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# Work functions of elements expressed in terms of the Fermi energy and the density of free electrons

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**Abstract.** On the basis of Brodie's definition of the work function and the length of spontaneous polarization of plasma, the following new formula for calculation of the work functions of elements has been derived:  $\phi/\text{eV} = 43.46\alpha r_s^{-3/2}(E_F/\text{eV})^{-1/2}$ , where  $r_s$  is the electron density parameter expressed in units of the Bohr radius,  $E_F$  is the Fermi energy and  $\alpha$  is an empirical constant ( $\alpha = 0.86$  for the alkali metals, Ca, Sr, Ba, Ra and Tl, whereas  $\alpha = 1.00$  for the remaining elements). The density parameter was calculated from the atomic mass, the bulk density of the element and the assessed number of free electrons per atom which is equal to the nominal valence of the element or, in the case of transition metals, close to this number (within  $\pm 0.5$ ).

The values obtained by using the above formula are in excellent agreement with experimental data for pure-metal polycrystalline surfaces, within 5% in most cases. A table with the work functions and with complete input data for most of the elements is presented.

## 1. Introduction

In the classical approach, the work function is defined as the smallest amount of energy that has to be given to an electron with the Fermi energy to enable it to be transported from the solid to the field-free region external to the surface, if the solid remains at 0 K and no electric fields are applied at the surface. The work function is a fundamental electronic property of a metallic surface, which is becoming increasingly useful in calculating corrosion rates, the yield of thermionic emission and spectral characteristics of photosensitive cells. Recently, it emerged that it is a very important value in scanning tunnelling microscopy. Therefore new accurate evaluations of the work functions for elements and alloys are very much needed.

A number of researchers have been interested in the calculation of work functions [1–5]. However, because one has to consider a large number of particles and the interactions between them in modelling the interface between the vacuum and the crystal, the *ab initio* methods that they used for calculating the work function, and other physical properties of crystalline solids, were both complex and time consuming. The technique most commonly used in calculations of electronic structures is the linear muffin-tin orbital (LMTO) method described by Sriver [6]. The results obtained by using the LMTO and other *ab initio* methods seem to be inconsistent with experimental data [4].

Recently, Brodie [3] redefined the idea of the work function, reducing it to the work done by an electron against the image forces. He expressed the work function in terms of the atomic radius, the Fermi energy and the effective mass of the electron. In this paper,

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we consider an entirely novel approach to the application of Brodie's definition, which is based on the concepts of plasma physics. The new formula derived below appears to be a fundamental relationship between the work function, the Fermi energy and the electron density parameter.

## 2. Derivation of the novel formula

It was long ago realized that the work done against forces acting between an electron emerging from a surface and its image charge contributes significantly to the work function for metals; see, e.g., [7]. In the case of a planar conducting surface kept at zero potential, the work required to remove an electron initially at a distance  $d_0$  to infinity is

$$W_{\text{image}} = \frac{e^2}{16\pi\epsilon_0 d_0} \quad (1)$$

where  $e$  is the elementary charge and  $\epsilon_0$  is the permittivity of vacuum. Formula (1) is applied in evaluation of the reduction of the work-function value that occurs when an external homogeneous electric field is acting between a planar metal surface and a remote anode (see reference [8], for example).

Recently, Brodie [3] has postulated that the minimum distance  $d_0$  at which the image force begins to act may be calculated on the basis of the uncertainty principle:

$$d_0 = \frac{\hbar}{\sqrt{2m^*E_F}} \quad (2)$$

where  $\hbar$  is Planck's constant,  $m^*$  is the effective mass of the electron and  $E_F$  is the kinetic Fermi energy. Identifying  $W_{\text{image}}$  with the work function,  $\varphi$ , one obtains values of  $\varphi$  that are systematically too high on the basis of equations (1) and (2). This discrepancy led Brodie to reconsider the work function as  $W_{\text{image}}$ , due to the interaction of the electron with the individual surface atoms, treated as spherical conducting balls [3].

In this paper we return to formula (1), which holds for planar surfaces, but formula (2) will no longer be used for the evaluation of the  $d_0$ -value. Instead, we recall some basic formulae from plasma physics, such as those for the length of spontaneous polarization and the screening length. The necessary modifications of these formulae will be made to make them applicable to a 'plasma' constituted of free electrons and ions in a metal lattice.

Locally, plasma can spontaneously polarize itself, which means that electrons are somewhat shifted against ions. The polarization requires energy, which in the case of gaseous plasma is derived from the thermal energy, i.e. the average kinetic energy per one degree of translational motion,  $\frac{1}{2}kT$ . In the case of free electrons in metals, such polarization can be produced only at the expense of a reduction in the kinetic energy of the electrons. Locally, the maximum possible gain of energy at 0 K is equal to the Fermi energy,  $E_F$ . At finite temperatures, this energy is defined with a precision of  $kT$ ; hence its relative uncertainty is  $kT/E_F$ , which is of the order of 1% at room temperatures, and 10% at the melting points of most refractory metals. The polarization length in a metal may be evaluated by replacing  $\frac{1}{2}kT$  by  $E_F$  in the classical formula from plasma physics; see reference [9], for example. This replacement leads to the expression

$$d = \sqrt{\frac{2\epsilon_0 E_F}{ne^2}} \quad (3)$$

where  $\epsilon_0$  is the permittivity of vacuum,  $n$  is the average density of free electrons in a metal lattice and  $e$  is the elementary charge.

Let us compare the  $d$ -value with the Thomas–Fermi screening length, which corresponds to the Debye length in plasma physics (see, e.g., reference [10]):

$$D = \sqrt{\frac{2\varepsilon_0 E_F}{3ne^2}}. \quad (4)$$

One can see that  $D = d/\sqrt{3}$ ; hence the ion is completely screened at a distance somewhat larger than  $d$  [10]. It should be emphasized that both the ion screening and the image forces appear due to the displacement of an electron from its average position. Therefore, we assume that when an electron is shifted from a remote plane (where, under normal conditions, the electron density tends to zero) by  $d_0 = d/\alpha$ , where  $\alpha$  is a factor of the order of unity and  $d$  is given by equation (3), the ‘mother’ ion is completely screened, whilst the image forces are just starting to act. In this way, the work function is calculated from formula (1), in which  $d_0 = d/\alpha$ . Before doing this calculation, let us rewrite formula (1) in a more convenient form:

$$\varphi = \frac{\alpha}{2} \frac{e^2}{8\pi\varepsilon_0 a_0} \frac{a_0}{d} = \frac{\alpha}{2} \text{Ryd} / \left( \frac{d}{a_0} \right) \quad (5)$$

where  $a_0$  is the Bohr radius (0.529 18 Å); the rydberg is the atomic unit of energy (1 Ryd = 13.6058 eV). The  $d$ -value is calculated using formula (3), in which the free-electron density,  $n$ , is replaced by the density parameter,  $r_s$ , defined as follows [11]:

$$\frac{1}{n} = \frac{4}{3}\pi r_s^3.$$

Now, formula (3) can be rewritten in the following way:

$$d = \sqrt{\frac{2\varepsilon_0 E_F \frac{4}{3}\pi r_s^3}{e^2}} = \sqrt{\frac{E_F}{\frac{1}{2}(e^2/4\pi\varepsilon_0 a_0)} \frac{r_s^3}{3a_0}} = \frac{a_0}{\sqrt{3}} \left( \frac{E_F}{\text{Ryd}} \right)^{1/2} \left( \frac{r_s}{a_0} \right)^{3/2}. \quad (6)$$

When this formula is substituted into (5), one obtains

$$\varphi = \frac{\alpha\sqrt{3}}{2} \text{Ryd} \left( \frac{E_F}{\text{Ryd}} \right)^{-1/2} \left( \frac{r_s}{a_0} \right)^{-3/2}. \quad (7)$$

For practical calculations, formula (7) may be rewritten in the form

$$\varphi/\text{eV} = \frac{11.783\alpha}{r_s^{3/2}(E_F/\text{Ryd})^{1/2}} = \frac{43.46\alpha}{r_s^{3/2}(E_F/\text{eV})^{1/2}} \quad (8)$$

where  $r_s$  is expressed in atomic units (Bohr radii). One can see that the work function is now expressed in terms of the density parameter,  $r_s$ , and the kinetic Fermi energy,  $E_F$ . The scaling factor  $\alpha$  was assumed to be equal to unity for all elements except the alkali metals, Ca, Sr, Ba, Ra and Tl, for which it was assumed to be equal to 0.86. In this paper the  $\alpha$ -factor is treated as just an empirical constant, which can probably be estimated theoretically; see the discussion section.

### 3. Results

The work function has been calculated for each element of the periodic table for which  $E_F$ -values were available. It should be noted that the error in the  $E_F$ -value is less critical than that in  $r_s$ , because it propagates to  $\varphi$  with the factor of  $\frac{1}{2}$ . Evaluation of  $r_s$  is critical, since it appears in formula (8) to the power of  $\frac{3}{2}$ , and because in many cases it was difficult

**Table 1.** Input values and the results of calculations.  $E_F$ -values below unity are expressed in rydbergs; the data are taken from reference [17] if not stated otherwise in the ‘Remarks’ column. The accepted values of  $\varphi$ ,  $A$  and  $\rho$  are taken from the *CRC Handbook* [12]. Key to ‘Remarks’ column: ‘ZOA’  $\equiv$  zero-order approximation used in the  $E_F$ -estimation, after reference [11]; ‘F’  $\equiv$  formula (8) used for the  $E_F$ -estimation; ‘Extrapolated’  $\equiv$  an extrapolated  $E_F$ -value was used in the  $\varphi$ -estimation; ‘Interpolated’  $\equiv$  an interpolated  $E_F$ -value was used in the  $\varphi$ -estimation.

Element	$A$	$\rho$ (g cm <sup>-3</sup> )	$z$	$r_s/a_0$	$E_F$ (eV)	$\varphi$ /eV		$\delta\varphi/\varphi$	Remarks
						Calculated	Accepted		
Li	6.94	0.534	1	3.26	4.74	2.92	2.9	0.00	ZOA
Na	22.99	0.9712	1	3.99	3.24	2.61	2.75	-0.05	ZOA
K	39.10	0.862	1	4.95	2.12	2.33	2.30	0.01	ZOA
Rb	85.74	1.533	1	5.31	1.85	2.25	2.16	0.04	ZOA
Cs	132.91	1.873	1	5.75	1.59	2.15	2.14	0.00	ZOA
Fr	223.02	2.6	1	6.12	1.5	2.0	—	—	Extrapolated
Be	9.012	1.852	2	1.87	12.0	4.91	4.98	-0.01	Reference [16]
Mg	24.312	1.745	2	2.65	7.1	3.77	3.66	0.03	ZOA
Ca	40.08	1.54	2	3.26	5.20	2.78	2.87	-0.03	
Sr	87.62	2.62	2	3.55	4.49	2.64	2.59	0.02	
Ba	137.33	3.512	2	3.73	3.84	2.65	2.7	-0.02	
Ra	226.025	5.0	2	3.92	3.0	2.8	—	—	Extrapolated
Sc	44.956	2.989	2	2.72	7.54	3.53	3.5	0.00	
Y	88.905	4.469	2	2.99	6.88	3.20	3.1	0.03	
La	138.91	6.15	2.5	2.89	6.10	3.58	3.5	0.02	
Ac	227	10.07	2.5	2.89	6.1	3.58	—	—	Extrapolated
Ti	47.90	4.54	2.5	2.24	8.84	4.36	4.33	0.00	
Zr	91.22	6.44	3	2.33	8.50	4.19	4.05	0.04	
Hf	178.49	13.312	2.5	2.43	8.69	3.89	3.9	0.00	
V	50.941	5.96	2.5	2.09	11.09	4.32	4.3	0.00	
Nb	92.906	8.57	3	2.13	10.82	4.25	4.3	-0.01	
Ta	180.948	16.6	3	2.13	10.19	4.37	4.25	0.03	
Cr	52.00	7.203	2.5	1.98	11.95	4.51	4.5	0.00	
Mo	95.94	10.22	3	2.03	11.36	4.46	4.6	-0.03	
W	183.85	19.352	3	2.04	11.47	4.41	4.55	-0.03	
Mn	54.938	7.20	2.5	2.01	12.2	4.37	4.1	0.03	
Tc	98.906	11.50	3	1.97	10.9	4.8	—	—	Interpolated
Re	186.2	20.53	3	2.01	10.9	4.62	4.72	-0.02	
Fe	55.85	7.90	2.5	1.96	11.81	4.61	4.5	0.02	
Ru	101.07	12.06	3	1.96	10.82	4.81	4.71	0.03	
Os	190.20	22.5	3	1.97	11.06	4.73	4.83	-0.01	
Co	58.93	8.71	2.5	1.93	10.52	5.00	5.0	0.00	
Rh	102.91	12.44	2.5	2.07	9.26	4.80	4.98	-0.04	
Ir	192.22	22.42	3.5	1.87	10.26	5.31	5.27	0.00	
Ni	58.71	8.90	2.5	1.92	9.66	5.26	5.15	0.02	
Pd	106.40	12.022	2.5	2.12	7.69	5.08	5.12	-0.01	
Pt	195.09	21.452	3.5	1.91	8.79	5.55	5.65	-0.02	
Cu	63.555	8.92	2	2.12	9.03	4.69	4.65	0.01	
Ag	107.868	10.52	2	2.39	7.48	4.30	4.26	0.01	
Au	196.97	19.296	2.5	2.22	7.25	4.88	5.1	-0.04	

Table 1. Continued.

Element	A	$\rho$ (g cm <sup>-3</sup> )	z	$r_s/a_0$	$E_F$ (eV)	$\varphi$ /eV		$\delta\varphi/\varphi$	Remarks
						Calculated	Accepted		
Zn	65.39	7.19	2	2.30	8.65	4.24	4.33	-0.02	
Cd	112.40	8.67	2	2.59	6.45	4.11	4.22	-0.03	
Hg	200.59	13.546	2.5	2.51	5.66	4.59	4.49	0.02	
B	10.81	2.34	2	1.84	15.4	4.44	4.45		F
Al	26.98	2.699	3	2.07	11.3	4.34	4.28	-0.01	Reference [8]
Ga	69.72	5.903	3	2.19	10.4	4.16	4.2	0.00	ZOA
In	114.82	7.28	3	2.41	8.6	4.0	4.12	-0.04	ZOA
Tl	204.37	11.85	3	2.49	6.0	3.88	3.84	0.01	
C	12.01	2.252	2	1.93	10.5	5.0	5.0		Graphite, F
Si	28.09	2.34	4	2.00	12.5	4.35	4.85	-0.11	Reference [8]
Ge	72.59	5.35	4	2.09	13.0	4.00	5.0	-0.25	Reference [8]
Sn	118.69	7.28	4	2.22	10.2	4.1	4.42	-0.07	ZOA
Pb	207.19	11.343	4	2.30	9.5	4.0	4.25	-0.05	ZOA
As	74.922	5.727	5	1.91	11.9	4.77	5.11 <sup>a</sup>	-0.07	Extrapolated
Sb	121.75	6.684	5	2.14	10.9	4.2	4.55	-0.08	ZOA
Bi	208.98	9.80	5	2.25	9.9	4.1	4.22	-0.03	ZOA
Se	78.96	4.812	6	1.94	7.5	5.9	5.9		F
Te	127.60	6.00	6	2.12	8.0	5.0	4.95		F
Po	210.05	8.8	6	2.20	7.0	5.0	—		Extrapolated

<sup>a</sup> Reference [18].

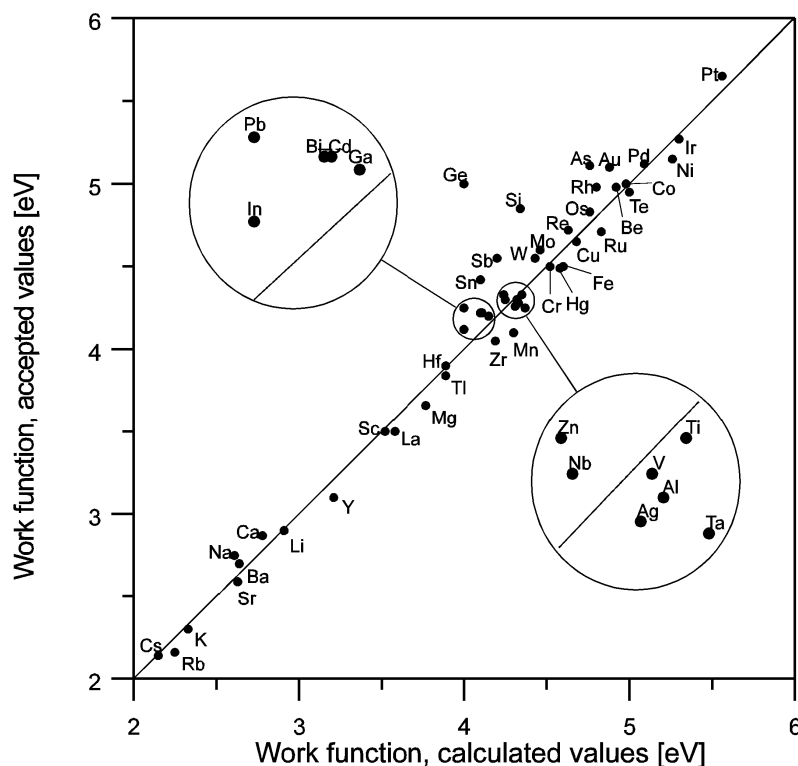
to estimate how many of the valence electrons (per atom) may be treated as free electrons. We calculated  $r_s$  from the following formula [11]:

$$r_s = 1.3882 a_0 \left( \frac{A}{z\rho} \right)^{1/3} \quad (9)$$

where  $a_0$  is the Bohr radius,  $A$  is the atomic mass given in grams,  $\rho$  is the bulk element density at 300 K in g cm<sup>-3</sup> (both of these latter values were taken from the *CRC Handbook* [12]) and  $z$  is the number of free electrons per atom.

It follows from formulae (8) and (9) that the error in the  $z$ -value propagates to  $\varphi$  with a factor of  $\frac{1}{2}$ . Therefore the maximum error in  $\varphi$  for the transition metals due to uncertainty in the  $z$ -value (assuming that  $\Delta z = \pm 0.5$ ) may be estimated as 12 and 8% for  $z = 2$  and 3, respectively. By careful selection of  $z$ , with the help of the periodic table, this error can be reduced by at least a factor of  $\frac{1}{2}$ . The remaining input values in formula (9),  $A$  and  $\rho$ , are known with high precision. The input data  $A$ ,  $\rho$  and  $z$ , together with  $r_s$ ,  $E_F$ ,  $\varphi$  calculated using formula (8) and  $\varphi$  accepted on the basis of experimental determinations, are given in table 1. In the penultimate column the relative differences between the calculated and accepted values are given. The accepted values were taken, if not stated otherwise, from the *CRC Handbook*.

Despite some difficulties being encountered in the selection of  $z$ -value, the results obtained are in excellent agreement with the accepted experimental  $\varphi$ -values for polycrystalline surfaces. The relative difference between the calculated and accepted values rarely exceeds 5% (see table 1). The agreement of  $\varphi$  with accepted values is much better than that obtained previously by LMTO methods [2] or by using Brodie's approach [3]. The comparison of the calculated values with the experimental data is also shown in figure 1.



**Figure 1.** Comparison of calculated and accepted work functions of the elements for which data on the Fermi energy were available to the authors.

Because the density parameter changes monotonically within groups of elements, we have used this property for extrapolation and interpolation purposes in the cases where insufficient data were available. The extrapolation was applied for Fr, Ra and Po. On the basis of the extrapolated  $r_s$ -values and atomic masses, the estimation of their densities was possible. Moreover, extrapolation of the Fermi energy, which also changes in a regular fashion, enables the work functions to be estimated. In similar way, the interpolation procedure was applied to Tc. These values are listed in table 1 in *italics*, to indicate that they are less well substantiated than the remaining data.

#### 4. Discussion

As was stated above, the selection of  $z$  is not a trivial task. This is particularly the case for the transition metals, where the hybridization of  $s$  and  $d$  orbitals may explain some departures of the  $z$ -value from the nominal valence. Our best selection is shown again, together with calculated  $r_s$ -values, in the format of a periodic table which is usually used for displaying the electronic configurations of atoms (table 2). One can see that in several cases fractional numbers were used. Use of fractional numbers for  $z$  leads to a smoothing of the  $r_s$ -values among groups and to better agreement of the calculated  $\varphi$ -values with experimental data.

The next point, which would merit further study, is the evaluation of the scaling constant,  $\alpha$ . This defines the fraction of the polarization length from which the integration of the

image force should be done:

$$\varphi = W_{\text{image}} = \int_{d/\alpha}^{\infty} \frac{e^2}{4\pi\epsilon_0(2r)^2} dr \quad (10)$$

where  $d$  is defined by formula (3). The integration leads to formula (1) and, in consequence, to formula (8) for the calculation of the work function in which the scaling factor appears.

Initially in this study, we assumed  $\alpha = 1$  for all of the elements for which data on  $E_F$  are available. However, we noticed that the values for the alkali metals and heavier alkaline-earth metals significantly depart from the plot of calculated versus accepted work functions. Fortunately, these elements and Tl were found to be shifted to the ‘line of agreement’ (figure 1) by multiplying the calculated values by a common factor of  $\alpha = 0.86$ . Since all of these metals are weakly bound, we assume that the common factor 0.86 may be evaluated theoretically. In the case of weak binding of atoms in the crystal lattice, this does not lead to a substantial change in the interlayer distance between the first and second layer of atoms. Therefore we may use the bulk element density in the  $r_s$ -calculation (formula (9)). For the remaining elements, however, we cannot ignore the interatomic forces, which lead to some increase of the surface density—by about 10%. Such a conclusion is in accordance with data on the relaxation of the topmost interlayer spacing (see, e.g., chapter 19 in reference [10]).

For a comparison of the present approach with the traditional theories for the work function, let us calculate the value of  $d/\alpha$  from equation (5):

$$b = d/(\alpha a_0) = \frac{13.61 \text{ eV}}{2\varphi}. \quad (11)$$

According to this formula, for  $\varphi$  ranging from 2 to 5 eV, the corresponding  $b$ -value varies from 3.4 to 1.4, respectively (table 3). Most of the calculations of the electron density profiles were done using the jellium model, which is a good approximation in the case of simple metals. The calculated profiles are cut off at a distance of  $0.5 \lambda_F$ , i.e. half of the Fermi wavelength [13];  $\lambda_F = 2\pi/k_F$ , where  $k_F$  is the Fermi momentum expressed in atomic units. From the Sommerfeld theory,  $k_F$  may be related to the  $r_s$ -value as follows:

$$k_F = \frac{1.919}{r_s}. \quad (12)$$

Hence  $\lambda_F = 2\pi 0.521 r_s/a_0$ . Taking the  $r_s$ -values for the alkali metals from table 1, one obtains the cut-off lengths of the electron density profiles. These values may be compared with the  $b$ -values. As is seen from table 3, these values represent a nearly constant fraction of the cut-off length of the electron density. A similar fraction is obtained for the Al(111) surface on the basis of density profiles calculated by Chelikowski *et al* [14] and using equation (11).

It is very tempting to conclude from the above comparisons that the work function is controlled as much by the range of the density profile (the cut-off value) as by the length of polarization,  $d$ , scaled by the factor  $\alpha$ . The values of the sum  $a + b$  given in table 4 are always double the values of the covalency radius,  $R$ . In the case of Al, the distance  $a + b$  is measured from the plane of the surface atom nuclei, while in the remaining cases it is measured from the edge of the positive background (in jellium model terminology). The influence of the dipole barrier which forms at the metal surface [19] seems to be negligible at the distance  $a + b$ , because the strength of the electric field decays rapidly (with  $r^{-3}$ , where  $r$  is the distance from the dipole centre). However, this barrier may modify our  $d$ -value by a factor slightly different from unity.

As was estimated above, at the distance  $a + b$  the ‘mother ion’ on the metal surface is completely screened by electrons. If an electron emerges beyond this distance, then image forces are induced. We assume that, starting from this point, the classical Coulomb formula may be used. The origin of the image potential and the limitations of the classical picture are thoroughly discussed by Kiejna and Wojciechowski in chapter 12 of their monograph [20]. It follows from that discussion that at large distances (above  $10 \lambda_F$ ) the classical formula derived from the Coulomb law is in rather good agreement with recent quantum mechanical calculations. For smaller distances, the quantum mechanical curve may depart substantially or negligibly (depending on the assumptions and methods used) from the classical one. A discrepancy between these curves for small distances may be corrected by using a common (universal) factor, because the theoretical curves are plotted versus distance expressed in Fermi wavelengths,  $\lambda_F$ , rather than in fixed units like ångströms or  $a_0$ . Such correction seems to be possible, because our  $d$ -values are also related to  $\lambda_F$ . A detailed discussion of this problem is beyond the scope of this paper. For the moment, the excellent agreement between the experimentally determined  $\varphi$ -values and those calculated here may be considered as proof that  $\varphi$  does indeed equal the work done against the image forces.

Table 2. Continued.

	s <sup>1</sup>	s <sup>2</sup>	p	p <sup>2</sup>	p <sup>3</sup>	p <sup>4</sup>	p <sup>5</sup>	p <sup>6</sup>	d <sup>1</sup>	d <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	d <sup>10</sup>
5s, 4d	1 Rb	2 Sr						5s <sup>0</sup>										2.5 Pd
	5.31	3.55						5s <sup>1</sup>				3 Nb	3 Mo		3 Ru	2.5 Rh		2 Ag
								5s <sup>2</sup>	2 Y	3 Zr			3 Tc		1.96 Ru	2.07 Rh		2.39 Cd
									2.99	2.33			1.97					2.59
5p			3 In	4 Sn	5 Sb	6 Te	I	Xe										
			2.41	2.22	2.14	2.12												
6s, 4f, 5d	1 Cs	2 Ba						6s <sup>1</sup>									3.5 Pt	2.5 Au
	5.75	3.73						6s <sup>2</sup>	2.5 La	2.5 Hf	3 Ta	3 W	3 Re	3 Os	3.5 Ir		1.91 Pt	2.22 Au
									2.89	2.43	2.13	2.04	2.01	1.97	1.87			2.51
6p			3 Tl	4 Pb	5 Bi	6 Po	At	Rn										
			2.49	2.30	2.25	2.20												
7s, 5f, 6d	1 Fr	2 Ra						7s <sup>1</sup>										
	6.12	3.92						7s <sup>2</sup>	2.5 Ac									
									2.89									

The plot in figure 1 reveals that the agreement in the case of semiconductors (Ge, Si) is not as good as that for metals; the calculated values are clearly too low. This discrepancy may be explained in the framework of the present model as follows. The valence electrons in semiconductors are strongly localized as a result of the covalent bonding of the atoms. Therefore the efficiency of the screening by the valence electrons is very poor. In consequence, an electron emerging at distances up to  $d/\alpha$  is not totally screened from the mother ion. Hence, the work required to remove an electron from this distance to infinity is higher than that calculated using formula (8), which was derived under the assumption of total screening.

It is also worth discussing the dependence of the work function on the density parameter for polycrystalline metals. The calculated values are plotted versus  $r_s$  in figure 2. This relationship can be explained simply, by noting that  $E_F$  in Sommerfeld's zero-order

**Table 3.** The distance at which the image forces start to act, expressed in Bohr radii and in ångströms.

$\varphi/\text{eV}$	$d/(\alpha a_0)$	$d/(\alpha \text{ Å})$
2.00	3.40	1.79
3.00	2.26	1.20
4.00	1.70	0.90
5.00	1.36	0.72

**Table 4.** A comparison of the cut-off lengths of the electron density profiles,  $a = 0.5 \lambda_F/a_0$ , with the values of  $b = d/(\alpha a_0)$  for simple metals;  $R$  is the covalency radius.

Element	$a$	$b$	$b/a$	$a + b$	$R/a_0^a$
Li	5.33	2.34	0.44	7.67	2.65
Na	6.53	2.47	0.38	9.00	2.91
K	8.10	2.96	0.37	11.06	3.74
Rb	8.69	3.15	0.36	11.84	4.15
Cs	9.41	3.18	0.34	12.59	5.00
Al(111)	3.39 <sup>b</sup>	1.59	0.44	4.98	2.46

<sup>a</sup> Reference [14].<sup>b</sup> Reference [21].

approximation can be expressed solely in terms of the  $r_s$ -value, as follows:

$$E_F = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}. \quad (13)$$

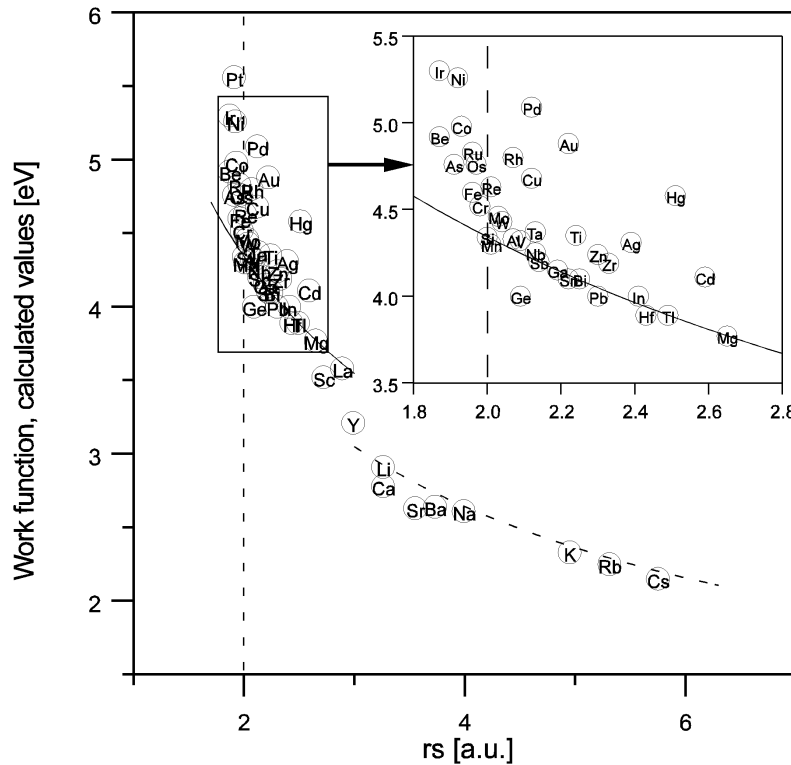
Hence, according to formula (8), the functional dependence  $\varphi(r_s)$  is given by

$$\varphi/\text{eV} = 6.15\alpha \left( \frac{r_s}{a_0} \right)^{-1/2}. \quad (14)$$

The curves calculated according to equation (14) with  $\alpha = 0.86$  and  $\alpha = 1$  are plotted in figure 2. The plot for the group of alkali metals, Ca, Mg, Sr and Ba, fits the experimental data fairly well. For the other elements, however, there are large departures from this relationship, which can be attributed to the complexity of their electronic structures. Recently, a similar relationship between  $r_s$  and the work function was obtained in the framework of ideal-metal theory [15].

## 5. Conclusions

1. We have derived a new formula which seems to be a fundamental relationship between the work function, the Fermi energy and the electron density parameter. Its applicability has been demonstrated for metals and semimetals, but not for semiconductors, for which the calculated values are too low due to low screening efficiency.
2. The present model is based on the definition of the work function (initially applied by Brodie) in which it is identified with the work done against image forces only. We estimated that excursions of an electron beyond the cut-off of the electron density profile (at about 40% of its extent) may be achieved entirely at the expense of loss of Fermi energy.



**Figure 2.** A plot of calculated work functions versus the density parameter. The curves were calculated using equation (14) for  $\alpha = 1$  (solid curve) and  $\alpha = 0.86$  (broken curve).

3. The agreement obtained in this study between the calculated work functions and the best experimental values is much better than what has been achieved so far by using LMTO methods or Brodie's approach.
4. By extrapolation (or interpolation) of the regularly varying electron density parameter among the groups of elements, and by the use of the new formula, it was possible to estimate the work functions for Fr, Po, Ra and Tc.

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