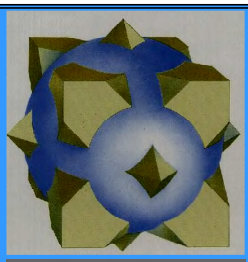
SOLID STATE PHYSICS



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Electron Levels in a Periodic Potential: General Properties

The Periodic Potential and Bloch's Theorem

Born-von Karman Boundary Condition

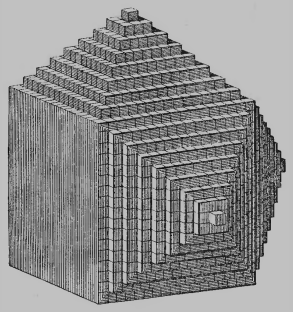
A Second Proof of Bloch's Theorem

Crystal Momentum, Band Index, and Velocity

The Fermi Surface

Density of Levels and van Hove Singularities

Because the ions in a perfect crystal are arranged in a regular periodic array, we are led to consider the problem of an electron in a potential $U(\mathbf{r})$ with the periodicity of the underlying Bravais lattice; i.e.,



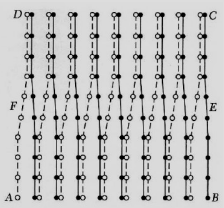
$$U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$$

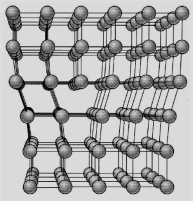
Since the scale of periodicity of the potential U ($\sim 10^{-8}$ cm) is the size of a typi
de Broglie wavelength of an electron in the Sommerfeld free electron model, it
essential to use quantum mechanics in accounting for the effect of periodicity
electronic motion. In this chapter we shall discuss those properties of the electro
levels that depend only on the periodicity of the potential, without regard to
particular form. The discussion will be continued in Chapters 9 and 10 in two limit
cases of great physical interest that provide more concrete illustrations of the gene
results of this chapter. In Chapter 11 some of the more important methods for
detailed calculation of electronic levels are summarized. In Chapters 12 and 13
shall discuss the bearing of these results on the problems of electronic transp
theory first raised in Chapters 1 and 2, indicating how many of the anomalies
free electron theory (Chapter 3) are thereby removed. In Chapters 14 and 15 we sh
examine the properties of specific metals that illustrate and confirm the general thec

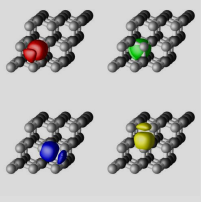
We emphasize at the outset that perfect periodicity is an idealization. Real solids are never absolutely pure, and in the neighborhood of the impurity atoms the solid is not the same as elsewhere in the crystal. Furthermore, there is always a slight temperature-dependent probability of finding missing or misplaced ions (Chapter 30) that destroy the perfect translational symmetry of even an absolutely pure crystal. Finally, the ions are not in fact stationary, but continually undergo thermal vibrations about their equilibrium positions.

These imperfections are all of great importance. They are, for example, ultimately responsible for the fact that the electrical conductivity of metals is not infinite. Progress is best made, however, by artificially dividing the problem into two parts: (a) the ideal fictitious perfect crystal, in which the potential is genuinely periodic, and (b) the effects on the properties of a hypothetical perfect crystal of all deviations from perfect periodicity, treated as small perturbations.

We also emphasize that the problem of electrons in a periodic potential does not arise only in the context of metals. Most of our general conclusions apply to all crystalline solids, and will play an important role in our subsequent discussions of insulators and semiconductors.





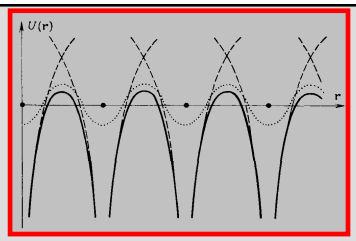


THE PERIODIC POTENTIAL

The problem of electrons in a solid is in principle a many-electron problem, for the full Hamiltonian of the solid contains not only the one-electron potentials describing the interactions of the electrons with the massive atomic nuclei, but also pair potentials describing the electron-electron interactions. In the independent electron approximation these interactions are represented by an effective one-electron potential $U(\mathbf{r})$. The problem of how best to choose this effective potential is a complicated one, which we shall return to in Chapters 11 and 17. Here we merely observe that whatever detailed form the one-electron effective potential may have, if the crystal is perfectly periodic it must satisfy (8.1). From this fact alone many important conclusions can already be drawn.

Qualitatively, however, a typical crystalline potential might be expected to have the form shown in Figure 8.1, resembling the individual atomic potentials as the ion is approached closely and flattening off in the region between ions.

A typical crystalline periodic potential, plotted along a line of ions and along a line midway between a plane of ions. (Closed circles are the equilibrium ion sites; the solid curves give the potential along the line of ions; the dotted curves give the potential along a line between planes of ions; the dashed curves give the potential of single isolated ions.)



We are thus led to examine general properties of the Schrödinger equation for a single electron,

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\psi = \mathcal{E}\psi$$

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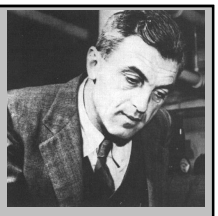
that follow from the fact that the potential U has the periodicity (8.1). The free electron Schrödinger equation (2.4) is a special case of (8.2) (although, as we shall see, in some respects a very pathological one), zero potential being the simplest example of a periodic one.

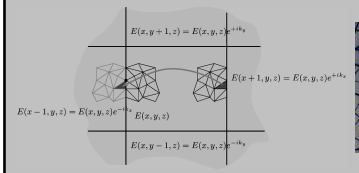
Independent electrons, each of which obeys a one electron Schrödinger equation with a periodic potential, are known as *Bloch electrons* (in contrast to "free electrons," to which Bloch electrons reduce when the periodic potential is identically zero). The stationary states of Bloch electrons have the following very important property as a general consequence of the periodicity of the potential U:

BLOCH'S THEOREM

'When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal.... By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation'

F. BLOCH





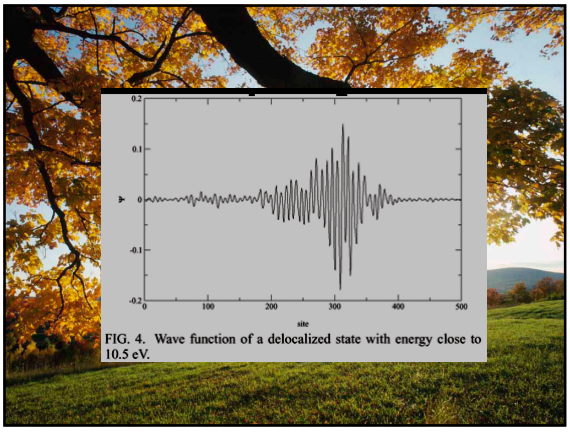


FIG. 4. Wave function of a delocalized state with energy close to 10.5 eV.

BLOCH'S THEOREM

Theorem.[1] The eigenstates ψ of the one-electron Hamiltonian $H = -\hbar^2\nabla^2/2m + U(\mathbf{r})$, where $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$ for all $\mathbf{R}$ in a Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r})$$

Bloch's theorem is sometimes stated in this alternative form:[3] the eigenstates of H can be chosen so that associated with each ψ is a wave vector $\mathbf{k}$ such that

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$$

Proof of Bloch's Theorem

$$T_{\mathbf{R}}\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{R})$$

$$T_{\mathbf{R}}H(\mathbf{r})\psi(\mathbf{r}) = \mathrm{H}(\mathbf{r}+\mathbf{R})\psi(\mathbf{r}+\mathbf{R}) = \mathrm{H}(\mathbf{r})\psi(\mathbf{r}+\mathbf{R}) = \mathrm{H}(\mathbf{r})\mathrm{T}_{\mathbf{R}}\psi(\mathbf{r})$$

Translation operator commutes with Hamiltonain

$$[\mathrm{H}, \mathrm{T}_{\mathbf{R}}] = 0$$

so they share the same eigenstates

$$H\psi(\mathbf{r}) = \mathrm{E}\psi(\mathbf{r}) \qquad T_{\mathbf{R}}\psi(\mathbf{r}) = \mathrm{c}(\mathbf{R})\psi(\mathbf{r})$$

$$T_{\mathbf{R}}T_{\mathbf{R}'}\psi(\mathbf{r}) = \mathrm{c}(\mathbf{R})\mathrm{T}_{\mathbf{R}'}\psi(\mathbf{r}) = \mathrm{c}(\mathbf{R})\mathrm{c}(\mathbf{R}')\psi(\mathbf{r})$$

$$T_{\mathbf{R}}T_{\mathbf{R}'}\psi(\mathbf{r}) = \mathrm{T}_{\mathbf{R}+\mathbf{R}'}\psi(\mathbf{r}) = \mathrm{c}(\mathbf{R}+\mathbf{R}')\psi(\mathbf{r})$$

$$c(\mathbf{R}+\mathbf{R}') = \mathrm{c}(\mathbf{R})\mathrm{c}(\mathbf{R}')$$

We can always write: $c(\mathbf{a}_i) = e^{2\pi i x_i}$

Now let $\mathbf{a}_i$ be three primitive vectors for the Bravais lattice.

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

We had proved that: $c(\mathbf{R}+\mathbf{R}') = \mathrm{c}(\mathbf{R})\mathrm{c}(\mathbf{R}')$

Thus: $\mathrm{C}(\mathbf{R}) = \mathrm{C}(\mathrm{n}_1\mathbf{a}_1 + \mathrm{n}_2\mathbf{a}_2 + \mathrm{n}_3\mathbf{a}_3) = \mathrm{C}(\mathrm{n}_1\mathbf{a}_1)\mathrm{C}(\mathrm{n}_2\mathbf{a}_2)\mathrm{C}(\mathrm{n}_3\mathbf{a}_3)$

$\mathrm{C}(\mathrm{n}_i\mathbf{a}_i) = \mathrm{C}(\mathbf{a}_i)^{\mathrm{n}_i}$ Why ?

$$\mathrm{C}(\mathrm{n}_i\mathbf{a}_i) = \mathrm{C}(\underbrace{\mathbf{a}_i + \mathbf{a}_i + \ldots + \mathbf{a}_i}_{\mathrm{n}_i}) = \underbrace{\mathrm{C}(\mathbf{a}_i)\mathrm{C}(\mathbf{a}_i)\ldots\mathrm{C}(\mathbf{a}_i)}_{\mathrm{n}_i} = \mathrm{C}(\mathrm{a}_i)^{\mathrm{n}_i}$$

$$c(\mathbf{R}) = c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3}$$

$$\mathrm{C}(\mathbf{R}) = \exp\{2\pi i \mathrm{x}_1\}^{\mathrm{n}_1} \exp\{2\pi i \mathrm{x}_2\}^{\mathrm{n}_2} \exp\{2\pi i \mathrm{x}_3\}^{\mathrm{n}_3}$$

$$\mathrm{C}(\mathbf{R}) = \exp\{2\pi i \mathrm{x}_1\}^{\mathrm{n}_1} \exp\{2\pi i \mathrm{x}_2\}^{\mathrm{n}_2} \exp\{2\pi i \mathrm{x}_3\}^{\mathrm{n}_3}$$

$$\mathrm{C}(\mathbf{R}) = \exp\{2\pi i \mathrm{n}_1 \mathrm{x}_1\} \exp\{2\pi i \mathrm{n}_2 \mathrm{x}_2\} \exp\{2\pi i \mathrm{n}_3 \mathrm{x}_3\}$$

$$\mathrm{C}(\mathbf{R}) = \exp\{2\pi i(\mathrm{n}_1\mathrm{x}_1 + \mathrm{n}_2\mathrm{x}_2 + \mathrm{n}_3\mathrm{x}_3)\}$$

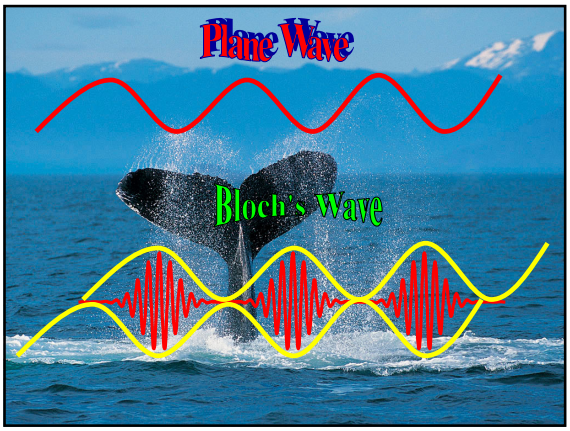
$$c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}$$

$\mathbf{K}.\mathbf{R} = 2\pi i(\mathrm{n}_1\mathrm{x}_1 + \mathrm{n}_2\mathrm{x}_2 + \mathrm{n}_3\mathrm{x}_3)\}$ Why ?

$$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3 \qquad \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

$$T_{\mathbf{R}}\psi = \psi(\mathbf{r}+\mathbf{R}) = c(\mathbf{R})\psi = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$$



THE BORN–VON KARMAN BOUNDARY CONDITION

By imposing an appropriate boundary condition on the wave functions we can demonstrate that the wave vector **k** must be real, and arrive at a condition restricting the allowed values of **k**. The condition generally chosen is the natural generalization of the condition (2.5) used in the Sommerfeld theory of free electrons in a cubical box. As in that case, we introduce the volume containing the electrons into the theory through a Born–von Karman boundary condition of macroscopic periodicity (page 33). Unless, however, the Bravais lattice is cubic and L is an integral multiple of the lattice constant a, it is not convenient to continue to work in a cubical volume of side L. Instead, it is more convenient to work in a volume commensurate with a primitive cell of the underlying Bravais lattice. We therefore generalize the periodic boundary condition (2.5) to

$$\psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}), \quad i = 1, 2, 3$$

$$\psi_{n\mathbf{k}}(\mathbf{r} + N_i\mathbf{a}_i) = e^{iN_i\mathbf{k}\cdot\mathbf{a}_i}\psi_{n\mathbf{k}}(\mathbf{r}), \quad i = 1, 2, 3$$

$$e^{iN_i\mathbf{k}\cdot\mathbf{a}_i} = 1, \quad i = 1, 2, 3$$

$$e^{2\pi i N_i x_i} = 1 \qquad x_i = \frac{m_i}{N_i}$$

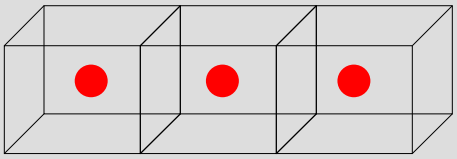
$$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\mathbf{b}_i$$

$$\Delta\mathbf{k} = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3}\right) = \frac{1}{N}\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$$

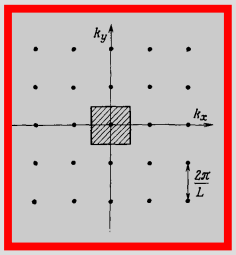
$$\Delta\mathbf{k} = \frac{(2\pi)^3}{V}$$

This is precisely the result (2.18) we found in the free electron case.

Periodic Boudary Conditions



$$\psi(x, y, z+L) = \psi(x, y, z),$$
$$\psi(x, y+L, z) = \psi(x, y, z),$$
$$\psi(x+L, y, z) = \psi(x, y, z).$$



$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}};$$

$$\mathscr{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m},$$

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3}$$

$$\Omega = 4/3\pi k_F^3$$

$$N = 2\times 4/3\pi k_F^3 \frac{V}{8\pi^3}$$

$$\frac{N}{V} = 2\times 4/3\pi k_F^3 \frac{1}{8\pi^3}$$

$$n = \frac{k_F^3}{3\pi^2}$$

$$\psi(x, y, z+L) = \psi(x, y, z),$$
$$\psi(x, y+L, z) = \psi(x, y, z),$$
$$\psi(x+L, y, z) = \psi(x, y, z).$$

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}$$