

P.G. Sem. III.

MPHYCC11

Condensed Matter Physics

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## # Calculations of Energy Bands

~~The~~ Some Methods - the NFE and TB models are discussed for calculating energy bands.

However, these methods - the NFE and TB models - are too crude to be useful in calculations of actual bands which are to be compared with experimental results. Therefore some common methods are employed in calculations of actual bands.

### # The cellular method

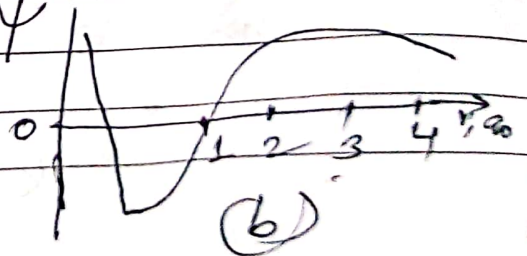
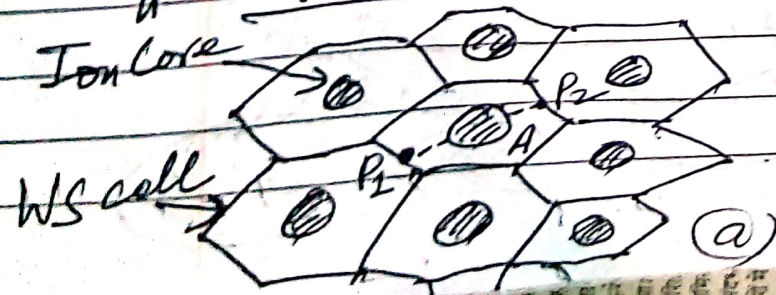


Fig. (1) (a) The WS cell. (b) The wave function  $\psi_0$  at the bottom of the 3s band in Na versus the radial distance, in units of the Bohr radius.

The cellular method was employed in band calculations (Wigner and Seitz, 1935). It was applied to the alkali metals, particularly Na and K. Here Na has been used as an example.

The Schrödinger equation whose solution we seek is

$$\left[ -\frac{\hbar^2}{2m_0} \nabla^2 + V(r) \right] \psi_k = E(k) \psi_k, \rightarrow (1)$$

where  $V(r)$  is the crystal potential and  $\psi_k$  the Bloch function. Say here we are interested only in the 3s band. It is at once evident that this equation cannot be solved analytically. We must therefore use an approximate procedure.

When we use the cellular method we divide the crystal into unit cells; each atom is centered at the middle of its cell, as shown in Fig. (1). Such a cell, known as the Wigner-Seitz (WS) cell, is constructed by drawing bisecting planes normal to the lines connecting an atom A, say, to its neighbors, and "picking out" the volume enclosed by these planes. The procedure for constructing the WS cell is analogous to that used in constructing the Brillouin zone in

$k$ -space. For Na, which has a bcc structure, the WS cell has the shape of a regular dodecahedron (similar to Fig. 1(a); but in real space).

In order to solve Eqn. (1); we now assume that the electron, when in a particular cell, say A, is influenced by the potential of the ion in that cell only. The ions in other cells have a negligible effect on the electron in cell A because each of these cells is occupied, on the average, by another conduction electron which tends to screen the ion, thereby reducing its potential drastically. To ensure that the function  $\psi_k$  satisfies the Bloch form, it is necessary that  $u_k$  - where  $\psi_k = e^{i\vec{k}\cdot\vec{r}} u_k$  - be periodic, that is,  $u_k$  has the same points on opposite faces of the cell, e.g., points  $P_1$  and  $P_2$  in Fig. 1(a).

The procedure is now clear in principle:

We attempt to solve Eqn. (1) in a single cell, using for  $V(r)$  the potential of a free ion, which can be found from atomic physics. In Na, for instance,  $V(r)$  is the potential of the ion core  $Na^+$ .

It is still very difficult, however, to impose the requirements of periodicity on the function for the actual shape of the cell -

the truncated octahedron, and to overcome this hurdle Wigner and Seitz replaced the cell by a Wigner sphere of the same volume as the actual cell, i.e., one employs a Wigner sphere. Using these simplifying assumptions concerning the potential and the periodic conditions, one then solves the Schrödinger equation numerically, since an analytical solution cannot usually be found. The resulting wave function  $\psi_0$  at the bottom of the band,  $k=0$ , is shown in Fig. 1(b). The wave functions at other values of  $k$  near the bottom of the band may then be approximated by

$$\psi_k \approx \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \psi_0 \quad \text{--- (2)}$$

which has the Bloch form.

The procedure is also capable of yielding the energy  $E(\mathbf{k})$ . The energy  $E_0$  of the bottom of the band is obtained from the same calculations which give  $\psi_0$ , and the energy at any other point  $\mathbf{k}$  is obtained by using

$$E(\mathbf{k}) = \left\langle \psi_k \left| -\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right| \psi_k \right\rangle \quad \text{--- (3)}$$

where the wave function  $\psi_k$  is to be substituted from (2). The energy found in this manner was used by Wigner and Seitz to evaluate the cohesive energy, and the results are in satisfactory agreement with experiment.

One noteworthy feature of these results is the shape of the wave function in Fig. 1(b). The wave function oscillated at the ion core, but once outside the core the function is essentially a constant. This constancy of the wave function holds true for almost 90% of the cell volume. Thus the wave function behaves like a plane wave, as can be observed from (2), over most of the cell, and hence over most of the crystal. Looking at this in terms of the potential, we can observe that where the function is a plane wave, the potential must be a constant. Thus, the effective potential acting on the electron is essentially a constant, except in the region of the ion core itself. Viewing the motion of the electron in the crystal as a whole, we can conclude that the electron moves in a region of constant potential throughout most of the crystal; only at the cores themselves does the electron experience any appreciable potential. This surprising result explains why the conduction electrons in Na, for example, may be regarded as essentially free electrons. Mathematically, it is a consequence of the periodic conditions imposed on the wave function.

in the cell, and this is particularly apparent when one realizes that the wave function for the  $3s$  electron in a free Na atom is very unlike  $\psi_0$  outside the ion core. The flatness of  $\psi_0$  is thus due to the imposition of the periodic conditions, and thus render the potential a constant, not to any special property of the ionic potential. The effect of the periodic condition is to cancel out the ionic potential outside the core, and thus render the potential a constant. This result is very useful in the development of other methods of band calculation.

Despite its usefulness, the cellular method is greatly oversimplified, and is not currently much in use. One of its chief disadvantages is that when one replaces the Wigner cell by a sphere, one ignores the crystal structure entirely and all anisotropic effects, for instance, are completely masked out.