

# Chapter 11

## The Solid State. Home Work Solutions

### 11.1 Problem 11.5

Consider a one-dimensional chain of alternating positive and negative ions. Show that the potential energy of an ion in this hypothetical crystal is

$$U(r) = -k\alpha \frac{e^2}{r}$$

where  $\alpha = 2 \ln 2$  (the Madelung constant), and  $r$  is the interionic spacing. [*Hint*: Make use of the series expansion for  $\ln(1+x)$ .]

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### Solution

Each ion, in a one-dimensional array of alternating positive and negative ions, is surrounded by two ions of the opposite charge followed by two ions of the same charge at double the distance then two ions of opposite charge at triple the distance, and so on. The potential energy of such ion is then the sum of all the potential energies due to the presence of other ions, i.e.

$$\begin{aligned} U(r) &= -\frac{ke^2}{r} - \frac{ke^2}{r} + \frac{ke^2}{2r} + \frac{ke^2}{2r} - \frac{ke^2}{3r} - \frac{ke^2}{3r} + \frac{ke^2}{4r} + \frac{ke^2}{4r} - \dots \\ &= -2\frac{ke^2}{e} \left[ 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right] \end{aligned}$$

Since,

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

taking  $x = 1$ , then:

$$U(r) = -2 \ln 2 \frac{ke^2}{r}$$

## 11.2 Problem 11.8

The Madelung constant for the NaCl structure may be found by summing an infinite alternating series of terms giving the electrostatic potential energy between an  $\text{Na}^+$  ion and its 6 nearest  $\text{Cl}^-$  neighbors, its 12 next-nearest  $\text{Na}^+$  neighbors, and so on (see Figure (11.1)).

- (a) From this expression, show that the first three terms of the infinite series for the Madelung constant for the NaCl structure yield  $\alpha = 2.13$ .
- (b) Does this infinite series converge rapidly? Calculate the fourth term as a check.

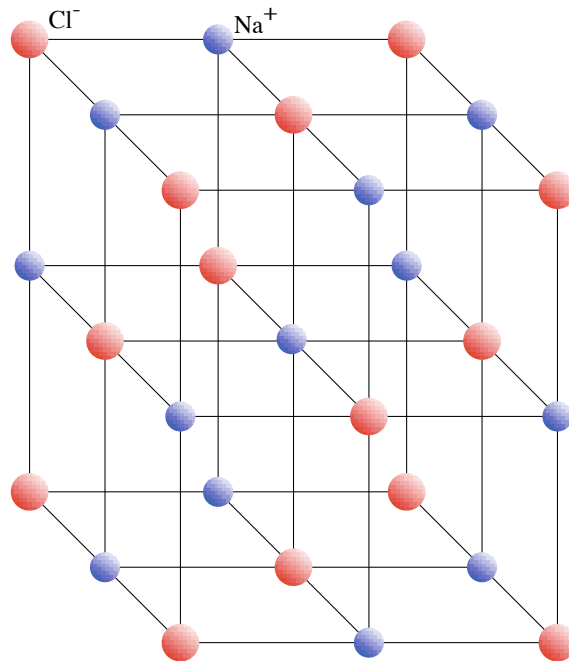


Figure 11.1: The crystal structure of NaCl

## Solution

- (a) Figure (11.1) represents the unit cell of a NaCl crystal. A unit cell is the smallest structure of the crystal than can be repeated in all direction to form large crystals. Let the  $r_0$  be the distance between an ion and its closest neighbor. Consider the  $\text{Na}^+$  ion at the center of the unit cell of NaCl crystal in Figure (11.1). This ion is surrounded by 6

$\text{Cl}^-$  ions at distance  $r_o$ . The potential energy  $U_{C1}$  of the  $\text{Na}^+$  ion at the center due to these six  $\text{Cl}^-$  ions is given by:

$$U_{C1} = -6 \frac{ke^2}{r_o}$$

There are also 12  $\text{Na}^+$  ions each at a distance  $\sqrt{2}r_o$  from the  $\text{Na}^+$  at the center. The potential energy  $U_{C2}$  of the ion at the center due to these 12 ions is:

$$U_{C2} = +12 \frac{ke^2}{\sqrt{2}r_o}$$

There are also 8  $\text{Cl}^-$ , at the corners of the unit cell, each at a distance of  $\sqrt{3}r_o$  from the central  $\text{Na}$  ion. The potential energy  $U_{C3}$  is:

$$U_{C3} = -8 \frac{ke^2}{\sqrt{3}r_o}$$

The total potential energy of the central ion is then:

$$\begin{aligned} U(r) &= U_{C1} + U_{C2} + U_{C3} \\ &= -6 \frac{ke^2}{r_o} + 12 \frac{ke^2}{\sqrt{2}r_o} - 8 \frac{ke^2}{\sqrt{3}r_o} \\ &= \left[ -6 + \frac{12}{\sqrt{2}} - \frac{8}{\sqrt{3}} \right] \frac{ke^2}{r_o} \\ &= -2.13 \frac{ke^2}{r_o} \end{aligned}$$

The first three terms produce a Madlung constant of 2.13.

- (b) The fourth term comes from the central  $\text{Na}^+$  ions at the centers of the neighboring unit cells (there can be 6 unit cell adjacent to the one shown in Figure (11.1)). Each of these 6 ions is at a distance of  $2r_o$ , the potential energy  $U_{C4}$  is then:

$$\begin{aligned} U_{C4} &= +6 \frac{ke^2}{2r_o} \\ &= +3 \frac{ke^2}{r_o} \end{aligned}$$

and the total energy is:

$$\begin{aligned} U(r) &= U_{C1} + U_{C2} + U_{C3} + U_{C4} \\ &= (-2.13 + 3) \frac{ke^2}{r_o} \\ &= +0.87 \frac{ke^2}{r_o} \end{aligned}$$

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It is obvious that the series does not converge rapidly. The addition of the fourth term made the total potential energy positive i.e. the total force is repulsive. The magnitude of the fourth term is actually larger than the magnitude of the sum of the first three terms. This means that a lot more ions has to be added until the series converges.

### 11.3 Problem 11.14

Sodium is a monovalent metal having a density of  $0.971 \text{ g/cm}^3$ , an atomic weight of  $23.0 \text{ g/mol}$ , and a resistivity of  $\rho = 4.20 \mu\Omega \cdot \text{cm} = 4.20 \times 10^{-8} \Omega \cdot \text{m}$  at  $300 \text{ K}$ . Use this information to calculate

- the free-electron density
- the Fermi energy  $E_F$  at  $0 \text{ K}$
- the Fermi velocity  $v_F$
- the average time between electronic collisions
- the mean free path of the electrons, assuming that  $E_F$  at  $0 \text{ K}$  is the same as  $E_F$  at  $300 \text{ K}$  and
- the thermal conductivity.

For comparison to (e), the nearest-neighbor distance in sodium is  $0.372 \text{ nm}$ .

### Solution

- Each monovalent atom contributes one electron to the free-electron density. So, the free electron density equals the number of atoms per unite volume,  $n$ .

$$n = \frac{A_v \times d}{w}$$

where  $A_v$  is Avogadro's number,  $d$  is the density in  $\text{g/cm}^3$ , and  $w$  is molecular weight in  $\text{g/mol}$ . We then have:

$$\begin{aligned} n &= \frac{6.02 \times 10^{23} \times 0.971}{23} \\ &= 2.54 \times 10^{22} \text{ e/cm}^3 \\ &= 2.54 \times 10^{28} \text{ e/m}^3 \end{aligned}$$

- The Fermi energy  $E_F$  at  $0 \text{ K}$  is defined as:

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

where  $h$  is Planck's constant,  $m_e$  is the electron mass, and  $N/V = n$  is the number of atoms per unit volume. so,  $E_F$  is:

$$\begin{aligned} E_F &= \frac{(6.625 \times 10^{-34})^2}{2 \times 9.11 \times 10^{-31}} \left( \frac{3 \times 2.54 \times 10^{28}}{8\pi} \right)^{2/3} \\ &= 5.046 \times 10^{-19} \text{ J} \\ &= \frac{5.046 \times 10^{-19}}{1.602 \times 10^{-19}} \text{ eV} \\ &= 3.15 \text{ eV} \end{aligned}$$

(c) The Fermi velocity  $v_F$  is given by:

$$\begin{aligned} v_F &= \sqrt{\frac{2E_F}{m_e}} \\ &= \sqrt{\frac{2 \times 5.046 \times 10^{-19}}{9.11 \times 10^{-31}}} \\ &= 1.05 \times 10^6 \text{ m/s} \end{aligned}$$

(d) The average time between collision  $\tau$  is defined by the mass of the electron, the number of atoms per unit volume, electric resistivity, and electron charge:

$$\begin{aligned} \tau &= \frac{m_e}{\rho n e^2} \\ &= \frac{9.11 \times 10^{-31}}{4.2 \times 10^{-8} \times 2.54 \times 10^{28} \times (1.602 \times 10^{-19})^2} \\ &= 3.33 \times 10^{-14} \text{ s} \end{aligned}$$

(e) The mean free path is given by:

$$\begin{aligned} L &= v_F \tau \\ &= 1.05 \times 10^6 \times 3.33 \times 10^{-14} \\ &= 3.5 \times 10^{-8} \text{ m} \\ &= 350 \text{ \AA} \end{aligned}$$

(f) Thermal conductivity  $K$  can be calculated from:

$$\begin{aligned}\frac{K}{\sigma T} &= \frac{1}{3} \left( \frac{\pi k}{e} \right)^2 \\ K &= \frac{\sigma T}{3} \left( \frac{\pi k}{e} \right)^2 \\ &= \frac{T}{3\rho} \left( \frac{\pi k}{e} \right)^2 \\ &= \frac{300}{3 \times 4.2 \times 10^{-8}} \left( \frac{\pi 1.381 \times 10^{-23}}{1.602 \times 10^{-19}} \right)^2 \\ &= 175 \text{ W/m} \cdot \text{K}\end{aligned}$$

where  $\sigma$  is the electric conductivity  $= 1/\rho$ .

Comparing the mean free path  $L$  with the nearest neighbor distance  $r_o = 0.372 \text{ nm}$ , we get:

$$\begin{aligned}\frac{L}{r_o} &= \frac{3.5 \times 10^{-8}}{0.372 \times 10^{-9}} \\ &= 94\end{aligned}$$



## 11.4 Problem 11.17

The simplest way to model the energy-level splitting that is produced when two originally isolated atoms are brought close together is with two finite wells. In this model, the Coulomb potential experienced by the outermost electron in each atom is approximated by a one-dimensional finite square well of depth  $U$  and width  $a$ . The energy levels for two atoms close together may be found by solving the time-independent Schrödinger equation for a potential consisting of two finite wells separated by a distance  $b$ .

- (a) Start this problem by “warming up” with a solution to the single finite well shown in Figure (11.17a). Justify the solutions listed for regions I, II, and III and apply the standard boundary conditions ( $\psi$  and  $d\psi/dx$  continuous at  $x = 0$  and  $x = a$ ) to obtain a transcendental equation for the bound-state energies.
- (b) Write a computer program to solve for the bound-state energies when an electron is confined to a well with  $U = 100 \text{ eV}$  and  $a = 1 \text{ \AA}$ . You should find two bound states at approximately 19 and 70 eV.
- (c) Now consider the finite wells separated by a distance  $b$  as shown in Figure (11.17b). Impose the conditions of continuity in  $\psi$  and  $d\psi/dx$  continuous at  $x = 0$  and  $x = a$  to obtain

$$\frac{D}{E'} = \frac{2e^{-2Ka} [\cos ka + \frac{1}{2}(K/k - k/K) \sin ka]}{(k/K + K/k) \sin ka}$$

Show that the boundary conditions at  $x = a + b$  yield

$$\frac{F}{G} = \frac{(D/E')e^{\beta}[\cos \alpha - (K/k) \sin \alpha] + e^{-\beta}[\cos \alpha + (K/k) \sin \alpha]}{(D/E')e^{\beta}[\sin \alpha + (K/k) \cos \alpha] + e^{-\beta}[\sin \alpha - (K/k) \cos \alpha]}$$

where  $\alpha = k(a + b)$  and  $\beta = K(a + b)$ . The boundary conditions at  $x = 2a + b$  yield

$$\frac{F}{G} = \frac{\cos k(2a + b) + (K/k) \sin k(2a + b)}{\sin k(2a + b) - (K/k) \cos k(2a + b)}$$

Thus, the two expressions for  $F/G$  may be set equal and the expression for  $D/E'$  used to obtain a transcendental equation for the energy  $E$

## Solution

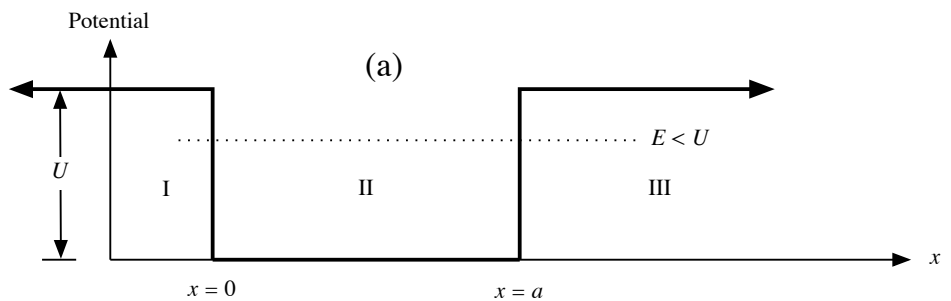
(a) In regions I and III (see Figure (11.17a)) the wave equation is:

$$\frac{d^2\psi(x)}{dx^2} = K^2\psi(x) \quad (11.1)$$

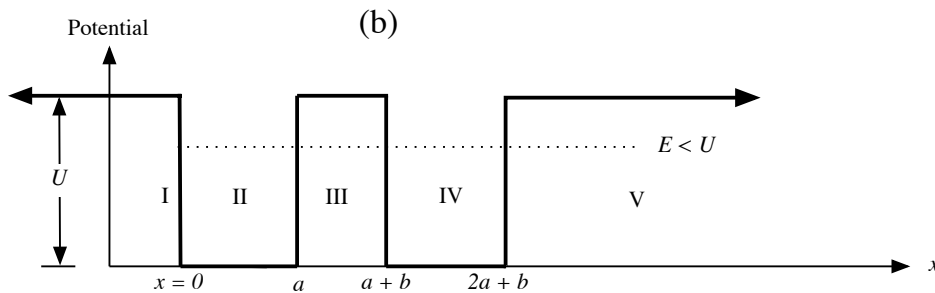
where

$$K = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (11.2)$$

The solutions to this equation are:



$$\begin{aligned} \square_{\text{I}} &= Ae^{Kx} & kh/2\pi &= [2m(U - E)]^{1/2} \\ \square_{\text{II}} &= B \cos kx + C \sin kx & kh/2\pi &= (2mE)^{1/2} \\ \square_{\text{III}} &= De^{-Kx} \end{aligned}$$



$$\begin{aligned} \square_{\text{I}} &= Ae^{Kx} & kh/2\pi &= [2m(U - E)]^{1/2} \\ \square_{\text{II}} &= B \cos kx + C \sin kx & kh/2\pi &= (2mE)^{1/2} \\ \square_{\text{III}} &= De^{Kx} + E' e^{-Kx} \\ \square_{\text{IV}} &= F \cos kx + G \sin kx \\ \square_{\text{V}} &= He^{-Kx} \end{aligned}$$

Figure 11.17: (a) Potential and eigenfunctions for single finite well depth  $U$ , where  $E < U$ . (b) Potential and eigenfunctions for two finite wells. The width of each well is  $a$ , and the wells are separated by a distance  $b$ .

$$\psi_I = Ae^{Kx} \quad \text{for } x \leq 0 \text{ (region I)} \quad (11.3)$$

$$\psi_{III} = De^{-Kx} \quad \text{for } x \geq 0 \text{ (region III)} \quad (11.4)$$

In region II where  $U = 0$ , the wave equation becomes:

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \quad (11.5)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (11.6)$$

and the solution is:

$$\psi_{II} = B \cos kx + C \sin kx \quad 0 \leq x \leq a$$

Each wave function and its slope must be continuous everywhere including the well edges  $x = 0$  and  $x = a$ :

$$A = B \quad [\text{continuity of } \psi(x) \text{ at } x = 0] \quad (11.7)$$

$$KA = kC \quad [\text{continuity of } d\psi(x)/dx \text{ at } x = 0] \quad (11.8)$$

$$De^{-Ka} = B \cos ka + C \sin ka \quad [\text{continuity of } \psi(x) \text{ at } x = a] \quad (11.9)$$

$$DKe^{-Ka} = B \sin ka - C \cos ka \quad [\text{continuity of } d\psi(x)/dx \text{ at } x = a] \quad (11.10)$$

These are four equations in the for unknown coefficients  $A, B, C, D$ . Dividing 11.8 by 11.7 and 11.10 by 11.9 we get:

$$B = \frac{k}{K} C \quad (11.11)$$

$$-K = \frac{-Bk \sin ka + C \cos ka}{B \cos ka + C \sin ka} \quad (11.12)$$

Rearranging 11.12 and using 11.11 to eliminate  $B$  we get:

$$\begin{aligned} -K \left( \frac{k}{K} \right) C \cos ka - KC \sin ka &= - \left( \frac{k}{K} \right) Ck \sin ka + Ck \cos ka \\ (k^2 - K^2) \sin ka &= 2kK \cos ka \\ \tan ka &= 2 \frac{kK}{k^2 - K^2} \end{aligned} \quad (11.13)$$

Using Equations (11.2 and 11.6) we get:

$$\begin{aligned}
 \tan ka &= 2 \frac{\sqrt{\frac{2mE}{\hbar^2}} \sqrt{\frac{2m(U-E)}{\hbar^2}}}{\frac{2mE}{\hbar^2} - \frac{2m(U-E)}{\hbar^2}} \\
 &= 2 \frac{2m\sqrt{E(U-E)}}{2mE - 2mU - 2mE} \\
 &= 2 \frac{\sqrt{E(U-E)}}{-U} \\
 \tan^2 ka &= \frac{4E(U-E)}{U^2} \\
 \tan^2 \left( \sqrt{\frac{2mE}{\hbar^2}} a \right) &= \frac{4E(U-E)}{U^2} \tag{11.14}
 \end{aligned}$$

11.14 is the required equation, that relates the energy  $E$  to the height  $U$  and width  $a$  of the potential.

(c) The boundary conditions are:

$$\psi_I(0) = \psi_{II}(0) \tag{11.15}$$

$$\psi_{II}(a) = \psi_{III}(a) \tag{11.16}$$

$$\psi_{III}(a+b) = \psi_{IV}(a+b) \tag{11.17}$$

$$\psi_{IV}(2a+b) = \psi_V(2a+b) \tag{11.18}$$

$$\left( \frac{d\psi_I(x)}{dx} \right)_{x=0} = \left( \frac{d\psi_{II}(x)}{dx} \right)_{x=0} \tag{11.19}$$

$$\left( \frac{d\psi_{II}(x)}{dx} \right)_{x=a} = \left( \frac{d\psi_{III}(x)}{dx} \right)_{x=a} \tag{11.20}$$

$$\left( \frac{d\psi_{III}(x)}{dx} \right)_{x=a+b} = \left( \frac{d\psi_{IV}(x)}{dx} \right)_{x=a+b} \tag{11.21}$$

$$\left( \frac{d\psi_{IV}(x)}{dx} \right)_{x=2a+b} = \left( \frac{d\psi_V(x)}{dx} \right)_{x=2a+b} \tag{11.22}$$

Applying Equations (11.15 and 11.19) we get:

$$A = B \tag{11.23}$$

$$KA = kC \tag{11.24}$$

and applying Equations (11.16 and 11.20) we get:

$$B \cos ka + C \sin ka = D e^{Ka} + E' e^{-Ka} \tag{11.25}$$

$$-Bk \sin ka + Ck \cos ka = K D e^{Ka} - K E' e^{-Ka} \tag{11.26}$$

Using Equations (11.23 and 11.24) in Equations (11.25 and 11.26) we get:

$$A \cos ka + \frac{KA}{k} \sin ka = De^{Ka} + E'e^{-Ka} \quad (11.27)$$

$$-Ak \sin ka + KA \cos ka = KDe^{Ka} - KE'e^{-Ka} \quad (11.28)$$

Eliminating  $A$  from Equations (11.27 and 11.28), we get:

$$\begin{aligned} \frac{De^{Ka} + E'e^{-Ka}}{\cos ka + \frac{K}{k} \sin ka} &= \frac{KDe^{Ka} - KE'e^{-Ka}}{K \cos ka - k \sin ka} \\ \frac{\frac{D}{E'}e^{Ka} + e^{-Ka}}{\cos ka + \frac{K}{k} \sin ka} &= \frac{\frac{D}{E'}e^{Ka} - e^{-Ka}}{\cos ka - \frac{k}{K} \sin ka} \\ \left( \frac{D}{E'}e^{Ka} + e^{-Ka} \right) \left( \cos ka - \frac{k}{K} \sin ka \right) &= \left( \frac{D}{E'}e^{Ka} - e^{-Ka} \right) \left( \cos ka + \frac{K}{k} \sin ka \right) \end{aligned}$$

$$\begin{aligned} \frac{D}{E'}e^{Ka} \left[ \left( \cos ka - \frac{k}{K} \sin ka \right) - \left( \cos ka + \frac{K}{k} \sin ka \right) \right] \\ = -e^{-Ka} \left[ \left( \cos ka - \frac{k}{K} \sin ka \right) + \left( \cos ka + \frac{K}{k} \sin ka \right) \right] \\ - \frac{D}{E'}e^{Ka} \left( \frac{K}{k} + \frac{k}{K} \right) \sin ka = -e^{-Ka} \left[ 2 \cos ka + \left( \frac{K}{k} - \frac{k}{K} \right) \sin ka \right] \\ \frac{D}{E'} = \frac{e^{-Ka} \left[ 2 \cos ka + \left( \frac{K}{k} - \frac{k}{K} \right) \sin ka \right]}{e^{Ka} \left( \frac{K}{k} + \frac{k}{K} \right) \sin ka} \\ = \frac{2e^{-2Ka} \left[ \cos ka + \frac{1}{2} \left( \frac{K}{k} - \frac{k}{K} \right) \sin ka \right]}{\left( \frac{K}{k} + \frac{k}{K} \right) \sin ka} \quad (11.29) \end{aligned}$$

Now, applying Equations (11.17 and 11.21) and use  $\alpha = k(a+b)$  and  $\beta = K(a+b)$  we get:

$$\begin{aligned} \frac{De^\beta + E'e^{-\beta}}{F \cos \alpha + G \sin \alpha} &= 1 \\ \frac{KDe^\beta - KE'e^{-\beta}}{-Fk \sin \alpha + Gk \cos \alpha} &= 1 \end{aligned} \quad (11.30)$$

$$\begin{aligned} \frac{KDe^\beta - KE'e^{-\beta}}{-Fk \sin \alpha + Gk \cos \alpha} &= 1 \end{aligned} \quad (11.31)$$

From Equations (11.30 and 11.31) we get:

$$\begin{aligned} \frac{De^\beta + E'e^{-\beta}}{F \cos \alpha + G \sin \alpha} &= \frac{KDe^\beta - KE'e^{-\beta}}{-Fk \sin \alpha + Gk \cos \alpha} \\ \frac{\frac{D}{E'}e^\beta + e^{-\beta}}{\frac{F}{G} \cos \alpha + \sin \alpha} &= \frac{\frac{K}{k} \frac{D}{E'}e^\beta - \frac{K}{k}e^{-\beta}}{-\frac{F}{G} \sin \alpha + \cos \alpha} \quad (11.32) \end{aligned}$$

11.32 can be rearranged as:

$$\begin{aligned}
& \left( \frac{D}{E'} e^\beta + e^{-\beta} \right) \left( -\frac{F}{G} \sin \alpha + \cos \alpha \right) = \left( \frac{K D}{k E'} e^\beta - \frac{K}{k} e^{-\beta} \right) \left( \frac{F}{G} \cos \alpha + \sin \alpha \right) \\
& -\frac{F}{G} \sin \alpha \left( \frac{D}{E'} e^\beta + e^{-\beta} \right) + \cos \alpha \left( \frac{D}{E'} e^\beta + e^{-\beta} \right) \\
& \qquad \qquad \qquad = \frac{F}{G} \cos \alpha \left( \frac{K D}{k E'} e^\beta - \frac{K}{k} e^{-\beta} \right) + \sin \alpha \left( \frac{K D}{k E'} e^\beta - \frac{K}{k} e^{-\beta} \right) \\
& \frac{F}{G} \sin \alpha \left( \frac{D}{E'} e^\beta + e^{-\beta} \right) + \frac{F K}{G k} \cos \alpha \left( \frac{D}{E'} e^\beta - e^{-\beta} \right) \\
& \qquad \qquad \qquad = -\frac{K}{k} \sin \alpha \left( \frac{D}{E'} e^\beta - e^{-\beta} \right) + \cos \alpha \left( \frac{D}{E'} e^\beta + e^{-\beta} \right) \\
& \frac{F}{G} \left[ \frac{D}{E'} e^\beta \left( \sin \alpha + \frac{K}{k} \cos \alpha \right) + e^{-\beta} \left( \sin \alpha - \frac{K}{k} \cos \alpha \right) \right] \\
& \qquad \qquad \qquad = \frac{D}{E'} e^\beta \left( \cos \alpha - \frac{K}{k} \sin \alpha \right) + e^{-\beta} \left( \cos \alpha + \frac{K}{k} \sin \alpha \right) \\
& \frac{F}{G} = \frac{\frac{D}{E'} e^\beta \left( \cos \alpha - \frac{K}{k} \sin \alpha \right) + e^{-\beta} \left( \cos \alpha + \frac{K}{k} \sin \alpha \right)}{\frac{D}{E'} e^\beta \left( \sin \alpha + \frac{K}{k} \cos \alpha \right) + e^{-\beta} \left( \sin \alpha - \frac{K}{k} \cos \alpha \right)} \tag{11.33}
\end{aligned}$$

Now, using Equations (11.18 and 11.22) we get:

$$H e^{-K(2a+b)} = F \cos k(2a+b) + G \sin k(2a+b) \tag{11.34}$$

$$-K H e^{-K(2a+b)} = -k F \sin k(2a+b) + k G \cos k(2a+b)$$

$$H e^{-K(2a+b)} = \frac{k}{K} [F \sin k(2a+b) - G \cos k(2a+b)] \tag{11.35}$$

Equating the right hand sides of Equations (11.34 and 11.35) we get:

$$\begin{aligned}
F \cos k(2a+b) + G \sin k(2a+b) &= \frac{k}{K} [F \sin k(2a+b) - G \cos k(2a+b)] \\
\frac{K}{k} [F \cos k(2a+b) + G \sin k(2a+b)] &= F \sin k(2a+b) - G \cos k(2a+b) \\
\frac{K}{k} \left[ \frac{F}{G} \cos k(2a+b) + \sin k(2a+b) \right] &= \frac{F}{G} \sin k(2a+b) - \cos k(2a+b) \\
\frac{K F}{k G} \cos k(2a+b) + \frac{K}{k} \sin k(2a+b) &= \frac{F}{G} \sin k(2a+b) - \cos k(2a+b) \\
\frac{F}{G} \left( \sin k(2a+b) - \frac{K}{k} \cos k(2a+b) \right) &= \cos k(2a+b) + \frac{K}{k} \sin k(2a+b)
\end{aligned}$$

$$\frac{F}{G} = \frac{\cos k(2a + b) + \frac{K}{k} \sin k(2a + b)}{\sin k(2a + b) - \frac{K}{k} \cos k(2a + b)} \quad (11.36)$$

From Equations (11.33 and 11.36) we get:

$$\frac{\cos k(2a + b) + \frac{K}{k} \sin k(2a + b)}{\sin k(2a + b) - \frac{K}{k} \cos k(2a + b)} = \frac{\frac{D}{E'} e^\beta (\cos \alpha - \frac{K}{k} \sin \alpha) + e^{-\beta} (\cos \alpha + \frac{K}{k} \sin \alpha)}{\frac{D}{E'} e^\beta (\sin \alpha + \frac{K}{k} \cos \alpha) + e^{-\beta} (\sin \alpha - \frac{K}{k} \cos \alpha)} \quad (11.37)$$

or one can write 11.37 as:

$$f(E) = \frac{\frac{D}{E'} e^\beta (\cos \alpha - \frac{K}{k} \sin \alpha) + e^{-\beta} (\cos \alpha + \frac{K}{k} \sin \alpha)}{\frac{D}{E'} e^\beta (\sin \alpha + \frac{K}{k} \cos \alpha) + e^{-\beta} (\sin \alpha - \frac{K}{k} \cos \alpha)} - \frac{\cos k(2a + b) + \frac{K}{k} \sin k(2a + b)}{\sin k(2a + b) - \frac{K}{k} \cos k(2a + b)} \quad (11.38)$$

The parameters in 11.38 are  $a$ ,  $b$ ,  $U$ , and  $E$ . The equation can be solved numerically such that for certain values of  $a$ ,  $b$ , and  $U$  one finds the values of  $E$  that makes  $f(E) = 0$ .

## 11.5 Problem 11.18

One can roughly calculate the weak binding energy of a donor electron as well as its orbital radius in a semiconductor on the basis of the Bohr theory of the atom. Recall that, for a single electron bound to a nucleus of charge  $Z$  the binding energy of the ground state is given by

$$\frac{ke^2Z^2}{2a_0} = 13.6Z^2 \text{ eV}$$

and the ground-state radius by

$$r_1 = \frac{a_0}{Z}$$

For the case of a phosphorus donor atom in silicon, the outermost donor electron is attracted by a nuclear charge of  $Z = 1$ . However, because the phosphorus nucleus is embedded in the polarizable silicon, the effective nuclear charge seen by the electron is reduced to  $Z/\kappa$ , where  $\kappa$  is the dielectric constant.

- (a) Calculate the binding energy of a donor electron in Si ( $\kappa = 12$ ) and Ge ( $\kappa = 16$ ) and compare to the thermal energy available at room temperature.
- (b) Calculate the radius of the first Bohr orbit of a donor electron in Si and Ge. How does the Bohr orbit radius compare to the nearest-neighbor distance in Si(2.34 Å) and in Ge(2.43 Å)?

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### Solution

- (a) The binding energy  $B.E.$  is given by:

$$\begin{aligned} B.E. &= 13.6 \left( \frac{Z}{\kappa} \right)^2 \\ B.E._{Si} &= 13.6 \left( \frac{1}{12} \right)^2 \\ &= 0.094 \text{ eV} \\ B.E._{Ge} &= 13.6 \left( \frac{1}{16} \right)^2 \\ &= 0.053 \text{ eV} \end{aligned}$$



The thermal energy at room temperature of  $300\text{ K}$  is  $0.025\text{ eV}$ . Although the thermal energy is smaller than the  $B.E.$ , many electrons will be able to make the transition to the conduction band due to the statistical nature of the distribution of electrons among available energy levels (See chapter 9).

(b) The first Bohr radius  $r_1$  is given by:

$$\begin{aligned}r_1 &= \frac{\kappa a_0}{Z} \\r_{1Si} &= 12 \times 0.529 \\&= 6.4 \text{ \AA} \\r_{1Ge} &= 16 \times 0.529 \\&= 8.5 \text{ \AA}\end{aligned}$$

The donor electrons are not localized around their own atoms but they roam around 3 or 4 semiconductor atoms.