

Modern Physics in Modern Technology

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Chapter 1

Semiconductor

1.1 Electrons are fermions

Properties of solids cannot be understood without resorting entirely to quantum mechanics. When we talk about conduction properties, in particular, we are first asking about the behavior of electrons inside the solid. By solid we loosely mean a collection of atoms forming a regular structure and some free electrons moving under the influence of Coulomb potentials arising from the positively charged ionic cores. This problem can be solved more or less satisfactorily by relatively simple application of quantum mechanics. Of equally fundamental importance in understanding the electronic property of solids is the fact that there are many, many electrons occupying a given solid, and that *electrons are fermions*. Fermions obey the Pauli exclusion principle. As a result, a given quantum state can only be occupied by at most one electron. This fact alone leads to some powerful consequences about the behavior of many-electron system.

1.2 One-dimensional quantum mechanics

Think of a simple problem of putting a particle in a box of length L as in Fig. ?? In quantum mechanics, such a particle obeys the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x). \quad (1.1)$$

We already know that the eigenstates of this particle are described by harmonic functions (sin's and cos's) and that a wave function with more nodes (this is roughly speaking the number of wavelengths that fit inside the box) generally has higher energy, etc.

Outside the box the particle cannot exist and, since $|\psi(x)|^2$ represents the probability of the particle's existence at a given position x , it must vanish when x lies outside of the range $[0, L]$. Let's assume further that our wave function can only change continuously, i.e. $\psi(x)$ cannot change by a discontinuous amount at any point in space. Then, by continuity, we will have to require $\psi(0) = \psi(L) = 0$, and only certain types of wave functions are consistent with these *boundary conditions*. We find $\psi(x) = \sin(kx)$, and further $\sin(kL) = 0$, hence

$$k = \frac{\pi}{L}n \quad (1.2)$$

where n is an integer. Since positive n and negative n give the same wave function $\psi(x)$ up to the overall phase, we can restrict n to be positive integers: $n = 1, 2, \dots$. What we described above is actually a very general procedure in dealing with a quantum-mechanical problem. First we reduce the problem to some sort of differential equation. The solutions of this equation are the eigenfunctions of the problem at hand. Finally there are some *constraints*, such as the vanishing of the wave function at the two ends of the box, that restrict the allowed quantum numbers. It is an essential point to keep in mind that the quantization in quantum mechanics arises from the boundary conditions. The origin of the quantization is therefore the same as the quantization of eigenmodes in the vibrating string or drum.

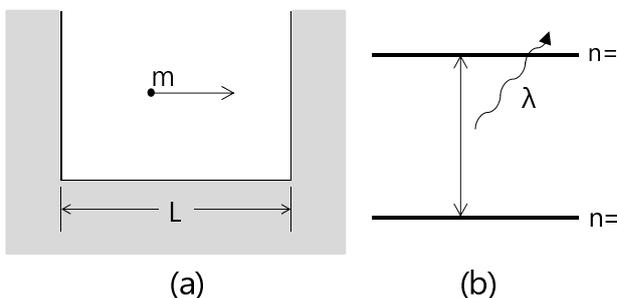


Figure 1.1: (a) A particle of mass m moving in a one-dimensional potential well of length L . (b) Quantized energy levels for such a particle. The difference between energy levels can be measured by the wavelength λ of the light being emitted.

As a related problem let's solve the quantum-mechanical problem of a particle confined to a ring of radius R as shown in Fig. ???. The position of the particle can be labelled by the angle θ , or by $x \equiv R\theta$. The Schrödinger equation expressed in terms of x will read¹

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x). \quad (1.3)$$

This equation can be simplified by writing $k^2 = \frac{2mE}{\hbar^2}$, then we will have

$$\left(\frac{d^2}{dx^2} + k^2 \right) \psi(x) = 0. \quad (1.4)$$

The solution of this differential equation is e^{ikx} , e^{-ikx} , or some linear combination of the two, $Ae^{ikx} + Be^{-ikx}$. Because we are dealing with a particle on a ring, we must also require that eigenfunction obey the property $\psi(x + 2\pi R) = \psi(x)$. This is the uniqueness condition of the wave function. Taking $L \equiv 2\pi R$, we immediately see that only a special selection of k values will obey this constraint:

¹I typically omit the fine distinction between a total derivative dx and the partial derivative ∂x . It will be obvious from the context.

$$kL = 2\pi n, \quad n = \text{integer.} \quad (1.5)$$

In this case all the integer values are allowed for n . As a result eigenenergies must also occur at special, quantized values

$$E_n = \frac{\hbar^2 \left(\frac{2\pi n}{L}\right)^2}{2m} = \frac{h^2}{2mL^2} n^2. \quad (1.6)$$

It is instructive to consider the actual scales of the energy difference between the levels. In the case of an electron, between $n = 0$ and $n = 1$, we obtain the energy difference

$$\Delta E_{10} = \frac{(6.6 \times 10^{-34} \text{J} \cdot \text{s})^2}{2(9.1 \times 10^{-31} \text{kg})L^2} = \frac{2.4 \times 10^{-37} \text{J} \cdot \text{m}^2}{L^2} = \frac{1.5 \times 10^{-18} \text{eV} \cdot \text{m}^2}{L^2}. \quad (1.7)$$

In the atomic world L is 10^{-10}m and we obtain $\Delta E_{10} \sim 100 \text{ eV}$. In the macroscopic world we can choose $L = 10^{-3} \text{m}$ and $\Delta E_{10} \sim 10^{-12} \text{eV}$. A useful way to get a sense of how big (or small) this energy scale is is to convert it to wavelength of light.

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{(4.1 \times 10^{-15} \text{eV} \cdot \text{s})(3 \times 10^8 \text{m/s})}{\lambda} = \frac{1.23 \times 10^{-6} \text{eV} \cdot \text{m}}{\lambda}. \quad (1.8)$$

We can directly equate the difference of quantized energy levels with the photon energy,

$$\frac{h^2}{2mL^2} = \frac{hc}{\lambda} \quad (1.9)$$

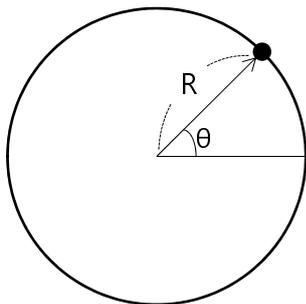
and arrive at the wavelength

$$\lambda = \frac{mc}{h} L^2 = \left(\frac{L}{2\pi\alpha a_B}\right) \times L, \quad (1.10)$$

where we used the relation $\hbar/mc\alpha = a_B$ as the Bohr radius and α is the fine structure constant. Hence, the energy difference of 10^{-12} eV corresponds to light emission of wavelength 10^6 m . Such long wavelength light will be hardly detectable. The quantization of particle energy becomes less and less obvious as we approach the macroscopic system size. The fact that in many solids there are clearly defined energy ranges where electrons cannot find a state is therefore surprising.

1.3 Many-particle quantum mechanics

Whether we like it or not, we have to deal with many-particle system in order to describe the real world. It should be immediately obvious that one needs more than one coordinate to describe the system, so let's introduce x_1 and x_2 to denote the position of the particles. The Schrödinger equation for the two-particle case will go something like

Figure 1.2: Particle moving on a ring of radius R .

$$-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) \psi(x_1, x_2) = E\psi(x_1, x_2). \quad (1.11)$$

The eigenfunction $\psi(x_1, x_2)$ depends on two coordinates because there are two particles in the system. On the other hand one cannot help the notion that each particle behaves more or less like what it did before when there was only one particle on a ring. This will be particularly true provided the two particles do not interact with each other. For example if these two particles were charged, then there will be a Coulomb potential $\frac{e_1 e_2}{|x_1 - x_2|}$ between the two, and one can no longer say that the motions of the particles are independent.

For now we ignore this interaction effect and proceed to verify our intuition about the independence of two particles. Writing $\psi(x_1, x_2) = \varphi(x_1)\varphi(x_2)$ - this is just separation of variables - and substituting it into Eq. (1.11) yields

$$\begin{aligned} \left(\frac{d^2}{dx_1^2} + k_1^2 \right) \varphi(x_1) &= 0, \\ \left(\frac{d^2}{dx_2^2} + k_2^2 \right) \varphi(x_2) &= 0, \end{aligned} \quad (1.12)$$

and $E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2)$. The energy is the sum of the energies of the individual state $\varphi(x_1)$ and $\varphi(x_2)$, as should be the case if the two particles were indeed non-interacting. Building on our experience with the one-particle problem we know that each eigenfunction is characterized by a quantum number n , where n is given by $k = 2\pi n/L$. Since there are two particles we better have two numbers, (n_1, n_2) , to completely specify the eigenstate of the system.

The associated two-particle eigenfunction can be written down as $\phi_{n_1}(x_1)\phi_{n_2}(x_2)$. This will indicate the physical state where particle number 1 resides in the eigenstate of quantum number n_1 , and the particle number 2 in the state with quantum number n_2 . One can also ask to write down the eigenstate with the two particles located in n_2 and n_1 . However, since the two particles are assumed *identical*, this is really the same state as the the first state we wrote down. Loosely speaking, we have

$$\phi_{n_1}(x_1)\phi_{n_2}(x_2) \sim \phi_{n_1}(x_2)\phi_{n_2}(x_1). \quad (1.13)$$

So which state do we choose to describe the state that is characterized by the occupation of the two quantum states (n_1, n_2) : $|n_1 n_2\rangle$? The answer is given by Pauli's exclusion principle that states that no two electrons shall occupy the same quantum state. This statement finds its mathematical incarnation in the following linear combination:

$$\begin{aligned}\psi_{n_1, n_2}(x_1, x_2) &= \frac{1}{\sqrt{2}}[\phi_{n_1}(x_1)\phi_{n_2}(x_2) - \phi_{n_1}(x_2)\phi_{n_2}(x_1)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{n_1}(x_1) & \phi_{n_1}(x_2) \\ \phi_{n_2}(x_1) & \phi_{n_2}(x_2) \end{vmatrix}.\end{aligned}$$

From the well-known theorem of linear algebra one finds that this wave function vanishes if $n_1 = n_2$ (two rows are equal). Vanishing of the wave function implies zero probability of its occurring, so it will never happen. Similarly one finds that the wave function vanishes if $x_1 = x_2$ (two columns are equal). This sometimes leads to the alternative version of Pauli's principle that says that no two electrons shall occupy the same place in space. The overall factor $1/\sqrt{2}$ is inserted so that the two-particle wave function $\psi(x_1, x_2)$ is once again normalized: $\int dx_1 dx_2 |\psi(x_1, x_2)|^2 = 1$. One can check this as an exercise problem.

For three particles on a ring, the same reasoning (and a little bit of mathematical ingenuity) will allow you to write down the wave function that also obeys Pauli's principle:

$$\psi_{n_1, n_2, n_3}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{n_1}(x_1) & \phi_{n_1}(x_2) & \phi_{n_1}(x_3) \\ \phi_{n_2}(x_1) & \phi_{n_2}(x_2) & \phi_{n_2}(x_3) \\ \phi_{n_3}(x_1) & \phi_{n_3}(x_2) & \phi_{n_3}(x_3) \end{vmatrix}.$$

Generalization to arbitrary N -electron system should now be obvious. Professor Slater realized this is the right way to write down the wave function for N -electron problems, so this type of determinant expression for the wave function is often known as the Slater determinant. Although the Slater determinant wave function is correct, working with it is another matter: It is too cumbersome! So a more convenient method of expression will have to be invented.

One soon realizes that the actual content of the Slater determinant is in the counting of the occupation numbers for each quantum state ϕ_n . So if a particular quantum state is occupied, we label it as such and the whole set of information about a particular many-body state is in the counting of all the states being occupied by the electrons. For instance, three particles occupying the states $n = 0, 2, 4$ can be simply written $|0, 2, 4\rangle$ instead of the lengthy Slater determinant, Eq. (1.14).

With spin degrees of freedom included, the quantum state labels can be expanded to include the spin orientations as $\sigma = +, -$, or $\sigma = \uparrow, \downarrow$. Then each state is labeled by one orbital quantum number n and one spin quantum number σ : $\phi_{n, \sigma}$. Slater determinant can be suitably generalized. Due to the spin degree of freedom, each orbital state can be occupied by two electrons, as long as their spin orientations are opposite.

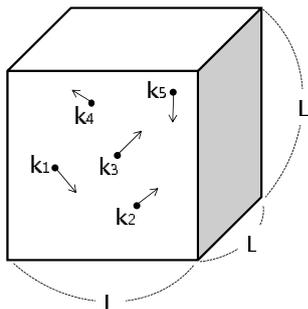


Figure 1.3: Particle freely moving inside the box of length L on each side. Each particle carries a well-defined momentum $\hbar\mathbf{k}$.

1.4 Free electron sea of a metal

The qualitative picture of the behavior of electrons in a metal has been proposed a long time ago, almost immediately after the birth of quantum mechanics. Ignoring the Coulomb repulsion between two electrons for a moment, each electron in a metal is considered a free particle. The quantum-mechanical description of a free particle in three dimensions is given by the Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z) \quad (1.14)$$

with a solution $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}$ and the corresponding energy $E_{\mathbf{k}} = \hbar^2\mathbf{k}^2/2m$. The volume of the box in which the electrons are enclosed is V .

The quantum-mechanical state with one electron in a particular \mathbf{k} -state is denoted $|\mathbf{k}\rangle$. Remember that electrons have spin (one up and one down), and the same momentum state \mathbf{k} can be occupied by one spin-up electron and one spin-down electron. Let's say we are putting an electron in momentum- \mathbf{k} and spin- \uparrow state. Such a state is given by $|\mathbf{k}\uparrow\rangle$.

We have an Avogadro's number of electrons each waiting for its place in this box, so we have to decide where to put the second electron in this box. One can only put an electron in one of the eigenstates of the Hamiltonian (1.14). That's simply what the eigenstate means. We can put the second electron, for instance, in the same \mathbf{k} state, but with a different spin, and the result would be a state $|\mathbf{k}\downarrow, \mathbf{k}\uparrow\rangle$. A third electron inserted in momentum- \mathbf{p} , spin- \uparrow state will turn it into $|\mathbf{p}\uparrow, \mathbf{k}\downarrow, \mathbf{k}\uparrow\rangle$. Now the rule is almost self-evident. For N electrons occupying a set of levels defined by $\{\mathbf{k}_i, \sigma_i\}$, $i = 1, \dots, N$, the N -electronic state is given by

$$|\psi\rangle = |\mathbf{k}_i\sigma_i\rangle. \quad (1.15)$$

The product runs over N different labels of $\{\mathbf{k}\sigma\}$. The lowest energy state is obtained if we categorically place two electrons of opposite spins in the successively higher energy states, starting from the very lowest energy. Such a state is the lowest possible energy state for N non-interacting electrons, *i.e.* it is the ground state. The highest-energy state occupied by the electron has an energy E_f related to the Fermi momentum k_f by

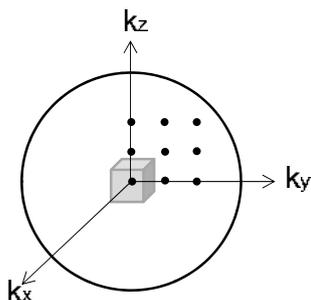


Figure 1.4: Schematic diagram of the \mathbf{k} -space where each dot represents a possible eigenstate of the free electron. The block of cube represents the \mathbf{k} -space volume occupied by each state.

$$E_f = \frac{\hbar^2 k_f^2}{2m}$$

and is called the Fermi energy. The contour consisting of \mathbf{k} -states having the same energy is in the shape of a sphere in three-dimensional space spanned by (k_x, k_y, k_z) . The highest-energy states form such a sphere too, which is called the Fermi surface. Some experimental techniques can directly measure the Fermi surface contour of a given metal.

Fermi momentum k_f has a close connection to the average electron density $\rho = N/V$. To see how to relate k_f to ρ , first think about a sphere of radius k_f in momentum space. All electrons live inside this sphere, so the total electron number is proportional to the volume of the sphere. The volume is given by $4\pi k_f^3/3$. If we divide this by the volume occupied by each electron, then we must obtain $N/2$. The extra factor 2 is due to the spin degeneracy.

So what is the volume of \mathbf{k} -space occupied by each electronic state? To find the answer to this, go back to the free-electron Schrödinger equation, whose solution for a box of sides (L_x, L_y, L_z) is characterized by \mathbf{k} :

$$\mathbf{k} = 2\pi \left(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right).$$

Using this result it is easy to see that the volume associated with each state is just $(2\pi)^3/L_x L_y L_z = (2\pi)^3/V$. So we have

$$\frac{N}{2} = \frac{(4\pi k_f^3/3)}{(2\pi)^3/V} = \frac{V k_f^3}{6\pi^2}.$$

Since $N/V = \rho$, the density is indeed related to k_f through

$$\rho = \frac{k_f^3}{3\pi^2}, \quad k_f^3 = 3\pi^2 \rho. \quad (1.16)$$

Due to this relation the Fermi energy is also related to the electron density via

$$E_f = \frac{\hbar^2}{2m} (2\pi^2 \rho)^{2/3}. \quad (1.17)$$

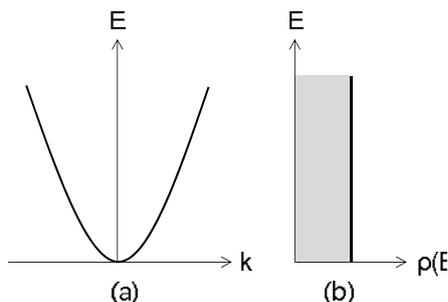


Figure 1.5: (a) Free electron energy dispersion and (b) the corresponding density of states $\rho(E)$ (schematic). There can be no gap in the density of states for free electron model.

In typical metals the Fermi momentum is roughly the inverse of the lattice spacing, $k_f \sim 1/a$. The Fermi energy is typically of order $\hbar^2/2ma^2$. Recall that the ground state level of the hydrogen atom also has an energy of order e^2/a . Due to the virial relation this is also the amount of the kinetic energy $\hbar^2/2ma^2$, so we infer that the Fermi energy is roughly 10 eV for a typical metal. To make this argument more precise, we write

$$E_f = \frac{\hbar^2}{2ma_B^2}(k_f a_B)^2 = \frac{e^2}{2a_B}(k_f a_B)^2 \quad (1.18)$$

using the Bohr radius of hydrogen atom a_B and the known relation between potential and kinetic energies $\hbar^2/2ma_B^2 = e^2/2a_B$. The energy unit $e^2/2a_B$ is known as the Rydberg (Ry), equal to 13.6 eV. As I said, $k_f a_B \sim 1$, and $E_f \sim 1$ Ry.

There's also the concept known as the Fermi temperature that's related to the Fermi energy by $E_f = k_B T_f$, k_B being a Boltzmann's constant. The typical conversion factor is 10^4 Kelvin for 1 electron volt, so the Fermi energy of 10 eV corresponds to 10^5 degrees. An extensive list of Fermi energies and Fermi wavevector for an assortment of metals is given in p. 139, Kittel (8th Ed.), or on p. 38, Ashcroft & Mermin.

Some of the modifications brought about in a real crystal are ionic potentials, various imperfections of both magnetic and non-magnetic characters, and multiple band structures, to name a few. We will cover as much of these as time allows.

1.5 Theory of electrons in periodic media

The most distinguishing feature separating electrons traveling in free space from the one inside a solid is the presence of periodic potential. For one dimension this implies that the electronic wave function obeys the differential equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x), \quad (1.19)$$

where $V(x)$ possesses the periodic property $V(x+a) = V(x)$. The constant a is the lattice constant measuring the distance of one atomic site to the next.

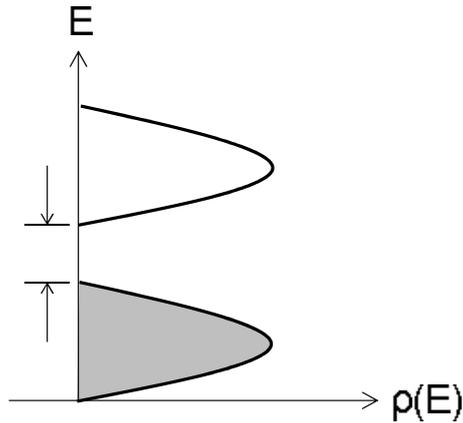


Figure 1.6: Schematic plot of the density of states for the bands separated by a band gap. Shaded energy regions are occupied while the un-shaded regions are empty. An energy gap separates the occupied from the empty bands.

Without the periodic function one obtains the plane-wave solution $\psi_k(x) = e^{ikx}/\sqrt{L}$ where L is the assumed length of the chain on which the electrons reside. For calculational convenience one can always choose L to be an integer multiple of a , $L = Na$, in which case N becomes the number of lattice sites.

Energy of the free electron is given by $E_k = \hbar^2 k^2/2m$, a continuous function of k that grows without bound. From the boundary condition one can quantize k as multiples of $2\pi/L$, $k = 2\pi n/L$, and for a given number of electrons N_e one can imagine occupying the lowest N_e levels until all the states below some energy E_F , called the Fermi energy, is completely occupied. This is in fact a roughly picture of how the electrons are arranged in a metal.

Now let's study the changes brought about by the periodic potential. Since $V(x)$ is a periodic function and its period is a , we must be able to Fourier-decompose it as

$$V(x) = \sum_{m=-\infty}^{\infty} V_m e^{imGx} \quad (1.20)$$

where G , called the reciprocal lattice vector, refers to $G = 2\pi/a$. V_m are some coefficients whose exact value depends on the exact form of $V(x)$ and obeys the relation $V_{-m} = V_m^*$. For simplicity we only keep the first harmonics and write $V(x) = 2V_1 \cos[Gx]$. Inserting the cosine function in the Schrödinger equation gives

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V_1 (e^{iGx} + e^{-iGx}) \psi(x) = E \psi(x). \quad (1.21)$$

Before, we were able to use $\psi_k(x) = e^{ikx}$ as the eigenfunction but now we find it gets multiplied by $e^{\pm iGx}$ and yields a different function, $e^{i(k\pm G)x}$. We often say that the perturbation, $V(x)$, "mixes" different eigenstates. The true eigenstate, in the presence of $V(x)$, becomes a mixture of many different $\psi_k(x)$'s.

There is a way to see the effect of mixing by graphical method. Since we know that the perturbation mixes the momentum eigenstate k with $k \pm G$, we plot two additional energy curves, $\hbar^2(k + G)^2/2m$ and $\hbar^2(k - G)^2/2m$, in addition to $\hbar^2k^2/2m$, on the same graph. The different curves cross at $k = \pm G/2$, called the Brillouin zone boundary. The effect of mixing introduced by $V(x)$ is particularly severe at the BZ boundary, and we want to isolate these special k -points to examine the influence of perturbation more carefully. Choosing $k = G/2$, we find the Schrödinger equation

$$\frac{\hbar^2(G/2)^2}{2m}\psi_{G/2}(x) + V_1\psi_{-G/2}(x) \simeq E\psi_{G/2}(x). \quad (1.22)$$

We dropped $e^{3iGx/2}$ in the above. The perturbation “connects” the state at $k = G/2$ to another state at $k = -G/2$, which happens to be another zone boundary point where the energy levels cross. Hence we write down another equation now for $k = -G/2$:

$$\frac{\hbar^2(G/2)^2}{2m}\psi_{-G/2}(x) + V_1\psi_{G/2}(x) \simeq E\psi_{-G/2}(x). \quad (1.23)$$

The two equations can be combined as a matrix,

$$\begin{pmatrix} \frac{\hbar^2(G/2)^2}{2m} & V_1 \\ V_1 & \frac{\hbar^2(G/2)^2}{2m} \end{pmatrix} \begin{pmatrix} \psi_{G/2}(x) \\ \psi_{-G/2}(x) \end{pmatrix} = E \begin{pmatrix} \psi_{G/2}(x) \\ \psi_{-G/2}(x) \end{pmatrix}. \quad (1.24)$$

The new energy solutions are readily found,

$$E_k^\pm = \frac{\hbar^2(G/2)^2}{2m} \pm V_1, \quad (1.25)$$

along with the corresponding wave functions

$$\psi^\pm(x) = \frac{1}{\sqrt{2}}[\psi_{G/2}(x) \pm \psi_{-G/2}(x)]. \quad (1.26)$$

Where there was once a continuous change of energy with k , now we find a gap, separating the lower (-) branch from the upper (+) one, of size $2|V_1|$. The new energy spectrum after the gap opening will look like Fig. ???. The exercise shows an important phenomenon of gap opening by the periodic potential in solid. As a result, electrons occupy a certain band and a certain momentum, and its state is characterized by two quantum numbers: n for the band index, and k for its momentum. Similarly, energies are denoted ε_{nk} . Typically there is an energy gap separating a given band n from the adjacent $n \pm 1$ -th band at the same k -point. It does not mean that all the energy states of $n + 1$ -th band lie higher than all the energy states of the n -th band. For each k , however, we can say that $\varepsilon_{i+1,k} \geq \varepsilon_{i,k}$.

1.6 Semiconductor Primer

Group IV elements such as C, Si, and Ge form a crystal where each atom is surrounded by four others. With one atom at the center of the tetrahedron, the four neighboring atoms are placed at the vertices of the tetrahedron, and the pattern continues to form a crystal structure. Carbon atoms arranged in such a fashion form a diamond with a wide band gap, and light passes through the material with little interaction with the electrons. Si has a small band gap of about 1.1 eV, interacts with light, and gives rise to a shiny surface. Ge has a slightly smaller energy gap. Materials made out of one group III and group V elements, such as GaAs and InSb, are also semiconductors.

When some of the Si atoms are replaced by the group V element like P(hosphorous), four of its valence electrons form the covalent bonds with the surrounding Si atoms but one electron remains, essentially playing the role of a free electron. Such material is said to be *n*-doped, since the extra carrier - the electron - has the negative charge. The opposite case of *p*-doping is realized by substituting group III elements like Al.