Theory of the Work Functions of Monovalent Metals

E. WIGNER AND J. BARDEEN, *Princeton University*

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The factors which determine the work function of a metal are described in a qualitative way. The work function is defined as the difference in energy between a lattice with an equal number of ions and electrons, and the lattice with the same number of ions, but with one electron removed. The work function is then found by first calculating the energy of a lattice with n_i ions and n_e electrons. The final formula gives the work functions of monovalent metals in terms of the heats of sublimation. This formula is approximate, and can claim validity only in a qualitative way, as one of the important factors, the electric double layer on the surface, is omitted entirely, and it is assumed that the Fermi energy is as great as if the electrons were entirely free. The values obtained from this formula check very closely with the experimental values for the alkalis, so that it can be concluded that the double layer is probably small for these metals. Finally, the deviations to be expected for other than monovalent metals are considered. A more exact calculation of the work function of one substance (Na) will be given by one of us in an ensuing paper.

(1)

It is perhaps not quite superfluous to have, in addition to a more exact calculation of a physical quantity, an approximate treatment which merely shows how the quantity in question is determined, and the lines along which a more exact calculation could be carried out. Such a treatment often leads to a simple formula by means of which the magnitude of the quantity may be readily determined. A treatment of this nature has been given by O. K. Rice[1] for the binding energies of the alkalis.

We intend to give here an approximate calculation, on somewhat different lines, of the work functions of monovalent metals, the main result being a formula which relates the work function with the heat of sublimation. We do this for two reasons; first, because a more exact treatment seems to involve a great deal of computational labor, and second, because the connection between the work function and other properties is empirically very pronounced. In fact, Sommerfeld,[2] in his original paper on the electron theory of metals, has already noticed that if one orders the metals according to their work functions (or according to their Volta potentials), the series is the same as if one orders them according to the Fermi energy of the electrons, calculated on the basis of the free electron theory. The greater the Fermi energy, the greater the work function. This fact was rather puzzling on the basis of the naïve free electron theories of that time, but an explanation was given later by Frenkel.[3] Although Sommerfeld and Bethe[4] have shown that the details of his calculations cannot be maintained, we feel that his basic idea is correct, namely that the binding energy of the electrons (i.e., work function) increases with the kinetic energy. The connection between the kinetic and potential energy, as given by the virial theorem in a Coulomb field, has been utilized by Tamm and Blochinzev[5] on the basis of the Fermi-Thomas model. It seems to us, however, that it is dangerous to use the Fermi-Thomas model in this connection, because this model does not yield the metallic bond.[6]

(2)

The work function may be defined as the difference in energy between a lattice with an equal number of ions and electrons, and the lattice with the same number of ions, but with one electron removed. It is assumed in both cases that the lowest electronic states are completely filled, so that the electron is removed from the highest energy state of the neutral metal. It is necessary to specify the position of the electron after its removal from the lattice, because, in general, the work function is different

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[1] O. K. Rice, Phys. Rev. **44**, 318 (1933).

[2] A. Sommerfeld, Naturwiss. **15**, 825 (1927); **16**, 374 (1928).

[3] J. Frenkel, Zeits. f. Physik **49**, 31 (1928).

[4] See article by A. Sommerfeld and H. Bethe in the *Handbuch der Physik*, Vol. 24, Berlin, 1933, p. 424.

[5] J. Tamm and D. Blochinzev, Zeits. f. Physik **77**, 774 (1932).

[6] For a discussion of the Fermi-Thomas model as applied to the metallic state, see J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935).

for different crystallographic planes. We shall suppose that the electron is at a point in the neighborhood of a surface plane of the crystal, the distance from this plane being small compared with the dimensions of the plane, but large in comparison with atomic dimensions. We shall calculate this energy difference by calculating the energy $E(n_i, n_e)$ of a lattice with n_i ions and n_e electrons where we may suppose that $|n_i - n_e| \ll n_i$ so that effects connected with the finite capacity of the sample may be neglected. For the calculation of $E(n_i, n_e)$ we shall use the method of orbital wave functions. This method requires hardly any modification of the scheme[7] used for $n_i = n_e$, i.e., for uncharged metals.

There is only one important difference, that due to the electric double layer which the electron cloud and the ions may form on the surface of the metal.[8] These double layers are due to the fact that the electron distribution will not be symmetric around the surface ions, as it is around the inner ones. It will extend partly outside of the limits of the spheres surrounding the ions* of the surface, and in the inside of the spheres it will have partly greater, partly smaller densities than in the inner s spheres. This alteration of the charge density may result in double layers on the surface of the metal. The double layers will be such that they generate a constant potential inside the metal. The potential outside the metal, however, will not be constant, but will vary in such a way that the potential differences between the outer neighborhoods of differently oriented crystal surfaces will be equal to the differences in the moments of the double layers of the corresponding surfaces. These differences are revealed experimentally as the differences in the work functions of the different surface planes of the same crystal. This shows, conversely, that the double layer is of the same order of magnitude as these differences, i.e., around $\frac{1}{2}$ to 1 electron volt.[9]

The total energy of the lattice with n_i ions and n_e electrons can be considered as containing three parts: (1) the energy which the lattice would have if the surface ions were surrounded with the same symmetric charge distribution which prevails in the interior; (2) the energy change of the inner ions and electrons due to the double layer on the surface; (3) the energy of this double layer. We shall assume that the electron comes from the interior of the metal, i.e., that the double layer remains unchanged, and that the density of the electrons changes in the interior only. This is, strictly speaking, incorrect, as one can easily see that the density will be practically unchanged in the interior, and that the electron will come from the surface. The result for the work function cannot be incorrect in spite of this, because the energy required to move an electron from the surface to the interior of a metal is of a much smaller order of magnitude than the energy required to remove an electron from the metal (or, the work function). If the energy necessary to move an electron from the surface to the interior were appreciable, the electrons would have already rearranged themselves in the neutral metal. We shall omit in the final result the change in energy of the second and third part of $E(n_i, n_e)$. This is not allowable, of course, but this part of the work function is just equal to the moment of the double layer, and cannot be taken into account without an explicit calculation of the latter, which is reserved for a later paper by one of us.

(3)

We can now use for the calculation of $E(n_i, n_e)$ the scheme of reference 7. The kinetic energy of the ions will be neglected, so that the total energy contains three parts, $\frac{1}{2}\Sigma e_i V_i$ for the ions, $\frac{1}{2}\Sigma e_i V_i$ for the electrons, and the kinetic energy of the latter. The first part can be calculated as follows: First one assumes that the density of electrons everywhere, except in the s sphere of the ion under consideration, is as great as it would be if $n_e = n_i$. Then, the charges outside this s sphere will have no effect on our ion, because the potential of the electrons in every other s sphere will be nullified by the potential of the ion inside.[10] Only the double

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[7] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934) (I and II); E. Wigner, Phys. Rev. **46**, 1002 (1934) (III); F. Seitz, Phys. Rev. **47**, 400 (1935) (IV).

[8] J. Frenkel, Zeits. f. Physik **51**, 232 (1928).

* "s spheres," reference 7, II.

[9] H. E. Farnsworth and B. A. Rose, Nat. Acad. Sci. **19**, 777 (1935); B. A. Rose, Phys. Rev. **44**, 585 (1933).

[10] We neglect the small correction of Appendix 2, reference 7, II.

layer of the surface will be effective, and we obtain as the first contribution to the energy of the crystal:

$$n_i[(n_e/2n_i)\int|\psi|^2Vdv+\tfrac{1}{2}eD], \tag{1}$$

where V is the potential of the ion core, D is the moment of the double layer, and the integration must be extended over the s sphere of the ion. The factor n_i comes in, because we have n_i ions, the factor n_e/n_i because there are only that many electrons in the mean in the s sphere; (1) should still be averaged over the wave functions of the different free electrons. The fact that there are $((n_i-1)/n_i)(n_i-n_e)$ electrons missing outside the s sphere introduces a further correction:

$$\tfrac{1}{2}\Sigma e_j\Phi_j, \tag{1a}$$

where Φ_j is the potential of the missing electrons at the jth ion, and is of the order of magnitude $(n_i-n_e)e/R$ where R is a lateral dimension of the crystal.

The potential energy of the electrons is more complicated. First, again, we can supplement the missing electrons outside the s sphere in which our electron happens to be. The potential energy due to the nearest ion is $\frac{1}{2}V(r)$. To this the electron interaction energy must be added, which, if the charge distribution is assumed to be uniform, amounts to $(n_e/n_i)(3e^2/2r_s-e^2r^2/2r_s^3)$ where r_s is the radius of the s sphere. These two terms give, together with the contribution from the double layer, if averaged over all positions of the electron under consideration in the s sphere:

$$n_e[\tfrac{1}{2}\int|\psi|^2Vdv+0.6e^2n_e/n_ir_s-\tfrac{1}{2}eD] \tag{2}$$

with definitions similar to those used in (1). The electrons missing outside the s sphere, yield the following correction to the energy:

$$-(n_e/2n_i)\Sigma e\Phi_j. \tag{2a}$$

Next we must take into account the effects of the different holes. The Fermi hole (exchange energy) gives $-0.458e^2/r_s$ if $n_e=n_i$. One easily sees that r_s must be replaced by $(n_i/n_e)^{\frac{1}{3}}r_s$ if $n_e\neq n_i$. Similarly, if we denote by $r_sf(r_s)$ the correlation function,[11] the correlation energy for one electron is $-e^2f((n_i/n_e)^{\frac{1}{3}}r_s)$. The total contribution from these sources is:

$$-n_e[(0.458e^2/r_s)(n_e/n_i)^{\frac{1}{3}}+e^2f((n_i/n_e)^{\frac{1}{3}}r_s)]. \tag{3}$$

Finally, the kinetic energy of the electrons gives:

$$-(\hbar^2n_e/2m)\int\psi^*\Delta\psi dv, \tag{4}$$

which again should be averaged over the different free electron wave functions.

The energy of the double layer due to the electrons and ions inside the crystal is simply:

$$-\tfrac{1}{2}eD(n_e-n_i).$$

This energy will change, even though the double layer itself is unchanged.

If we add all these quantities together, (4) together with the first terms of (1) and (2) gives, because of the Schrödinger equation $-(\hbar^2/2m)\Delta\psi+V\psi=E\psi$ just n_eE, where still the mean value of E over all occupied states of the electrons must be taken. This gives the energy E_0 of the lowest free electron level, augmented by the mean value of the Fermi energy, F, i.e.,

$$n_e(E_0+F(n_e/n_i)^{\frac{2}{3}});$$

$$F=(9\pi/10)(3/2\pi)^{\frac{1}{3}}(R_y/r_s^2). \tag{5}$$

Thus the total energy is:

$$\begin{aligned}E(n_i, n_e)=&\,n_e(E_0+F(n_e/n_i)^{\frac{2}{3}})\\&+(n_e^2/n_i)(0.6e^2/r_s)+(1/2n_i)(n_i-n_e)\Sigma\Phi_j\\&-n_e[(0.458e^2/r_s)(n_e/n_i)^{\frac{1}{3}}+e^2f((n_i/n_e)^{\frac{1}{3}}r_s)]\\&-eD(n_e-n_i).\end{aligned} \tag{6}$$

(4)

The derivative of $E(n_i, n_e)$ at $n_i=n_e$ is the work function φ with the negative sign.

$$\begin{aligned}-\varphi=&\,E_0+5F/3+1.2e^2/r_s-(4/3)(0.458e^2/r_s)\\&-e^2f(r_s)+e^2r_sf'(r_s)/3-eD.\end{aligned} \tag{7}$$

The derivative of the sum in (6) tends to zero with increasing size of the crystal, and has therefore been omitted. If we omit the double layer term, and replace the Fermi energy by its value for free electrons, the only unknown quantity in (7) is E_0. One can express E_0 in terms of the ionization energy I, and the heat of

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[11] Represented by the lower curve, Fig. 7, reference 7, III.

TABLE I. *Work functions of the alkalis.*

Metal	r_s	$I+H$	F	$\varphi_{\text{calc.}}$	$\varphi_{\text{exp.}}$
Li	3.28	7.04	2.07	2.19	2.28[1]
Na	4.00	6.25	1.89	2.15	2.25[2] 2.46[1]
K	4.97	5.27	1.22	2.20	2.24[1] 2.24[3] 2.17[2]
Rb	5.32	5.03	1.07	2.20	2.19[3] 2.16[1]
Cs	5.73	4.70	.92	2.15	1.96[3] 1.87[1] 1.81[4]

[1] A. R. Olpin (see reference 13).
[2] Z. Berkes, Math. Phys. Lapok 41, 131 (1934).
[3] J. J. Brady, Phys. Rev. 41, 613 (1932).
[4] K. H. Kingdon, Phys. Rev. 25, 892 (1925).

sublimation, H,

$$I+H=-(\partial/\partial n_i)E(n_i,\,n_e)-(\partial/\partial n_e)E(n_i,\,n_e)$$
$$=-E_0-F-0.6e^2/r_s+0.458e^2/r_s+e^2f(r_s),\quad(8)$$

which, of course, is the result of reference 7. We have, from (7) and (8)

$$\varphi=I+H-\tfrac{2}{3}F-0.6e^2/r_s+0.458e^2/3r_s$$
$$-e^2r_sf'(r_s)/3+eD.\quad(9)$$

Table I gives the work functions of the alkalis as calculated from (9) under the assumption that $D=0$. The Fermi energy for Li was taken from the work of F. Seitz,[12] and the free electron values were used for the remaining metals. The check with the experimental values[13] is extremely good, considering the approximate nature of the theory, and shows that the double layer is probably small for these metals. The double layer may, however, give an important contribution to the work functions of other metals.

The solid curve of Fig. 1 gives the theoretical values of $I+H-\varphi$ in electron volts plotted against r_s in Bohr units. It is assumed that the Fermi energy has its classical free electron value, and that $D=0$. The light broken line connects the experimental values for the monovalent metals. Most of the discrepancy for Li ($r_s=3.28$) is accounted for by the deviation of the Fermi energy from its free electron value.[12] The experimental values of $I+H-\varphi$ for other than monovalent metals are also shown in Fig. 1. A calculation similar to the preceding one could be made for these metals by treating all valence electrons as free. The work function could then be obtained as the difference of quantities which are even greater than those for monovalent metals. One can obtain an orientation, however, by considering only one electron as free, the rest belonging to the "ion" core. There will then be two main modifications of the foregoing considerations. First, the Fermi energy will be even further from its classical value. It will in general be smaller than this if the levels of the last electron all belong to the same Brillouin zone; it may be greater or smaller if they extend over both sides of a gap between two zones. Second, a large part of the cohesion will be due to the interaction of the "ions." Thus in (9), only that part of the heat of sublimation should be inserted which results from the outermost electron. This correction is, indeed, in the right direction to bring the experimental points for these metals closer to the theoretical curve.

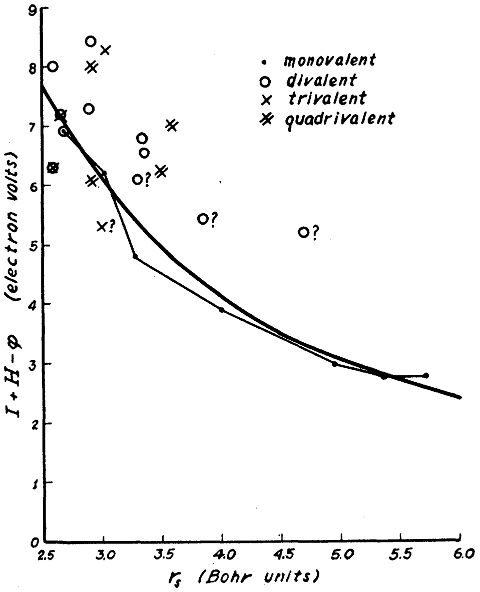

FIG. 1. Theoretical curve of $I+H-\varphi$ for monovalent metals, assuming no surface double layer. Broken line connects experimental values for these metals.

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[12] See reference 7, IV.

[13] For the experimental values of the work function, see A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, McGraw-Hill, 1932, p. 75. For the heats of sublimation, see J. Sherman, Chem. Rev. 11, 93 (1932).