

## Contacts Between Metals and Between a Metal and a Semiconductor

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The problem of contacts between metals and between a metal and a semiconductor is treated classically with the help of the results of wave mechanical theory of electron energy states in solids. The potential and electron density distributions in the two bodies near the contact are discussed. The bodies are assumed to be in immediate contact. The problem of a body in vacuum and the problem of two bodies separated by a gap are discussed qualitatively.

### INTRODUCTION

WE know that when two bodies are in contact their thermodynamic potentials of electrons should be the same and that the contact potential difference is equal to the difference of work functions at  $T=0^\circ\text{K}$ . We do not yet have a detailed picture of how the potential and electron density distributions near the surface of each body are affected by the contact. Frenkel<sup>1</sup> using the Thomas-Fermi method has discussed the situation at the surface of a metal in vacuum. On account of the approximate nature of the method he gets zero work function. Mott<sup>2</sup> has considered the contact between a metal and a semiconductor. He is mainly concerned with the situation in the semiconductor when certain boundary conditions at the contact are assumed. In a previous paper<sup>3</sup> we have discussed qualitatively contacts between metals and between a metal and a semiconductor. We shall now discuss the problem quantitatively treating it classically with the help of the results of wave mechanical theory of electron energy states in solids.

### GENERAL CONSIDERATION

The potential energy of an electron in a solid is periodic with the periodicity of the lattice, approaching large negative values near the nuclei at the lattice points. Bloch's treatment shows that energy levels of the electrons in such a potential field are divided into separate bands with gaps of forbidden energy caused by the periodic nature of the field. Changing the average potential simply shifts the whole energy

spectrum up or down. If there is a slow variation of the average potential such that it changes little over many unit cells, then to the first approximation the whole energy spectrum with the top and bottom levels of each band simply follows the variation and the density distribution of energy states in each band remains constant. We shall thus assume: (1) The top and bottom levels of each energy band follow the variation of the average potential. (2) The variation of the average potential affects only the density of electrons in the conduction band, since the number of energy states and hence the number of electrons per unit volume in the completely filled bands remains constant. These assumptions result in great simplification. They are, however, rough approximations especially when the average potential changes very rapidly as at the surface or the contact with another body, problems with which we are concerned.

We turn now to the question of electron density in the conduction band. The wave function of the electrons is of the form  $\psi = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$ , the energy being a function of  $\mathbf{k}$ . The number of energy states per unit volume in the energy interval  $(W_1 - W_2)$  is given by  $(\frac{1}{8}\pi^3)\Omega$ , where  $\Omega$  is the volume in  $\mathbf{k}$  space between two surfaces of constant energy corresponding to  $W_1$  and  $W_2$ .  $W$  is a complicated function of  $\mathbf{k}$  and can be determined only by a complete wave mechanical solution for the given solid. Therefore it is not easy to determine  $\Omega$ . We shall adopt the customary approximation

$$W = E + \frac{\hbar^2 k^2}{8\pi^2 m} \quad (1)$$

where  $E$  is the energy of the bottom level and  $m$  is the effective mass of electrons for the band

<sup>1</sup> J. Frenkel, *Zeits. f. Physik* **51**, 232 (1928).

<sup>2</sup> N. F. Mott, *Proc. Camb. Phil. Soc.* **34**, 568 (1938).

<sup>3</sup> H. Y. Fan, *Phys. Rev.* **61**, 365 (1942).

under consideration, which can be appreciably larger than the ordinary mass of an electron. This expression for energy is of the form for electrons moving in a space of constant potential ( $-E/e$ ). It must, however, be borne in mind that we use this expression only for finding approximately the number of energy states in a given energy interval. The actual average potential in the solid is quite different from ( $-E/e$ ) and we should not identify the two with each other when we are concerned with potential.

According to Eq. (1) the distribution of energy states is

$$f(W)dW = \frac{1}{4\pi^2} \left[ \frac{8\pi^2 m}{h^2} \right]^{3/2} (W-E)^{1/2} dW.$$

The number of electrons in the energy states between  $W$  and  $E$  is

$$n = \int_E^W 2f(W)dW.$$

With constant average potential the average density of electrons with energy in the interval  $W$  to  $E$  is

$$n = \frac{1}{2\pi^2} \left[ \frac{8\pi^2 m}{h^2} \right]^{3/2} \int_E^W \frac{(W-E)^{1/2} dW}{e^{(W-E)/kT} + 1}. \quad (2)$$

We shall treat our problem classically by extending the application of Eq. (2) to the case of variable average potential.

The electrons in the conduction band of metals are highly degenerate. We have

$$n = \frac{1}{2\pi^2} \left[ \frac{8\pi^2 m}{h^2} \right]^{3/2} \frac{2}{3} (\zeta - E)^{3/2} = \frac{8\pi(2m)^{3/2}}{3h^3} (\zeta - E)^{3/2}. \quad (3)$$

$E$  varies with the average potential and  $n$  varies with  $E$  according to this equation.

In a semiconductor there are few electrons in the conduction band. The lower energy bands are full. According to present theory the few electrons in the conduction band come mainly from impurity atoms. In the semiconductors with normal decrease of resistance with increase of temperature, the electron energy level of the impurity atoms is situated in the energy gap

below the conduction band. If the impurity is electropositive it can supply electrons to the conduction band and we have an efficacious semiconductor. With electronegative impurity atoms electrons from the lower band are absorbed by them leaving holes in the band and we have a deficient semiconductor. In general the impurity atoms may supply electrons to or absorb electrons from not only the normal energy bands but also localized energy levels due to imperfection of the crystal.<sup>4</sup> This may be of great significance in the theory of semiconductors. We shall, however, consider only efficacious semiconductors and shall use the simple model: the impurity atoms supply electrons only to the conduction band and in the normal state all electrons in the conduction band are supplied by the impurity atoms. Since there are few electrons in the conduction band we have  $\exp[(W-\zeta)/kT] \gg 1$ . Equation (2) gives

$$n = \frac{2}{h^3} (2\pi m k T)^{3/2} e^{(\zeta-E)/kT} = n_0 \exp[-(E-E_0)/kT], \quad (4)$$

where  $n_0$  is the normal value of  $n$  for  $E=E_0$ . Let the density of impurity atoms be  $N$  with localized energy levels at  $\Delta E$  below the bottom of the conduction band. The density of electrons in the impurity levels is

$$N \frac{1}{e^{(E-\Delta E-\zeta)/kT} + 1}.$$

In the normal state with  $E=E_0$  the total density of electrons in the conduction band and the impurity levels is  $N$ . When  $E$  is different from  $E_0$  the density of excess electrons is

$$-N + \left[ n + \frac{N}{\exp[(E-\Delta E-\zeta)/kT] + 1} \right] = \frac{1}{\exp[(E-\Delta E-\zeta)/kT] + 1} \times [n_0 \exp[(E_0-\Delta E-\zeta)/kT] + n_0 \exp[-(E-E_0)/kT] - N \exp[(E_0-\Delta E-\zeta)/kT] \times \exp[(E-E_0)/kT]. \quad (5)$$

<sup>4</sup>B. R. A. Nijboer, Proc. Phys. Soc. **51**, 575 (1939); A. H. Wilson, "Semiconductors and metals," Cambridge physical tract.

This should be equal to zero when  $E = E_0$

$$\begin{aligned} n_0 \exp[(E_0 - \Delta E - \zeta)/kT] + n_0 \\ = N \exp[(E_0 - \Delta E - \zeta)/kT] \\ \exp[(E_0 - \Delta E - \zeta)/kT] = n_0/(N - n_0). \end{aligned}$$

Since  $n_0 \ll N$  the first term in the bracket of the right-hand side of Eq. (5) is small compared with the other two and can be neglected. The number of excess electrons is then

$$\begin{aligned} \frac{n_0}{\exp[(E - \Delta E - \zeta)/kT] + 1} \\ \times [\exp[-(E - E_0)/kT] - \exp[(E - E_0)/kT]] \\ \approx n_0 \{ \exp[-(E - E_0)/kT] \\ - \exp[(E - E_0)/kT] \} \quad (6) \end{aligned}$$

provided  $\exp(E - \Delta E - \zeta)/kT \ll 1$ . It should be noted that when  $E - E_0$  is too large, then if it is negative the number of electrons in the conduction band may become so large that Eq. (4) based on the approximation of Maxwellian distribution ceases to hold and if it is positive the condition  $\exp(E - \Delta E - \zeta)/kT \ll 1$  may no longer be true.

#### EXCHANGE AND CORRELATION ENERGIES

The energy expression (1) can be improved by taking into account the effect of exchange and correlation energies. When the electrons are perfectly free and can be considered as a Fermi gas filling up each energy state with two electrons of opposite spins up to a maximum energy level, the exchange energy is given by<sup>5</sup>

$$\frac{e^2}{2\pi} \left[ 2k_m + \frac{k^2 - k_m^2}{k_m} \ln \frac{k_m - k}{k_m + k} \right],$$

where  $k$  is the wave number of the electron under consideration and  $k_m$  is that corresponding to the maximum energy. For the electron of maximum energy this expression gives  $e^2 k_m / \pi$ . Strictly this expression applies to electrons in a field free space. We shall follow the Thomas-Fermi-Dirac method<sup>6</sup> and extend its application

<sup>5</sup> P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930); A. H. Wilson, *The Theory of Metals*.

<sup>6</sup> J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935).

to electrons in a variable potential field. The correlation energy is more difficult to estimate. Wigner<sup>7</sup> has shown that in the limiting case when the electrons have no kinetic energy the correlation energy bears the ratio of 0.292 to 0.458 to the total exchange energy. For the ordinary density of electrons in the conduction band of a metal the correlation energy is much smaller.<sup>8</sup> We assume it to be equal to 25 percent of the exchange energy. For the maximum energy electron the sum of correlation and exchange energies is  $1.25e^2 k_m / \pi$ .

The above discussion may be applied to the electrons in the conduction band of a metal, which can be considered approximately as a Fermi gas. We do not have to consider the electrons in the filled bands. Their density being considered constant, they contribute a constant amount to the exchange and correlation energies of an electron. The highest occupied energy level in the conduction band is now

$$\zeta = E - \frac{1.25e^2}{\pi} k_m + \frac{h^2}{8\pi^2 m} k_m^2, \quad (7)$$

where  $E$  should follow the variation of the average potential. The volume in  $\mathbf{k}$  space between two constant energy surfaces corresponding to  $W(k = k_m)$  and  $W(k = 0)$  is  $4\pi k_m^3 / 3$ . The density of electrons in the conduction band is therefore

$$n = (8\pi/3) k_m^3.$$

With the help of Eq. (7) we get

$$n = \frac{8\pi}{3h^3} \left\{ \frac{2.5e^2 m}{h} + \left[ \frac{6.25e^4 m^2}{h^2} + 2m(\zeta - E) \right]^{1/2} \right\}^3. \quad (8)$$

In a semiconductor there are few electrons in the conduction band, which can be considered as a non-degenerate gas. The exchange and correlation energies are small and we shall not introduce such correction.

#### POTENTIAL EQUATION

We shall smear the positive charge of the nuclei and the negative charge of the electrons in the filled bands into a fixed uniform positive charge, the density of which is equal to the

<sup>7</sup> E. Wigner, Phys. Rev. **46**, 1002 (1934).

<sup>8</sup> E. Wigner, Phys. Rev. **46**, 1002 (1934), curve in Fig. 7.

normal negative charge density of the conduction electrons in the case of metals or equal to the sum of normal negative charge densities of the conduction electrons and the electrons in the impurity levels in the case of semiconductors.

Consider first a metal. With the help of Eq. (8) the Poisson equation can be written as (for one dimensional problem)

$$\frac{d^2 V}{dx^2} = 4\pi e \left[ \frac{8\pi}{3h^3} \left\{ \frac{2.5e^2 m}{h} + \left[ \frac{6.25e^4 m^2}{h^2} + 2m(\zeta - E) \right]^{1/2} \right\}^3 - \frac{8\pi}{3h^3} \left\{ \frac{2.5e^2 m}{h} + \left[ \frac{6.25e^4 m^2}{h^2} + 2m(\zeta - E_0) \right]^{1/2} \right\}^3 \right], \quad (9)$$

where  $V$  is the average potential inside the metal. It has been pointed out that  $E$  follows the variation of  $V$ ; i.e.,  $dE/dx = -edV/dx$ . Let

$$y = \frac{6.25e^4 m^2}{h^2} + 2m(\zeta - E). \quad (10)$$

Equation (9) can be rewritten

$$\frac{d^2 y}{dx^2} = \frac{64m\pi^2 e^2}{3h^3} \times \left[ \left( \frac{2.5e^2 m}{h} + y^{1/2} \right)^3 - \left( \frac{2.5e^2 m}{h} + y_0^{1/2} \right)^3 \right] = K_1 [(K_2 + y^{1/2})^3 - (K_2 + y_0^{1/2})^3]. \quad (11)$$

Integrating and using the boundary condition that  $dV/dx = 0$  where  $E = E_0$ , we get

$$\left( \frac{dy}{dx} \right)^2 = 2K_1 \left[ \frac{2}{5} y^{5/2} + \frac{3}{2} K_2 y^2 + 2K_2^2 y^{3/2} - (y_0^{3/2} + 3K_2 y_0 + 3K_2^2 y_0^{1/2}) y + \frac{3}{5} y_0^{5/2} + \frac{3}{2} K_2 y_0^2 + K_2^2 y_0^{3/2} \right]. \quad (12)$$

The right-hand side of this equation can be expressed in terms of the electron density  $n$ . From Eq. (8) and (10) we have

$$y^{1/2} = \left( \frac{3h^3}{8\pi} n \right)^{1/3} - \frac{2.5e^2 m}{h} = \frac{2.5e^2 m}{h} [N^{1/3} - 1] = K_2 [N^{1/3} - 1], \quad (13)$$

where

$$N = \left( \frac{h}{2.5e^2 m} \right)^3 \frac{3h^3}{8\pi} n = \frac{1}{K_2^3} \frac{3h^3}{8\pi} n. \quad (14)$$

Substituting (13) into (12) we get

$$\left( \frac{dy}{dx} \right)^2 = 2K_1 K_2^5 \left[ \frac{2}{5} N^{5/3} - \frac{1}{2} N^{4/3} - N_0 N^{2/3} + 2N_0 N^{1/3} + \frac{3}{5} N_0^{5/3} - \frac{3}{2} N_0^{4/3} \right]. \quad (15)$$

Put  $N = N_0 + \Delta N$  and expand the right-hand side of (15) in terms of  $\Delta N$

$$\left( \frac{dy}{dx} \right)^2 = 2K_1 K_2^5 \left[ \frac{1}{3} (N_0^{-1/3} - N_0^{-2/3}) \Delta N^2 - \frac{2}{27} (N_0^{-4/3} - 2N_0^{-5/3}) \Delta N^3 + \dots \right]. \quad (16)$$

On the other hand we have from (13)

$$\Delta y = K_2^2 \left[ \frac{2}{3} (N_0^{-1/3} - N_0^{-2/3}) \Delta N - \frac{1}{9} (N_0^{-4/3} - 2N_0^{-5/3}) \Delta N^2 + \dots \right]. \quad (17)$$

With  $\Delta N/N < 1$  both (16) and (17) converge rapidly. By taking the first term of each series and substituting (17) into (16) we get

$$\left( \frac{dy}{dx} \right)^2 \approx \left( \frac{d\Delta y}{dx} \right)^2 = \frac{3}{2} \frac{K_1 K_2}{N_0^{-1/3} - N_0^{-2/3}} \Delta y^2 = l^2 \Delta y^2, \quad (18)$$

where

$$l = \left( \frac{3}{2} \frac{K_1 K_2}{N_0^{-1/3} - N_0^{-2/3}} \right)^{1/2} = \frac{8.95\pi m e^2}{h^2} \left( \frac{N_0^{2/3}}{N_0^{1/3} - 1} \right)^{1/2}. \quad (19)$$

Equation (18) gives after integration

$$\Delta y \approx A' \epsilon^{\pm lx} \quad (20)$$

or

$$\Delta V \approx \frac{A'}{2me} \epsilon^{\pm lx} = A \epsilon^{\pm lx}. \quad (21)$$

For semiconductors with the help of (6) the Poisson equation is

$$\frac{d^2 V}{dx^2} = 4\pi e n_0 \left[ \epsilon^{-(E-E_0)/kT} - \epsilon^{(E-E_0)/kT} \right]. \quad (22)$$

Here we have assumed that the bottom level of the conduction band  $E$  follows the variation of  $V$ , i.e.,  $dE/dx = -edV/dx$ . We can therefore

write

$$\frac{d^2z}{dx^2} = K(e^z - e^{-z}), \quad (23)$$

where

$$z = (E - E_0)/kT \quad (24)$$

and

$$K = 4\pi e^2 n_0 / kT. \quad (25)$$

Integrating and using the boundary condition that  $dV/dx=0$  where  $E=E_0$ , we get

$$dz/dx = \pm (8K)^{1/2} \sinh(z/2). \quad (26)$$

Integrating again we have

$$\tanh(z/4) = \tanh(-e\Delta V/4kT) = B e^{\pm(2K)^{1/2}z}. \quad (27)$$

#### CONTACT BETWEEN TWO BODIES

Our problem is to determine the charge density and potential distributions near the contact surface. We have a second-order differential Eq. (9) or (22) for each of the two bodies. The constants of the first integration are determined by the boundary condition inside each body:  $dV/dx=0$  where  $V=V_0$ . Two more conditions are required for determining the constants of second integration, constant  $A$  of Eq. (21) or constant  $B$  of Eq. (27). These are supplied by the requirement of continuity of  $V$  and its derivative at the contact. The latter is the condition for the two bodies being electrically neutral as a whole. Let body 1 extend from  $-\infty$  to 0 and body 2 from 0 to  $\infty$ . We have

$$\begin{aligned} -4\pi q_1 &= \left(\frac{dV_1}{dx}\right)_{x=0} - \left(\frac{dV_1}{dx}\right)_{x=-\infty} = \left(\frac{dV_1}{dx}\right)_{x=0}, \\ -4\pi q_2 &= \left(\frac{dV_2}{dx}\right)_{x=\infty} - \left(\frac{dV_2}{dx}\right)_{x=0} = -\left(\frac{dV_2}{dx}\right)_{x=0}. \end{aligned}$$

If  $q_1 + q_2 = 0$ , then

$$\left(\frac{dV_1}{dx}\right)_{x=0} = \left(\frac{dV_2}{dx}\right)_{x=0}. \quad (28)$$

The condition of continuity of  $V$  is

$$V_1 + (\Delta V_1)_{x=0} = V_2 + (\Delta V_2)_{x=0}$$

or

$$\begin{aligned} (\Delta V_1 - \Delta V_2)_{x=0} \\ = -\frac{1}{e} \{ [\zeta_1 - (-eV_1)] - [\zeta_2 - (-eV_2)] \} \quad (29) \end{aligned}$$

since  $\zeta_1 = \zeta_2$  is the condition of equilibrium.

Let us consider first two metals in contact. If we use the approximate Eq. (18) then the condition (28) gives

$$\Delta V_1 / \Delta V_2 = -l_2 / l_1. \quad (30)$$

The minus sign is due to the fact that we have to choose the negative sign when taking the square root of the right-hand side of Eq. (18) for metal 2 and the positive sign for metal 1. From (29) and (30) the values of  $\Delta V_1$  and  $\Delta V_2$  and hence the integration constants  $A$  for the two metals can be determined. For the solution of the problem we need to know  $[\zeta - (-eV)]$  and the normal density  $n_0$  and effective mass of the conduction electrons. According to the approximate Eq. (21) at a distance  $x=1/l$  from the contact,  $\Delta V$  falls to  $1/\epsilon$  of its value. Taking  $n_0 = 2.62 \times 10^{22}$  (the value for sodium) and the ordinary electron mass for  $m$  we get  $1/l = 0.29 \times 10^{-8}$  cm. Thus the potential and charge density differ from their normal values only in the immediate neighborhood of the contact, within one atomic distance. Bethe<sup>9</sup> has shown that the Thomas Fermi method used by Frenkel gives  $1/l = 0.74 \times 10^{-8}$  cm. Within such short distance from the contact the electron density can, however, differ considerably from the normal value. If  $[\zeta - (-eV)]$  of the two metals differ by a fraction of an electron volt,  $\Delta V$  will be of the order of a few tenths of a volt. With the numerical data as assumed above, for  $\Delta V = 0.1$  volt,  $\Delta n$  is about twenty percent of  $n_0$ . Owing to the fact that the charge due to  $\Delta n$  is concentrated over a short distance near the surface, a large amount of charge of opposite signs on the two sides of the contact is required to form a sufficient double layer for compensating the difference between  $[\zeta - (-eV)]$  of the two metals.

In the case of contact between a metal and a semiconductor the condition of continuity of  $dV/dx$  gives

$$\frac{kT}{e} (8K)^{1/2} \sinh \frac{-e\Delta V_s}{2kT} = l\Delta V_m. \quad (31)$$

If  $e\Delta V_s/2kT < 1$  we may put  $\sinh(e\Delta V_s/2kT) \approx e\Delta V_s/2kT$ . Then

$$\Delta V_s / \Delta V_m = -l / (2K)^{1/2}. \quad (32)$$

<sup>9</sup> H. Bethe, *Handbuch der Physik* 24/2, p. 420.

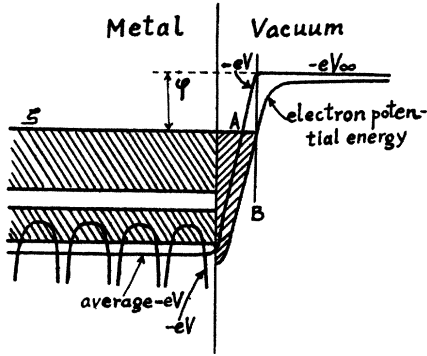


FIG. 1. Conditions at boundary between a vacuum and metal surface.

Putting  $n_0 = 10^{14}$  and  $T = 300^\circ\text{K}$  we get  $(2K)^{\frac{1}{2}} = 1.18 \times 10^5$ . With the value of  $l$  estimated above we have  $|\Delta V_s / \Delta V_m| = 2.96 \times 10^3$ . Thus  $\Delta V_m$  is negligible compared with  $\Delta V_s$ ; all the difference between  $[\zeta - (-eV)]$  of the two bodies is evened out by potential variation in the semiconductor.

At  $T = 300^\circ\text{K}$ ,  $e\Delta V_s / 2kT = 19.3\Delta V_s$  where  $\Delta V_s$  is in volts. It is possible that this factor is much larger than one, in which case we may put

$$\sinh \frac{-e\Delta V_s}{2kT} \approx -e^{\Delta V_s / 2kT}.$$

Hence

$$\frac{e\Delta V_s}{2kT} = \ln \frac{l}{(2K)^{\frac{1}{2}}} + \ln \frac{e(-\Delta V_m)}{2kT} \quad (33)$$

with the same values for  $l$  and  $K$  used above. According to this equation  $|\Delta V_s / \Delta V_m| \approx 1$  at  $e\Delta V_s / 2kT = 10.3$  corresponding to  $\Delta V_s = 0.515$  volt. Thus for the case of small difference between  $[\zeta - (-eV)]$  of the two bodies most of the potential drop takes place in the semiconductor, whereas for a large difference the potential drop in the two substances may become comparable.

Let us assume that  $e\Delta V_s / 4kT < 1$ ; we may put  $\tanh e\Delta V_s / 4kT \approx e\Delta V_s / 4kT$  in Eq. (27), whence

$$\Delta V_s = -\frac{e}{4kT} B \exp[-(2K)^{\frac{1}{2}} x].$$

In a distance of  $1/(2K)^{\frac{1}{2}}$ ,  $\Delta V_s$  drops to  $1/e$  of its value. Comparing the estimated values of  $l$  and  $1/(2K)^{\frac{1}{2}}$  we see that the potential variation and space charge extend over a much wider region in a semiconductor than in a metal. The poorer the conductivity of the semiconductor

or the smaller  $n_0$  the larger will be  $1/(2K)^{\frac{1}{2}}$  and  $|\Delta V_s / \Delta V_m|$ .

In the above discussion we took account of the exchange and correlation energies for metals by Eq. (7) and made them proportional to  $k_m$  or to the third power of the electron density. This applies strictly only to electrons in field free space with constant density. When the density varies these energies will depend not only upon the density at the given point but also upon the density distribution. Hence our approximation is the better justified the smaller the density variation or when the difference between  $[\zeta - (-eV)]$  of the two bodies in contact is small.

#### CONTACT WITH VACUUM

For the vacuum space in contact with a body  $[\zeta - (-eV)]$  is equal to the negative work function of the substance,  $-\varphi$ .

$$[\zeta - (-eV)] - (-\varphi) = [\zeta - (-eV)] + \varphi$$

is of the order of several electron volts. Within a very short distance at the surface of the body the electron density changes from its normal value inside the substance to a negligible value. A more accurate method of evaluating the exchange and correlation energies is therefore necessary. In fact it can be easily shown that unless this is done we should get zero work function.<sup>10</sup>

Consider the surface surrounding the body, outside of which there are no electrons. If the body is not charged then according to Gauss's law  $\int dV/dnds = 0$ . It follows that  $dV/dn = 0$  at this surface. Moreover, outside this surface  $\nabla^2 V = 0$ . Therefore the potential at this surface is equal to the potential at infinity. Our expression for electron density, Eq. (8), gives  $[\zeta - (-eV)] = 0^{11}$  for  $n = 0$ . Hence at this surface  $\zeta = -eV = -eV_\infty$  and the work function is equal to zero.

The actual condition is represented by Fig. 1. At surface A  $\zeta = -eV$  but the electron density has not yet dropped to zero, contrary to Eq. (8). The potential  $V$  continues to drop ( $-eV$  continues to rise). At surface B the maximum energy level is equal to the potential energy which is the sum of  $-eV$  and the exchange and correlation

<sup>10</sup> Cf. H. Bethe, *Handbuch der Physik* 24/2, p. 417.

<sup>11</sup> For vacuum  $E$  in Eq. (8) is equal to  $(-eV)$ .

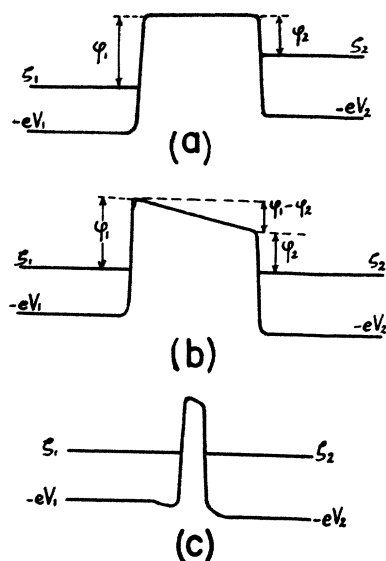


FIG. 2. Conditions at gap between two bodies.

energies. Beyond  $B$  there are no electrons and  $V$  remains constant. The continuity of  $V$  and its derivative serve as boundary condition at the surface. It is clear from this discussion that for the treatment of this problem we have to wait for the development of a better method of taking care of the exchange and correlation energies. Bardeen<sup>12</sup> has given a wave mechanical calculation of the work function for sodium.

Consider two bodies separated by a gap. If there is no interchange of electrons the condition will be shown by Fig. 2a. Except at absolute zero temperature there will be an electron atmosphere in the gap, which is in equilibrium with electrons in the two bodies. This requires  $\zeta_1 = \zeta_2$ . Under the condition shown by Fig. 2a more electrons flow from body 2 to 1. As a result the two bodies become oppositely charged and a potential difference is set up across the gap bringing  $\zeta_1 = \zeta_2$ . If the gap is not too narrow

the amount of charge acquired by each body will be too small to affect appreciably the electron density and potential distributions at its surface. We may then assume the work functions to remain constant and the potential difference across the gap is  $\varphi_1 - \varphi_2$  (Fig. 2b).

With decreasing distance the charges acquired by the two bodies increase in order to maintain the same potential difference across the gap. For parallel plates the surface charge density is

$$q = (\varphi_1 - \varphi_2) / 4\pi d.$$

If the charge is concentrated within a layer of  $10^{-8}$ -cm thickness the corresponding electron density will be of the order

$$n = \frac{\varphi_1 - \varphi_2}{4\pi d} \frac{1}{e} \cdot 10^8.$$

With a difference of one volt between the work functions and a gap of  $10^{-7}$  cm the charge acquired due to the contact gives rise to an additional electron density of the order of  $10^{21}$ . This approaches the order of magnitude of the normal density of electrons in metals. Therefore with such small gaps we can no longer assume that the potential and electron density distributions at the surfaces remain unchanged (Fig. 2c). The treatment of such problem has difficulties explained above.

The treatment developed in the previous paragraphs applies to two bodies in immediate contact. We have to know  $[\zeta - (-eV)]$  for each of the two bodies or the difference. This quantity for a substance is given by a wave mechanical solution of the electron energy states. It should be related to the work function and we would be able to determine it from the experimental data of the latter if we could derive the relation between the two. Experiments on contact phenomena such as contact rectification should yield useful information.

<sup>12</sup> J. Bardeen, Phys. Rev. **49**, 653 (1936).