also an *antiferromagnet*.