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Work Function of Metals and Strain based on Brodies Model using Free Electron Theory

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Abstract: In this study, Brodie model based on plasma physics concept is extended to the study of work function of metals since the model redefined the work function of metals by reducing it to the work done by electron against the image forces. The scaling factor of each metals is obtained by directly substituting the experimental value of Fermi energy, work function and electron density parameter of each metals into the model used in this work. Result obtained revealed that there is a good agreement between computed and experimental value of work function. The trend display by work function of metals in this work revealed that it depend on the number of valence electron per unit cell, conduction electron, material composition and nature of metallic surface. The work function of metals decreases as the strain increases. The decrease in work function as strain increases may be due to the effect of strain on some properties that work function of metals relied upon. Platinum has the highest work function while Potassium has the lowest work function when subjected to different strain.
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Introduction

Metals are important materials characterized by high electrical and thermal conductivity Kittel (1976). Metals at high temperature obey Wiedemann–Franz law. Metals are ductile and deform plastically instead of fracturing Ashcroft and Mermin (1976). Metals is opaque to light for frequencies below the plasma frequency. Some properties of metals can be understood by considering metals as a collection of positive ions in a sea of electrons (the jellium model) Efthimios (2003). Metals are material that, when freshly prepared, polished, or fractured, shows lustrous appearance, and conducts electricity Patterson and Bailey (2010). Metals can be drawn into wires and can be hammered into thin sheets. Metals could be a chemical element or a molecular compound. Metals could be deformed under stress without cleaving Rogalski and Palmer (2000). The non-directional nature of metallic bonding contribute significantly to the ductility of metallic solids Kittel (1976). Reversible elastic deformation in metals can be described by Hooke's Law for restoring forces, where stress is linearly proportional to strain Pillai (2010). Heat or forces larger than metal's elastic limit may cause a permanent deformation, known as plastic deformation or plasticity Kittel (1976). Temperature change affect the movement or displacement of structural defects in metal and the energy required to extract an electron originates deep in the metal interior is determined by surface and its bulk conditions Madelung (1995). Work function is the minimum energy required to remove an electron from the interior of solid to a position at a distance from the surface that is large on the atomic scale but small compared with the linear dimensions of the crystal Ashcroft and Mermin, (1976). Work function is the smallest amount of energy possess by electron with 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 is applied at the surface Kakani, and Kakani (2004). Work function is a fundamental electronic property of metallic surface useful in the computation of corrosion rates, yield of thermionic emission and spectral characteristics of photosensitive cells Halas and Durakiewicz (1998). Work function is the difference between the work needed to remove to infinity an electron at the lowest energy state in the valance band and Fermi energy Uichiro (2003). In experiment, there are three types of work function: (i) the mean or polycrystalline work function obtained as a result of measuring

polycrystalline samples, (ii) the total work function determined by measurements of total thermo-emission current from a single-crystal tip, and (iii) the work function measured from face dependent and face-independent crystals with Miller indices (hkl) structures Kachhava, (1992). The work function of metal is strongly face-dependent and is important in devices like old televisions and when studying how light makes metals to release electrons Elliott (1997). Before now, theoretical studies of some surface properties of metals have been investigated by different researchers, theorist and experimentalist using different techniques. Wojciechowski and Bogdanów (1994) performed a variational calculation of face-dependent work function based on pseudopotential corrections. A comparison between the calculated work function values and the experimental polycrystalline data is also obtained. They also find that the use of simple variational method and Ashcroft pseudopotential for the description of metallic ions gives good agreement between theory and experimental value and also provide an explanation on the increasing or decreasing tendency of work function values in different simple metals. Halas and Durakiewicz (1998) theoretically studied the work functions of elements in terms of Fermi energy and density of free electrons of elements base on Brodie's definition of the work function and the length of spontaneous polarization of plasma. And derive an expression for computing the work functions of elements and the scaling factor is treated as an empirical constant. The result obtained is in excellent agreement with experimental data for pure-metal polycrystalline surfaces. Surma et al (2018) computed the work function and some physicochemical data for several most prominent crystal planes of three metals of typical structures within the linear approximation by employing the surface dipole and two dimensional gas models. The result obtained revealed that the work function obtained from the thermodynamics based formula are in good agreement with the result of the quantum mechanics based formula and experimental value. Although there is a specific deviation in the case of field emission method for most packed plane. Hałas (2006) performed an early inquires on the nature of work function since it was earlier assume that the image force introduced by Thomson for macroscopic bodies could be the main reason for the barrier at the metal surface. He found that the idea of the image potential as the main contribution to work function was restored by Brodie and subsequently improved by Halas and Durakiewicz where a distance from which the image force can be integrated is found from the uncertainty principle and from the length of spontaneous metallic plasma polarization. This approach was adjudged to be very useful in computing the work function of conducting compounds and ionization potentials of metallic clusters. Korolevych et. al. (2017) developed a one-dimensional finite crystal model based on inter-site aspect of crystal lattice and considered two extreme cases of crystal structure. He studied the field of forces acting on an electron in a crystal and obtain a relationship between the electron work function and the lattice constant. This result shows a matching between theoretical values of work function and practical data. Olubosede et. al. (2011) developed a model for computing the work function of metals using metallic plasma model. The results obtained were compared with the results of the stabilized jellium model (SJM), Ab-initio model and the experimental values. Result obtained 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. Adesakin (2018) study the effects of deformation on electronic heat capacity of different elemental metals based on Einstein model formalism. The electron density parameters of deformed metals under the application of different strains were obtained for different metals. The poison ratio relating the transversal compression to elongation in the direction of applied deformation for different elemental metals were computed using elastic moduli for homogeneous isotropic material. The results obtained revealed that there is a good agreement between the computed and experimental values of electronic heat capacity of metals. This shows that Einstein model can be used in the theoretical prediction of heat capacity of metals. The result obtained shows that the electronic heat capacity of metals increases as the temperature increases. The electronic heat capacity of all the metals increases with an increase in deformation (strain). This could be due to the fact that as deformation increases, the collision between the interacting electron increases which forces the mean atomic velocity, amplitude of atomic vibration and electron thermal excitation to increase and there by result in the increase in the electronic heat capacity of the metals as deformation increases. This study focuses on work function of metals where the scaling factor is involved unlike some theorist that assume values for scaling factor which their-by reduces the input parameter to only electron density parameter.

Theoretical Consideration

The motion of an electron in free space, where the potential V is zero everywhere, can be described by the simplest form of the Schrödinger equation:

$$-\left(\frac{\hbar^2}{2m_e}\right)\nabla^2\psi(x,y,z) = -\left(\frac{\hbar^2}{2m_e}\right)\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z) \quad (1)$$

where $\hbar$ is the Planck's constant divided by 2π, m_e is the mass of electron, E is the energy eigenvalue and $\psi(x,y,z)$ is the wave function. Equation (1) can be decomposed into three independent equations involving only a single variable x, y or z by setting $\psi(x,y,z) = X(x)Y(y)Z(z)$ and $E = E_x + E_y + E_z$. The total wave function $\psi(x,y,z) = X(x)Y(y)Z(z)$ is now expressed as a linear combination of eight different plane waves

$$\psi(x,y,z) = \sum_{j=1}^{8} c_j e^{i(\pm k_x x \pm k_y y \pm k_z z)} \quad (2)$$

where c_j ($j = 1$ up to 8) is a numerical coefficient. Equation (2) represents a plane wave, which is characterized by wave numbers k_x, k_y *and* k_z corresponding to x, y *and* z components of the wave vector k.

The energy of an electron in three-dimensional free space is given by

$$E = \left(\frac{\hbar^2}{2m_e}\right)k_x^2 + k_y^2 + k_z^2 = \frac{\hbar^2 k^2}{2m_e} \quad (3)$$

where the wave vector k satisfies the relation $k^2 = k_x^2 + k_y^2 + k_z^2$. The wave number k is related to the wavelength λ through the equation $k = {}^{2\pi}/_{\lambda}$.

The probability density of an electron at the position r with a wave vector k turns out to be constant.

$$|\psi_k(r)|^2 = \psi_k^*(r)\psi_k(r) = \frac{1}{V} \quad (4)$$

Where V is volume. The total wave function is written as

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} sin\left(\frac{\pi n_x x}{L}\right) sin\left(\frac{\pi n_y y}{L}\right) sin\left(\frac{\pi n_z z}{L}\right) \quad (5)$$

The energy of free electron confined in a cube with edge length L is easily calculated as

$$E = \frac{\int \psi^*\left(\frac{-\hbar^2}{2m_e}\right)\nabla^2\psi dV}{\int \psi^*\psi dV} = \left(\frac{\hbar^2}{2m_e}\right)\left(\frac{\pi}{L}\right)^2\left(n_x^2 + n_y^2 + n_z^2\right) \quad (6)$$

The Fermi radius k_F is obtained as

$$k_F = \left[3\pi^2\left(\frac{N_0}{V}\right)\right]^{1/3} \quad (7)$$

where N_0 is obviously the total number of electrons in volume V, and volume $V = L^3$.

The energy of a free electron with the Fermi radius k_F is calculated by inserting equation (7) into equation (3)

$$E_F = \frac{\hbar^2 {k_F}^2}{2m_e} = \left(\frac{\hbar^2}{2m_e}\right)\left[3\pi^2\left(\frac{N_0}{V}\right)\right]^{2/3} = \frac{50.1}{r_s^2}eV \quad (8)$$

Where N_0 *is* obviously the total number of electrons in volume V, E_F is the Fermi energy and r_s is the electron density parameter.

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

$$W_{image} = \frac{e^2}{16\pi\varepsilon_0 d_0} \quad (9)$$

where e is the elementary charge and ε0 is the permittivity of vacuum and d_0 is the minimum distance at which the image force begins to act which may be calculated on the basis of the uncertainty principle by using the expression

$$d_0 = \frac{h}{\sqrt{2m_e E_F}} \quad (10)$$

where h is Planck's constant, m_e is mass of electron and E_F is the Fermi energy

The polarization length d in a metal may be obtained by

$$d = \sqrt{\frac{2\varepsilon_0 E_F}{ne^2}} \quad (11)$$

where $\varepsilon_0$the permittivity of vacuum, e is the electronic charge and n is the average density of free electrons in metal given by

$$n = \frac{3}{4\pi r_s^3} \quad (12)$$

where r_s is the electron density parameter. When electron is shifted from a remote plane, it is assumed that the scaling factor α is

$$\alpha = \frac{d}{d_0} \quad (13)$$

By substituting equation (10) and (11) into equation (13), the scaling factor α becomes

$$\alpha = \frac{2E_F}{\sqrt{n}} \quad (14)$$

For practical calculations, the work function ϕ of metals may be expressed as

$$\phi = \frac{43.46\alpha}{r_s^{3/2}E_F^{1/2}}eV \quad (15)$$

where r_s is the electron density parameter, α is the scaling factor and E_F is the Fermi energy.

In this paper, the work function of metals from different groups and period were computed and studied using equation (15). The scaling factor for each metals ia obtained computed unlike some researchers that have assume that the scaling factor of alkaline metals is 0.86 while for other metals is assumed to be equal to unity. This assumption makes the theory to be dependent on only one input parameter and the physical quantities involved become continuous functions of this parameter.

Results and Discussion

Figure 1 shows the plot of work Function as ordinate and Electron Density Parameter as Abscissa for metals from different groups and periods. Figure 1 revealed that there is a good agreement between the computed and experimental value of work function. The experimental value of work function used in this work is obtain from solid state Physics by Aschcroft and Mermin (1976). The agreement between the computed and experimental value of work function in this work revealed that Brodie model takes some specified factors into account that work function of metals depends upon. Such as density of states, carrier concentration, nature of the surface, elemental composition and charge carrier concentration. Figure 1, revealed that work function of metals is more concentrated in the region of high density limit than low density limit. These indicate that the work function of metals relied on the configuration of valence electron density, density of conduction electron, number of conduction electrons per unit volume, Fermi level, Fermi energy and atoms at metallic surface. Another thing that may be responsible for the high value of work function of metals in the region of high density limit in figure 1 may be due to their atoms that are closely packed, nature of crystal face and high surface reconstruction. The low work function of metals in the region of low density limit in figure 1 may be due to the open lattice structure possess by the metals. The trend display by metals in Figure 1 also shows that work function of metals depend on the number of valence electron, electronic concentration and configurations of atoms at the surface of the material. Figure 2 shows the plot of work Function as ordinate and strain as Abscissa for different elemental metals from different groups and periods. Figure 2 revealed that work function of metals decreases as the strain increases for all the metals investigated. These decrease in work function as the strain increases may be due to an increase in the temperature between the interacting electrons as electron collision increases. The decrease in work function of metals as the strain increases in figure 2 can also be due to an increase in the inter atomic distance between the electron in metals which causes a surface distortion effect on the metals and then reduces the electron atomic packing density and strength to an open lattice structure. Also, the decrease in work function of metals as strain increases in figure 2 could be due to the fact that as the electron move through the surface region during deformation, its energy is influenced by optical, electrical and mechanical characteristics which then reduces the work function as strain increases. The decrease in work function of metals as strain increases in figure 2 could be due to impurity and lattice localization contamination at the metals surface. Furthermore, the decrease in work function of metals as strain increases in figure 2 may be due to the effect of strain on some properties that work function of metals relied upon. Such as absorbed or evaporated layers, surface reconstruction, surface charging, oxide layer imperfections, surface and bulk contamination, nature of metal surface or elemental composition, material composition, surface condition and temperature. In figure 2, Platinum has the highest work function among the metals computed and subjected to different strain while Potassium has the lowest work function. This may be due to the nature of its surface and properties. With the trend display by metals in figure 2, we conclude that work function of metals is highly affected by strain.

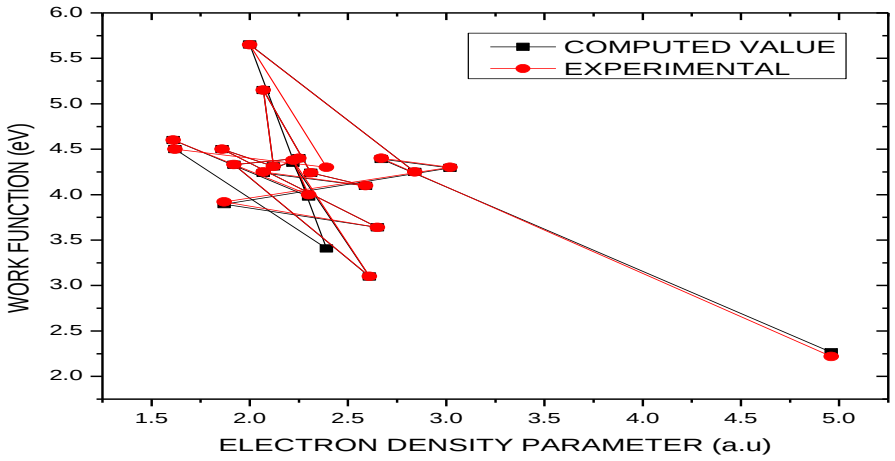
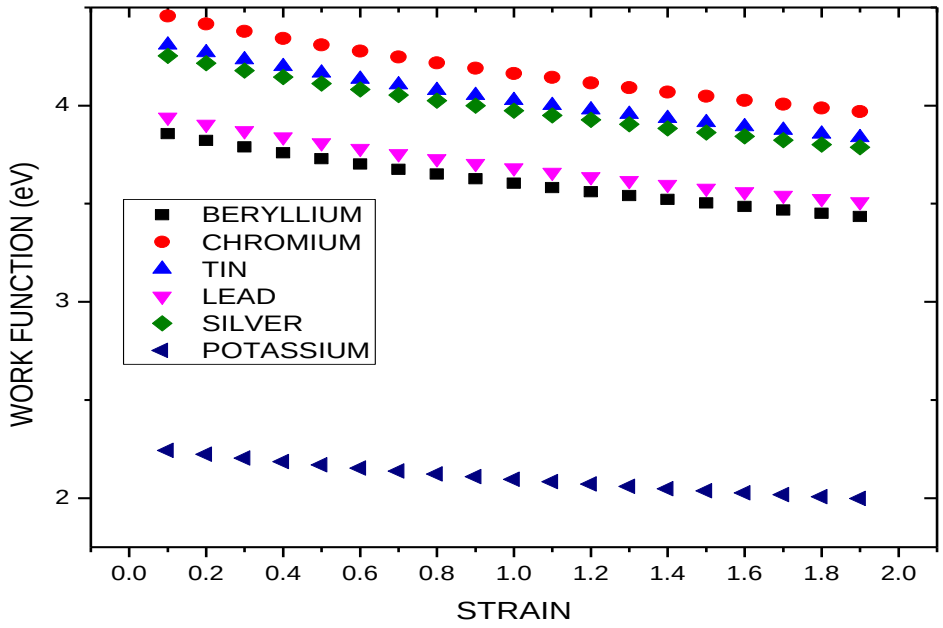
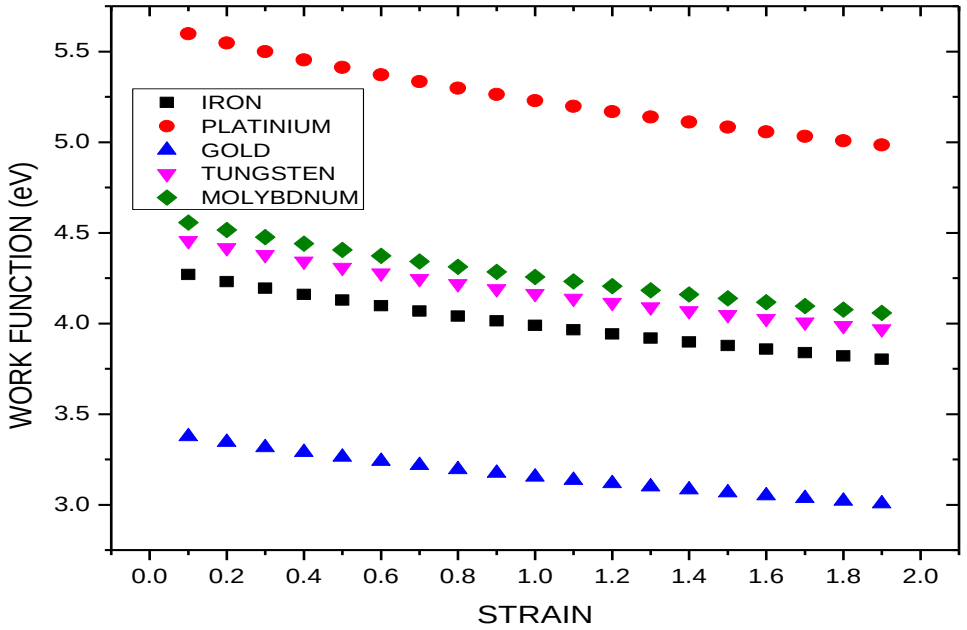
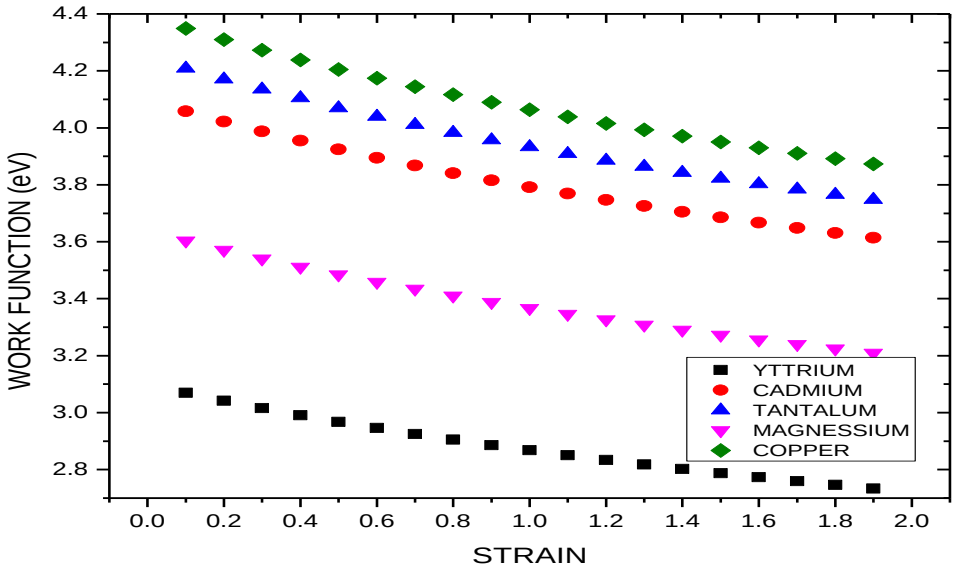


FIGURE 1: Work Function is plotted as ordinate and Electron Density Parameter is plotted as Abscissa for Metals


WORK FUNCTION (eV)
STRAIN
BERYLLIUM
CHROMIUM
TIN
LEAD
SILVER
POTASSIUM
2
3
4
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0


WORK FUNCTION (eV)
STRAIN
IRON
PLATINIUM
GOLD
TUNGSTEN
MOLYBDNUM
3.0
3.5
4.0
4.5
5.0
5.5
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0



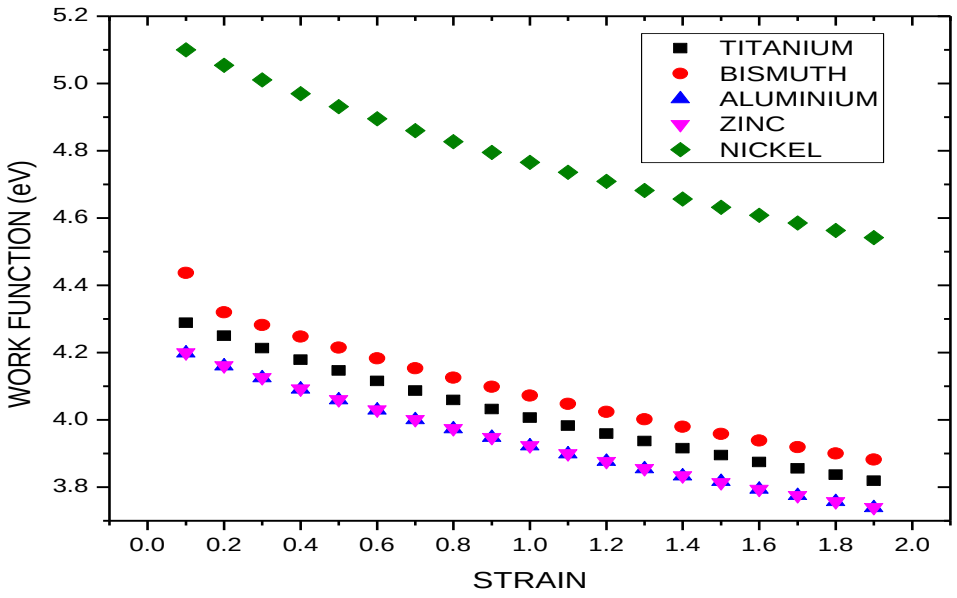


FIGURE 2: Work Function is plotted as ordinate and Strain is plotted as Abscissa for Metals

Table 1. **Work Function of Unstrained Metals**

Metals	**Electron Density Parameter (a.u)**	**Scaling Factor (eV)**	**Work Function (eV)**	
			Computed Value	**Experimental Value**
K	4.96	0.821587	2.26508	2.22
Cu	2.67	1.16864	4.39133	4.40
Ag	3.02	1.21557	4.29484	4.30
Be	1.87	0.867328	3.89434	3.92
Mg	2.65	0.964773	3.63892	3.64
Cr	1.86	0.999486	4.49978	4.50
Fe	2.12	1.02218	4.31053	4.31
Ni	2.07	1.20665	5.14952	5.15
Zn	2.31	1.04961	4.24026	4.24
Cd	2.59	1.07402	4.09764	4.10
Al	2.07	0.993218	4.23868	4.25
Bi	2.25	1.07511	4.40081	4.40
Ti	1.92	0.977147	4.32992	4.33
Y	2.61	0.815411	3.09904	3.10
Sn	2.22	1.05576	4.3507	4.38
Pb	2.3	0.982725	3.97868	4.00
Mo	1.61	0.950655	4.60024	4.60
W	1.62	0.932821	4.49999	4.50
Au	2.39	0.858127	3.40819	4.30
Pt	2	1.30160	5.65111	5.65
Ta	2.84	1.16633	4.24945	4.25

Table 2: Work Function of Strained Metals

		Strain								
Metals	*r_s (a.u)*	*0.2*	*0.4*	*0.6*	*0.8*	*1.0*	*1.2*	*1.4*	*1.6*	*1.8*
K	4.96	2.22312	2.18610	2.15303	2.12320	2.09606	2.09606	2.04828	2.02703	2.00726
Cu	2.67	4.30998	4.23820	4.17409	4.11626	4.06365	4.01545	3.97101	3.92983	3.89148
Ag	3.02	4.21528	4.14508	4.08238	4.02582	3.97437	3.92722	3.88376	3.84348	3.80154
Be	1.87	3.82219	3.75854	3.70169	3.65039	3.60374	3.56099	3.52159	3.48506	3.45106
Mg	2.65	3.57151	3.51203	3.45891	3.41098	3.36739	3.32745	3.29062	3.25650	3.22472
Cr	1.86	4.41642	4.34287	4.27718	4.21792	4.16401	4.11461	4.06908	4.02688	3.98759
Fe	2.12	4.23067	4.16022	4.09729	4.04052	3.98887	3.94160	3.89794	3.85752	3.81988
Ni	2.07	5.05413	4.97002	4.89478	4.82696	4.76526	4.70874	4.65663	4.60834	4.56338
Zn	2.31	4.16171	4.09240	4.03050	3.97465	3.92386	3.87731	3.83441	3.79464	3.75761
Cd	2.59	4.02172	3.95475	3.89493	3.84096	3.79187	3.74689	3.70543	3.66700	3.63122
Al	2.07	4.16015	4.09087	4.02899	3.97317	3.92238	3.87586	3.83297	3.79322	3.75621
Bi	2.25	4.31928	4.24734	4.18310	4.12515	4.07242	4.02411	3.97958	3.93831	3.89989
Ti	1.92	4.24971	4.17893	4.11572	4.05870	4.00683	3.95930	3.91548	3.87488	3.83707
Y	2.61	3.04163	2.99097	2.94573	2.90492	2.86779	2.83377	2.80241	2.77335	2.74629
Sn	2.22	4.27010	4.19899	4.13548	4.07818	4.02606	3.97830	3.93428	3.89347	3.85549
Pb	2.30	3.90497	3.83994	3.78186	3.72946	3.68179	3.63812	3.59786	3.56055	3.52581
Mo	1.61	4.51502	4.43983	4.37268	4.31208	4.25697	4.20648	4.15993	4.11679	4.07662
W	1.62	4.41663	4.34307	4.27738	4.21811	4.16420	4.11481	4.06928	4.02707	3.98778
Au	2.39	3.34505	3.28934	3.23959	3.19470	3.15387	3.11645	3.08197	3.05001	3.02025
Pt	2.00	5.54642	5.45405	5.37155	5.29713	5.22942	5.16739	5.11021	5.05721	5.00787
Ta	2.84	4.17073	4.10464	4.03924	3.98327	3.93236	3.88571	3.84271	3.80286	3.76576

Conclusion

In this paper, the effect of electron density parameter and strain on work function of metals is computed and studied. The scaling factor of each metals is obtained and used for compution unlike some researchers that assumed values for the scaling factor of metals. Result obtained revealed that there is a good agreement between computed and experimental value of work function. The work function of metals is more concentrated in the region of high density limit than the low density limit. These indicate that the work function of metals relied on the configuration of the density of valence electron and configurations of atoms at the surface of metals. The work function of metals decreases as strain increases. Platinum has the highest work function among the metals subjected to different strain while Potassium has the lowest work function. This may be due to the nature of its surface and properties.

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