

Comparison of Calculated Work Function of Metals Using Metallic Plasma Model with Stabilized Jellium, Ab-Initio Approach and Experimental Values

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Received: January 28, 2011 Accepted: February 14, 2011 Published: November 1, 2011

doi:10.5539/apr.v3n2p171

URL: <http://dx.doi.org/10.5539/apr.v3n2p171>

Abstract

The work function of metals was calculated using the metallic plasma model (MPM). The results obtained were compared with the available results of the stabilized jellium model (SJM), *Ab-initio* model and the experimental values. Result shows that the stabilized jellium model was in good agreement with experimental values for the simple metals, the transition, inner transition and rare-earth metals. The metallic plasma model gave results that are agreeable with experimental values for most of the metals especially the polycrystalline metals. The *ab-initio* results were higher than experimental values except for Ba, Ca and Sr, this shows that the metallic plasma model is more reliable in predicting the work function of metals.

Keywords: Metallic plasma model, Stabilized jellium model, Ab-initio model, Metallic surfaces, Work function, Electron density parameter

1. Introduction

Work function (W_f) is the minimum energy required to extract an electron from a crystal. It is essential in the determination of the physical and chemical properties of metallic surfaces. It is an intrinsic parameter which is affected by atomic arrangement in the metal and inter-atomic distances within the metal and very vital in understanding some surface phenomena such as the calculation of corrosion rates, properties of materials for light emitting and photosensitive devices (Halas, S. 2006, P. 951-968 and Michaelson H.B, 1977 P. 4729-4733). W_f can be measured absolutely using thermionic emission, photoelectric emission and field emission. It can also be measured relatively using the retarding potential and vibrating capacitor methods (Hudson J.B, 1992, P. 250-305). Measurement of work function is improving with advancement in technology and development of better methods of measurement (Yoshitake M and Yoshitake K, 2006 P. 144 and Nishiyama H and Inoue Y, 2006 P. 2644-2659).

Much attention has been paid to the theoretical study of work function. The first theory proposed for the work function of metals and the self-consistent many-electron calculation of the work function of metals from first principles within the free electron model produced results that were not in good agreement with experimental values (Wigner E. and Bardeen, J. 1935, P. 84-87 and Smith, J.R. 1969, P. 522-529). Lang and Kohn (Lang, N.D and Kohn.W. 1971 P. 1215-1223) developed the theory of work function of metals based on the jellium model. In the jellium model, the ionic point charges are replaced by a semi-infinite distribution of constant positive charges. The work function of metals was calculated by solving the Kohn-Sham equation self-consistently using the kinetic, exchange, and correlation energies based on the local density approximation. The results were only in good agreement with experimental values for some simple metals (Lang N.D and Kohn.W. 1970, P. 4555-4567). Mahan and Schaich (Mahan, G.D and Schaich, W.L. 1974, P. 2647-2651) also derived another formula for calculating work function based on the jellium model, which is an improvement to the formula of Lang and Kohn. The formula showed that work function might be related to the ground state energy per electron of the bulk metal. Work functions of Al, Li, Na, Mg, Pb, and Zn calculated using density functional theory of the inhomogeneous electron gas were not in good agreement with experimental values (Monnier R., Perdew, J.P., Langreth, D.C. and Wilkins, J.W. 1978, P. 656-66).

The stabilized jellium model (SJM) was developed by Perdew *et al* (Perdew, J.P., Tran, H.Q. and Smith, E.D. 1990 P.11627-11636). It evolved from the variational self-consistent method of the ground state properties of metals (Monnier R., Perdew, J.P., Langreth, D.C. and Wilkins, J.W. 1978, P. 656-66). The model has all the properties of the jellium model with an additional constant potential to the effective potential of the metal. Recently, Brodie (Brodie I 1995, P. 13660.) redefined the work function idea by reducing it to the work done by an electron against the image forces, expressing the work function in terms of the atomic radius, the Fermi energy and the effective mass of the electron.

In this work, a fundamental relationship between the work function, the Fermi energy and the electron density parameter is established taking the entire novel approach to the application of plasma physics concept. The results obtained were compared with the results obtained from other models like the pseudopotential (SJM), Ab-initio method as well as experimental values.

2. Theoretical Consideration

The work done against forces acting between an electron emerging from a metal surface and its image contributes significantly to the work function of the metal (Jackson J.D 1975, P. 179. For a planar conducting surface at zero potential, the work required to take an electron initially at a distance d_0 to infinity (Halas, S, T.Durakiewicz 1998, P.10815-10826) is

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

where e is the electronic charge and ϵ_0 is the permittivity of free space.

The polarization length in a metal may be evaluated by replacing $\frac{1}{2}kT$ by E_F in the classical formula for distance d , from plasma physics (Ibach, H. 1997, P. 193-263) by

$$d = \sqrt{\frac{2\varepsilon_0 E_F}{ne^2}} \quad (2)$$

n is the average density of free electrons in a metal lattice and e is the electronic charge.

Comparing the d -value with Thomas-Fermi screening length, equation 2 corresponds to Debye length in plasma physics (Kittel C. 1996, P. 235-236);

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

It can be seen that $D = d/\sqrt{3}$ hence the ion is completely screened at a distance somewhat larger than d (Kittel C. 1996, P. 235-236). 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 $d_0 = \frac{d}{\alpha}$ where α is a factor of the order of unity and d is given by equation (2), the ion is completely screened, whilst the image force are just starting to act.

By substituting $d_0 = \frac{d}{\alpha}$ and rewriting the equation (1) we have:

$$\varphi = \frac{1}{2} \frac{e^2}{8\pi\varepsilon_0 a_0} \frac{a_0}{d} = \frac{\alpha}{2} Ryd \left/ \left(\frac{d}{d_0} \right) \right. \quad (4)$$

where a_0 is the Bohr radius (0.52918 \AA), the Rydberg is the atomic unit of energy ($Ryd = 13.605 eV$). The d -value is calculated using equation (2), in which the free-electron density n , is replaced by the density parameter r_s defined as follows (Ashcroft N.W and Mermin N.D 1976, P. 345-368)

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

and Fermi Energy $E_F = \frac{1.84}{r_s^2}$ hartree.

Equation (2) can be rewritten as:

$$d = \sqrt{\frac{2\varepsilon_0 E_F \frac{4}{3} \pi r_s^3}{e^2}} = \sqrt{\frac{E_F}{\frac{1}{2} \left(\frac{e^2}{4\pi\varepsilon_0 a_0} \right)} \frac{r_s^3}{3a_0}} = \frac{a_0}{\sqrt{3}} \left(\frac{E_F}{Ryd} \right)^{1/2} \left(\frac{r_s}{a_0} \right)^{3/2} \quad (5)$$

Substituting equation (5) into equation (4) gives:

$$\varphi = \frac{\alpha\sqrt{3}}{2} Ryd \left(\frac{E_F}{Ryd} \right)^{-1/2} \left(\frac{r_s}{a_0} \right)^{-3/2} \quad (6)$$

The work function of elements in terms of Fermi energy E_F and electron density parameter r_s is expressed as.

$$\phi/eV = \frac{11.78\alpha}{r_s^{3/2} \left(E_F/Ryd \right)^{1/2}} = \frac{43.46\alpha}{r_s^{3/2} \left(E_F/eV \right)^{1/2}} \quad (7)$$

where r_s is Bohr radii, E_F is Fermi energy. The scaling factor α which defines the fraction of the polarization length from which the integration of the image force should be done was assumed to be equal to unity (Halas, S, T.Durakiewicz 1998, P.10815-10826) for all elements except the alkali metals, Ca, Sr, Ba, Ra and Tl, for which it was assumed to be equal to 0.86, the factor is treated as just an empirical constant. The equation (7) is the metallic plasma model (MPM) that was employed in this work to evaluate work function of metals.

3. Results and Discussion

The work function of metal that was calculated in this work using MPM was compared with those of SJM, *Ab-initio* model and experimental values reported in other papers. These results are presented in Table 1. Figure 1 shows the comparison of the MPM results and experimental values with electron density parameter. The MPM obtained results are in excellent agreement with the experimental work function values for pure-metal polycrystalline surfaces. The agreement in the case of semiconductors (Ge, Si) is not as good as that of metals as the values are clearly too low. This may be due to the fact that the valence electrons in semiconductors are strongly localized as a result of covalent bonding of the atoms, thereby making the efficiency of the screening by the valence electron poor. However, for the alkali metals, Ca, Mg, Sr and Ba, results fit fairly well with the experimental values.

For some metals, there are large departures from this relationship which could also be attributed to the complexity of their electronic structures. Figure 2 shows the Comparison of SJM and experimental Values with electron density parameter as seen from (Osiele, O.M. and Olubosedede, O. 2007, P. 9-16.). SJM agrees well with metals in the low density limit but not too accurate in the high density limit. This limitation of SJM is well observed in the high-density limit, $r_s \leq 3.0 \text{ au}$ where the agreement with the experimental values decreases with decrease in the electron density parameter. This may be due to the fact that the simple metals are in the low-density limit. In addition, the properties of non-simple metals are affected by band structure and crystal structure, which the SJM does not put into consideration. However, SJM conformed with the experimental values in the low density region $r_s \geq 3.0 \text{ au}$. Figure 3 shows the comparison of *Ab-initio* method and experimental values with electron density parameter. In this derived figure, *Ab-initio* results were all higher than the experimental values except in Ba Ca and Sr. For all the methods, the calculated work function value reduces with an increase in electron density parameter.

4. Conclusion

The MPM used in this work is a new formula which shows the relationship of the work function, Fermi energy as well as the electron density parameter. In this paper, the MPM has been successfully compared with the SJM (Osiele, O.M. and Olubosedede, O. 2007, P. 9-16.), *Ab-initio* (Ashcroft N.W and Mermin N.D 1976. P. 345-368) and Experimental values (Michaelson H.B, 1977 P. 4729-4733). The SJM proved to be more accurate for calculations of work function of simple metals, while MPM has agreeable results for pure-metals and polycrystalline surfaces. However, in the semiconductors (Ge and Si) it gives a lower value due to low screening efficiency. The work function of elemental metals obtained from the SJM calculation was in fairly good agreement with experimental values. Considering the cubic arrangements of lattice structures, the SJM gave more accurate results for the work functions of body centred cubic (bcc) metals, followed by hexagonal closed packed (hcp) metals and was least accurate for face centred cubic (fcc) metals. This shows that the SJM could be used to calculate and predict the work function of metals. Although MPM and SJM were in good agreement with the experimental values, MPM was more accurate than SJM for non-simple metals. This may be due to the band structure, crystal strength and crystal structure which the SJM does not put into consideration.

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Table 1. Input values and the results of calculations for the MPM model. SJM, *Ab-initio* and Experimental values are taken from references Osiele, O.M. and Olubosede, O. (2007). P. 9-16, Ashcroft N.W and Mermin N.D (1976). P. 345-368. and Michaelson H.B, (1977) P. 4729-4733 respectively.

Element	Z	r_s (a.u)	E_F (eV)	Calculated MPM (eV)	Calculated (eV) (Osiele,O.M., et al. 2007)	SJM Ref.	Ab-initio method Ref.(Ashcroft N.W et al. 1976)	Experimental Value (eV) Ref.(Michaelson H.B, 1977)
Li	1	3.26	4.74	2.92	2.92		3.33	2.9
Na	1	3.99	3.24	2.61	2.64		2.76	2.75
K	1	4.95	2.12	2.32	2.23		2.34	2.30
Rb	1	5.31	1.85	2.25	2.13		2.22	2.16
Cs	1	5.75	1.59	2.15	2.02		2.50	2.14
Fr	1	6.12	1.50	2.0	NA		NA	NA
Be	2	1.87	12.0	4.91	4.22		5.62	4.98
Mg	2	2.65	7.10	3.79	3.34		3.86	3.66
Ca	2	3.26	5.20	2.79	2.91		2.86	2.87
Sr	2	3.55	4.49	2.64	2.74		2.42	2.59
Ba	2	3.73	3.84	2.65	2.70		2.23	2.7
Ra	2	3.92	3.00	2.78	NA		NA	NA
Se	2	3.72	7.54	3.52	2.88		3.74	3.5
Y	2	2.99	6.88	3.21	3.39		3.38	3.1
La	3	2.89	6.10	3.57	NA		NA	NA
Ac	3	2.89	6.10	3.58	NA		NA	NA
Ti	3	2.24	8.84	4.28	4.16		4.59	4.33
Zr	3	2.33	8.50	4.18	3.90		4.15	4.07
Hf	3	2.43	8.69	3.89	NA		NA	3.9
V	3	2.09	11.09	4.32	4.63		5.2	4.3
Nb	3	2.13	10.82	4.25	3.88		4.63	4.3
Ta	3	2.13	10.19	4.38	4.39		5.08	4.25
Cr	3	1.98	11.95	4.50	4.25		NA	4.50
Mo	3	2.03	11.36	4.52	4.28		5.34	4.60
W	3	2.04	11.47	4.40	NA		NA	4.55
Mn	3	2.01	12.20	4.37	NA		NA	4.10
Tc	3	1.97	10.90	4.76	NA		NA	NA
Re	3	2.01	10.90	4.62	NA		NA	4.72
Fe	3	1.96	11.81	4.60	4.25		5.54	4.50
Ru	3	1.96	10.82	4.81	4.15		NA	4.71
Os	3	1.97	11.06	4.72	NA		NA	4.83
Co	3	1.93	10.52	5.00	NA		NA	5.00
Rh	3	2.07	9.26	4.80	4.12		NA	4.98
Ir	4	1.87	10.26	5.31	NA		NA	5.27
Ni	3	1.92	9.66	5.25	3.96		NA	5.25
Pd	3	2.12	7.69	5.08	3.71		NA	5.12
Pt	4	1.91	8.79	5.56	4.05		NA	5.65
Cu	2	2.12	9.03	4.69	3.90		NA	4.65
Ag	2	2.39	7.48	4.31	3.16		NA	4.26
Au	3	2.22	7.25	4.88	3.59		NA	5.1
Zn	2	2.30	8.65	4.24	NA		NA	4.33
Cd	2	2.59	6.45	4.10	3.40		NA	4.22
Hg	3	2.51	5.66	4.59	NA		NA	4.49
B	2	1.84	15.40	4.44	NA		NA	4.45
Al	3	2.07	11.30	4.34	3.96		NA	4.28
Ga	3	2.19	10.40	4.16	NA		NA	4.2
In	3	2.41	8.60	3.96	NA		NA	4.12
Tl	3	2.49	6.00	3.88	3.51		NA	3.84
C	2	1.93	10.50	5.0	NA		NA	5.0
Si	4	2.00	12.50	4.34	NA		NA	4.85
Ge	4	2.09	13.00	3.98	NA		NA	5.0
Sn	4	2.22	10.20	4.12	NA		NA	4.42
Pb	4	2.30	2.30	9.50	4.03		3.16	4.25
As	5	1.91	11.90	4.77	NA		NA	5.11
Sb	5	2.14	10.90	4.21	NA		NA	4.55
Bi	5	2.25	9.90	4.09	NA		NA	4.22
Se	6	1.94	7.50	5.87	NA		NA	5.9
Te	6	2.12	8.00	4.98	NA		NA	4.95
Po	6	2.20	7.00	5.03	NA		NA	NA

Note: NA means not available

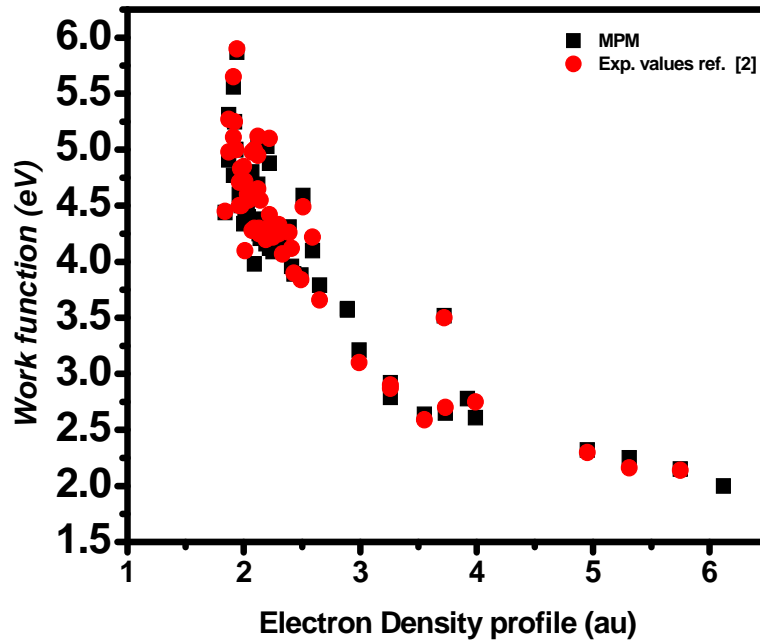


Figure 1. Comparison of MPM and experimental Values with electron density parameter

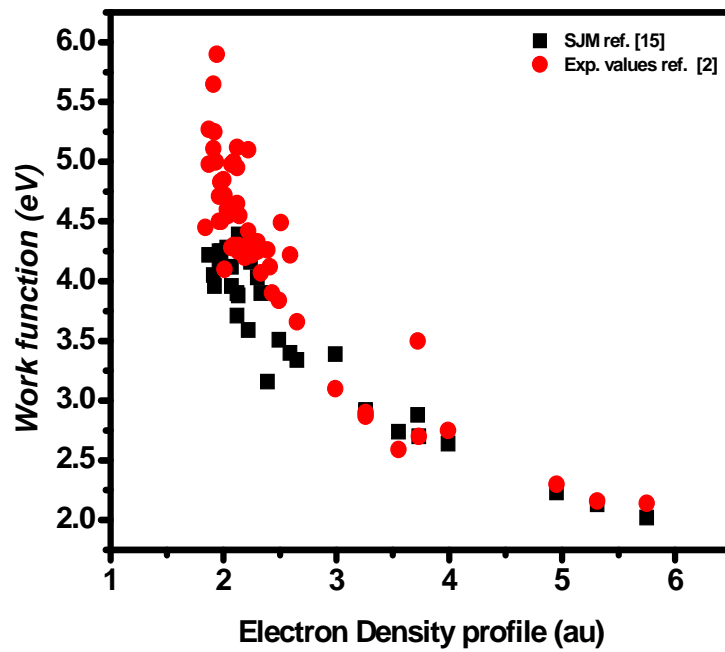


Figure 2. Comparison of SJM and experimental Values with electron density parameter

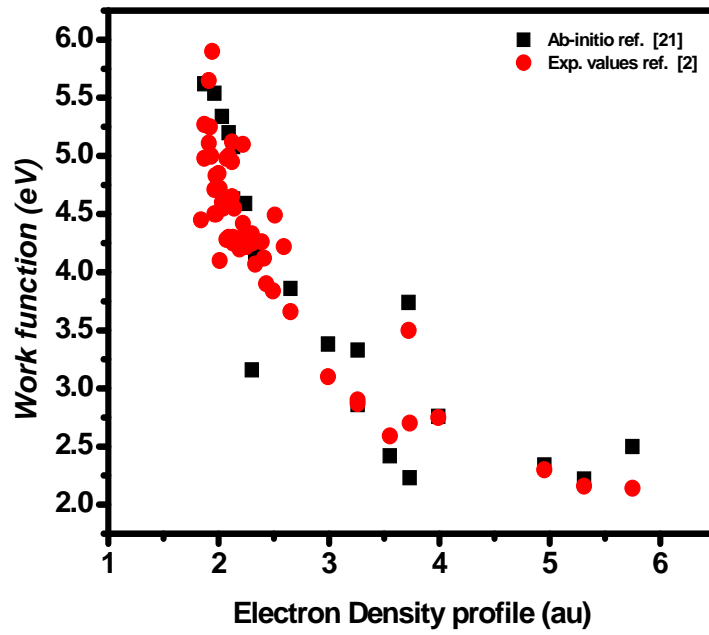


Figure 3. Comparison of Ab-initio and experimental Values with electron density parameter