

Work function of elemental metals and its face dependence: Stabilized Jellium approach

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Abstract

The stabilizing potentials and work functions of elemental metals were calculated for the flat surface, the (111), (100) and (110) faces using the stabilized jellium model. The calculated work functions were compared with experimental values and calculated values obtained using the ab initio method. The stabilizing potentials for the different faces of the metals revealed that the less densely packed faces require higher potential for stabilization in the stabilized jellium model. The calculated work functions for the flat surface of the metals were in perfect agreement with experimental values for metals in the low-density limit and the agreement with experimental values decreased towards the high-density limit. The calculated work functions for the body centred cubic metals were in good agreement with experimental values. The calculated work function for the hexagonal close packed metals were in fairly good agreement with experimental values while the degree of agreement with experimental values was least for face centred cubic metals. The work functions of metals calculated in this work revealed that the more closely packed faces have higher work functions. The results obtained in this work revealed that the stabilized jellium model could be used to predict fairly well the work function of metals and calculate other metallic properties.

Keywords: Stabilized jellium, metals, work function, metallic faces, electron gas parameter.

1.0 Introduction

Work function is one of the most important properties of metal surfaces. Work function determines the physical and chemical properties of metallic surfaces. Work function of metals is an intrinsic property and it is affected by atomic arrangement in the metal and inter-atomic distances within the metal. Work function is very vital in understanding some surface phenomenon. Work functions of metals are used to calculate corrosion rates, properties of materials for light emitting and photosensitive devices [1]. Work functions can be measured absolutely using thermionic emission, photoelectric emission and field emission. Work functions can be measured relatively using the retarding potential and vibrating capacitor methods [2]. Measurement of work functions is improving with improvement in technology and development of better methods of measurement [3-4].

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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 metals from first principles within the free electron model produced work function of metals that were not in good agreement with experimental values [5-6]. Lang and Kohn [7] 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 of metals calculated based on the jellium model by solving the Kohn-Sham equation self-consistently using the kinetic, exchange, and correlation energies based on the local density approximation were only in good agreement with experimental values for some simple metals [7]. Mahan and Schaich derived another formula for calculating work function based on the jellium model that is equivalent 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 [8]. 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 [9]. *Ab initio* calculation of the work function of metals was in fairly good agreement with experimental values [10].

The stabilized jellium model was developed by Perdew et al [11]. It evolved from the variational self-consistent method of the ground state properties of metals [12]. The model has all the properties of the jellium model with an additional constant potential to the effective potential of the metal. The stabilized jellium model has been successfully used to explain the physics of slabs, [13-14], clusters [15] and to calculate the bulk modulus of metals [16]. In this work, the stabilized jellium model will be used to calculate the work function of elemental metals at the flat surface, the (111), (110) and (100) faces. The stabilizing potential at these faces will also be calculated and studied. The calculated work functions will be compared with experimental values and work function of metals calculated using the *ab initio* method. The variation of the calculated work function for the flat surface with electron gas parameter will be studied.

2.0 Theory

The energy functional functional of a stabilized jellium is

$$E[n, n_+] + E_j[n, n_+] + (E_m + e_R) \int d^3r n_+(r) + \langle \delta v \rangle_{WS} \int d^3r \theta(r) [n(r) - n_+(r)] \quad (2.1)$$

where E_j is the total jellium energy given as

$$E_j = T_s[n] + E_{xc}[n] + \frac{1}{2} \int d^3r \theta([n, n_+], r) n(r) - n_+(r) \quad (2.2)$$

$T_s[n]$ is the kinetic energy functional E_{xc} is the exchange correlation energy functional $\theta([n, n_+], r)$ is the electrostatic potential of the jellium, E_m is the Madelung energy, w_R is the short-range repulsive part of the ionic potential, $\langle \delta v \rangle_{WS}$ is the average stabilizing potential over the volume of the Wigner-Seitz cell.

In the stabilized jellium model, the potential is the sum of the ionic potential $w(r)$ and the electrostatic potential $V(r)$

$$\delta V = w(r) + V(r) \quad (2.3)$$

The ionic pseudopotential consists of a long-range attractive part and a repulsive term $w_R(r)$

$$\text{acting at a short distance} \quad w(r) = -\frac{z}{r} + w_R(r) \quad (2.4)$$

where $w_R(r)$ is a pseudopotential whose repulsive part is

$$w_R = \frac{z}{|r|} \theta(r_c - r) \quad (2.5)$$

where $\theta(r_c - r)$ is a step function which is equal to one in the cell and zero outside. r_c is the radius

of the Ashcroft core radius. The electrostatic potential is given [11] as

$$V(r) = \frac{3}{2} \frac{z}{r_0} - \frac{zr^2}{2r_0^3} \quad (2.6)$$

The average of the potential δv over the Wigner-Seitz cell of radius r_0 is

$$\langle \delta v \rangle = \frac{1}{z} \int_0^{r_0} dr 4\pi r^2 n(w(r) + V(R)) = \varepsilon + E_m + W_R \quad (2.7)$$

where $\overline{W_R}$ is the average of the ionic potential E_m is the Madelung energy and ε is the average electrostatic energy which cancels the electrostatic energy of the uniform positive background. At equilibrium the stabilizing potential is

$$\langle \delta v \rangle - n \frac{d}{dn} E_j = n \frac{d}{dn} (t_s(n) + E_{xc}(n)) \quad (2.8)$$

where t_s and E_{xc} are the respective kinetic energy, exchange and correlation energy in the local density approximation. In this work, we used the correlation energy of Carperly and Alder as parameterized by Perdew and Zunger [17]. The stabilizing potential for a metal depends upon the exposed crystal face. The stabilizing potential for a face is expressed as [18]

$$\langle \delta v \rangle_{face} = \langle \delta v \rangle + \frac{3z}{10r_0} \left[1 - \frac{5}{12} \left(\frac{d}{r_0} \right)^2 \right] \quad (2.9)$$

where $r_0 = z^{1/3} r_s$, z is valency, r_s is the electron density parameter defined as $r_s = (3/4\pi n_{av})^{1/3}$ and n_{av} is the average valence electron density and d is the inter planar distance

In the stabilizes jellium model, the work function is

$$W = \Delta\phi - E_j + V_{xc} + \langle \delta v \rangle \quad (2.10)$$

where $\Delta\phi = 4\pi \int_{-\infty}^{\infty} x(n(x) - n_+(x)) dx$ is the surface dipole barrier, $n(x)$ is the electron density

and $n_+(x)$ is the density of the positively charged background. $E_f = \frac{k_f^2}{2}$ is the Fermi energy

and $v_{xc} = n \frac{d}{dn}$ is the exchange correlation potential. The face dependent work function is

$$W_{face} = \Delta\phi - E_j + V_{xc} + \langle \delta v \rangle_{face} \quad (2.11)$$

where $\langle \delta v \rangle_{face}$ is given by equation (2.9) above.

The stabilizing potential for the flat surface was calculated using equation (2.8), the stabilizing potential for the (111), (100) and (110) faces were calculated using equation (2.9). The work function for the flat surface of metals was calculated using equation (2.10) while the face dependent work function was calculated using equation (2.11).

3.0 Results and discussion

The stabilizing potential for body centred cubic (bcc) and face centred cubic (fcc) metals are shown respectively in figures 1 and 2. The stabilizing potentials for the flat surfaces of the metals increase as a rule with increase in the electron density parameter, r_s suggesting that in the stabilized jellium model, the stabilizing potential depend inversely on the electronic concentration. The most densely pack faces (fcc(111)) and (bcc(110)) follow the flat surfaces. The stabilizing potential for the bcc(110) is relatively constant for the bcc metals, but for the fcc(111) face, the stabilizing potential increases with r_s as a power law. The stabilizing potential for the less dense faces (bcc(111), bcc(100), fcc(110) and fcc(100)) has a different trend. In the low-density limit, the stabilizing potential of the less dense faces increases with increase in the electron density parameter gets to a peak value and starts to decrease with an increase in the electron density parameter. For the fcc metals, as shown in fig.2, the stabilizing potential for the different faces tend to a constant value in the range of $3.2a.u \leq r_s \leq 3.5a.u$. From fig.1, the stabilizing potential for the bcc metals follow the trend $\delta v_{111} > \delta v_{100} > \delta v_{110} > \delta v_{flat}$ while from fig.2, the stabilizing potential for the fcc metals follow the trend $\delta v_{110} > \delta v_{100} > \delta v_{111} > \delta v_{flat}$. These suggest that the less pack faces of bcc and fcc metals requires higher potential to attain stability in the stabilized jellium model.

Fig.3 is the variation of the calculated and experimental work function for flat surfaces of metals with electron density parameter, r_s . In the low-density limit, $r_s \geq 3.0a.u$, there is a good agreement between our calculated work function and experimental values. But in the high-density limit, $r_s \leq 3.0a.u$ the agreement between the calculated and the experimental values decreases with a decrease in the electron density parameter. This may be due to the fact that the simple metals are in the low-density limit while the non-simple metals are in the high-density limit. The simple metals approximate the jellium model on which the stabilized jellium model is based. The properties of non-simple metals are affected by band structure and crystal structure, which the stabilized jellium model does not put into consideration.

The stabilized jellium calculation, *ab initio* calculation of Skriver and Rosengaard [10] and the experimental [1] values for body centred cubic (bcc), face centred cubic (fcc) and hexagonal closed packed (hcp) metals is shown respectively in Tables 1, 2 and 3. In Table 1, the stabilized jellium calculation reproduced the experimental work function of Li, K, Rb, Cs, and Ba within the range of $\pm 0.1eV$. For the (111), (100), and (110) faces, the stabilized jellium is in fairly good agreement with available experimental results for Fe, Nb, Mo. The *ab initio* calculation for the above mentioned metals for the (111), (100) and (110) faces are generally higher than the available experimental values except for Nb(110). As shown in Table 1, the work functions calculated using the stabilized jellium model differed maximally by $\pm 0.76eV$ from the available experimental values while the *ab initio* calculations differed maximally from the available experimental values by $\pm 0.74eV$. As shown in Table 1, for the bcc metals, the work functions calculated using the stabilized jellium model follows the trend $W_{110} > W_{100} > W_{111}$ which is in agreement with the theory of Lang and Kohn, [7] that the more closely packed face have the highest work function. This seems to suggest that in the stabilized jellium model, the work function of a face depend inversely on the stabilizing potential of the face.

In Table 2, the agreement between the stabilized jellium model calculation of work function of fcc metals and experimental values is lower than those of bcc metals. The stabilized jellium model calculation reproduced only the experimental work function of Ca that differed by $0.1eV$ from experimental value. The *ab initio* calculation for the (111), (100) and (110) faces of the fcc metals are generally higher than available experimental values and are not in very good agreement with experimental values. The stabilized jellium model calculation for the work function of the (111), (100) and (110) faces of the fcc metals follows the trend $W_{111} > W_{100} > W_{110}$ in agreement that the more closely packed face have the highest work function [7].

In Table 3, our stabilized jellium model calculation gave the work function of Gb that differ from the experimental value by $0.01eV$. In Table 3, about 75% of the work function of metals calculated using the stabilized jellium model are in good agreement with experimental values for the hexagonal closed packed (hcp) metals apart from the work functions of Be, Co, Cd which differed from the experimental values by over $0.76eV$. In Table 3, the calculated work function for the flat surface is greater than the calculated work function of the (0001) face.

The difference in our calculated work functions and experimental values may be due to the fact that the experimental values are for polycrystalline samples and may be the average over different faces. Also, the experimental work functions are affected by purity of the sample, the method of measurement and surface distribution of crystal facets [1]. The results obtained for the following metals : Li, Na, K, Rb, Cs, Al, Pb, Zn, Mg, Ca, Sr and Ba compares very well with the results of Perdew et al.,[11],that calculated the work function of the above mentioned metals and did not compare the results they obtained with experimental values. Our calculated work function for Li, Na, K, Rb, Cs, Ca, Sr and Ba are close to experimental values although generally lower than experimental values. The work function of Li, Na, K, Rb, Cs, Ca, Sr and Ba calculated by Perdew et al.,[11] are generally higher than experimental values and they are not in good agreement with experimental values. The results of Perdew et al.,[11] for Pb, Zn, Al and Mg are lower than experimental values and are not in good agreement with experimental values. But our calculated work function for Pb, Zn, Al and Mg are close to experimental values but lower than the experimental values. The work function of Li, Na, K, Cs, Rb, Ca, Mg, Sr, Ba, Pb, Zn, Mg and Al calculated in this work are in better agreement with experimental values than that of Perdew et al.,[11], This may be due to stabilization potential of the different faces that was fully considered in this work.

The results obtained in this work is in better agreement with experimental values than the results of Serena et al.,[19] that performed full-self-consistent calculation of electron density and work functions of Li, Na, Cs,Al and Pb at (111), (110) and (100) faces. The stabilized jellium model results for the work functions of AL, Li, Pb, Zn, Mg, Na compares favourably well with experimental values than the results obtained by Monnier et al.,[9] that calculated the work functions of Al, Li, Pb, Zn, Mg, Na within the density-functional theory of the inhomogeneous electron gas.

Figure 1: Stabilizing potentials for body centred cubic (bcc) metals

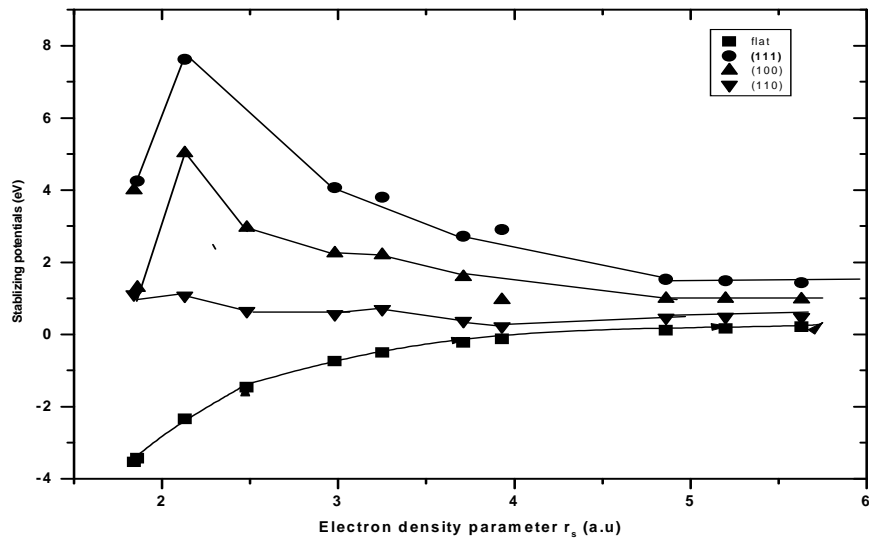


Figure 2: Stabilizing potentials for face centred cubic (fcc) metals

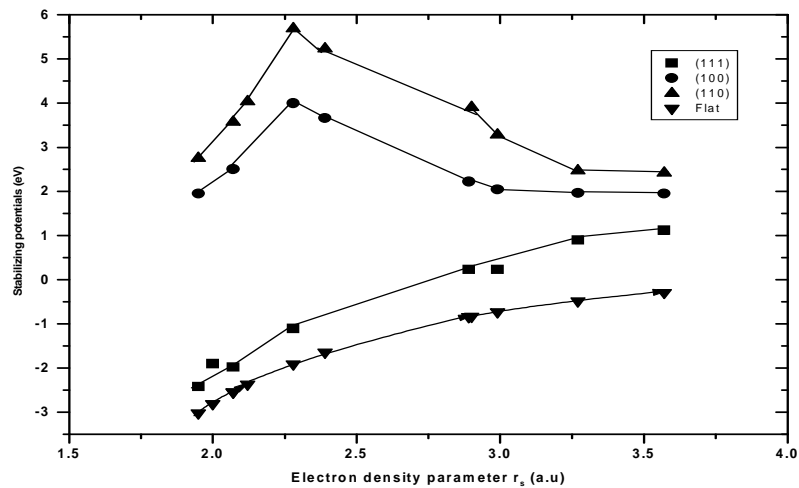


Figure 2: Stabilizing potentials for face centred cubic (FCC) metals

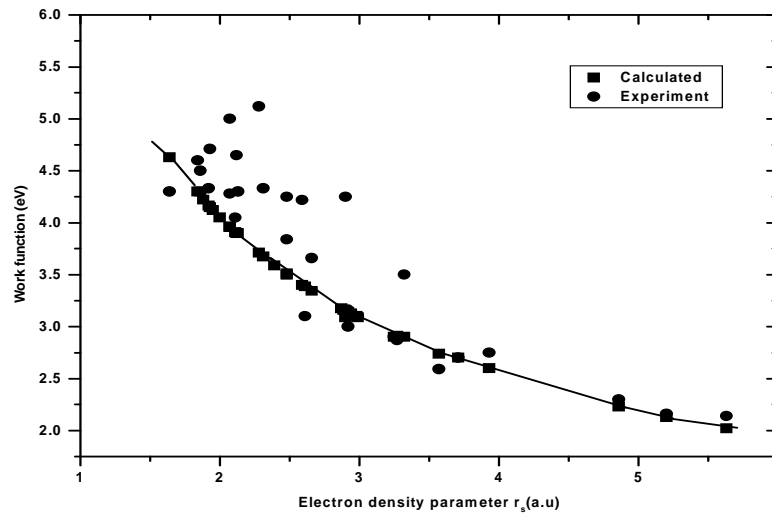


Figure 3: Variation of calculated work function for flat metal surfaces and experimental values with electron gas parameter.

4.0 Conclusion

The stabilized jellium model has been successfully used to calculate the stabilizing potential and work function of elemental metals and their face dependence. The stabilization potential for different faces depends inversely on the electronic concentration of the face. The calculated work functions for the (111), (100), and (110) faces for body centred cubic (bcc) and face centred cubic (fcc) metals revealed that the most closely packed faces have the highest work function. The work function of elemental metals obtained from the stabilized jellium model calculation was in fairly good agreement with experimental values. The stabilized jellium model gave more accurate results for the work functions of bcc metals, followed by hexagonal closed packed (hcp) metals and was least accurate for face centred cubic (fcc) metals, and majority of the fcc metals are in the high-density limit ($r_s < 3.0a.u.$). This shows that the stabilized jellium model could be used to calculate and predict the work function of metals and other metallic properties.

Table 1: Stabilized jellium, Abinito and experimental work function of body centred cubic (bcc) metals

Metal	crystal Structure	$r_s(a.u)$	Face	Work function W (eV)		
				Stabilized jellium	Ab inito[10]	Exp[1]
Li	Bcc	3.25	flat	2.92		2.9
			111	2.94		
			100	3.36	3.33	
			110	3.64	3.15	
Na	Bcc	3.93	Flat	2.57		2.75
			111	2.14		
			100	2.64	2.76	
			110	2.99	2.94	
K	Bcc	4.86	Flat	2.23		2.30
			111	1.45	2.41	
			100	2.08	2.34	
			110	2.49	2.38	

Rb	Bcc	5.20	Flat	2.13		2.16
			111	1.26	2.29	
			100	1.94	2.22	
			110	2.38	2.32	
Cs	Bcc	5.63	Flat	2.02		2.14
			111	1.08	2.10	
			100	1.79	2.03	
			110	2.28	2.09	
Ba	Bcc	3.71	Flat	2.70		2.7
			111	2.45	2.23	
			100	3.21		
			110	3.72	2.28	
Cr	Bcc	1.86	Flat	4.25		4.5
			111	4.42		
			100	4.19		
			100	5.25		
Fe	Bcc	1.86	Flat	4.25		4.5
			111	4.38	5.54	4.81
			100	4.75		4.67
			110	5.01	5.16,	5.78
Nb	Bcc	2.13	Flat	3.88		4.3
			111	4.17		4.36
			100	4.93		
			110	5.49	4.63	4.87
Mo	Bcc	1.84	Flat	4.28		4.6
			111	4.51		4.55
			100	5.21		4.53
			110	5.67	5.34	4.95
Ta	Bcc	2.48	Flat	3.51		4.25
			111	3.72		4.00
			100	4.39		4.15
			110	4.84	5.08	4.80
Eu	Bcc	2.98	Flat	3.10		2.5
			111	3.36		
			100	4.16		
			110	4.70	2.45	

Table 2: Stabilized jellium, Ab initio and experimental work function of face centred cubic (fcc) metals.

Metal	Crystal structure	$r_s(\text{a.u.})$	Face	Work function W (eV)		
				Stabilized jellium	Abinitio[10]	Expt[1]
Ca	Fcc	3.27	Flat	2.91		2.87
			110	2.92	2.86	
			100	3.27		
			111	3.81	2.84	
Sr	Fcc	3.57	Flat	2.74		2.59
			110	2.52	2.42	
			100	2.91		
			111	3.49	2.39	
Pb	Fcc	2.90	Flat	3.16		4.25
			110	3.28		
			100	3.87		
			111	4.34		
Ni	Fcc	2.07	Flat	3.96		5.51
			110	4.05		5.35

			100	4.27		5.22
			111	4.60		5.04
Cu	Fcc	2.12	Flat	3.90		4.65
			110	3.99		4.98
			100	4.22		4.59
			111	4.56		4.48
Rh	Fcc	1.95	Flat	4.12		4.98
			110	4.25	5.91	
			100	4.59		
			111	5.10	6.14	
Pd	Fcc	2.28	Flat	3.71		5.12
			110	3.87	5.90	5.6
			100	4.30	5.96	
			111	4.85		
Ag	Fcc	2.89	Flat	3.16		4.26
			110	3.24	5.01	4.74
			100	3.44	5.02	4.64
			111	3.73	4.40	4.52
Pt	Fcc	2.0	Flat	4.05		5.65
			110	4.19	6.74	5.7
			100	4.53	6.97	
			111	5.05		
Au	Fcc	2.39	Flat	3.59		5.1
			110	3.66	6.01	5.31
			100	3.82	6.16	5.47
			111	4.06	5.40	5.40
Yb	Fcc	2.99	Flat	3.09		
			110	3.17	2.51	
			100	3.38		
			111	3.68	2.45	
Al	Fcc	2.07	Flat	3.96		4.28
			110	4.08	4.54	4.24
			100	4.37		4.41
			111	4.81		4.06

Table 3: Stabilized jellium, Ab initio and experimental work function of Hexagonal closed packed (hcp) metals.

Metal	crystal structure	$r_s(a.u)$	Face	Work fuction W(eV)		
				Stabilized jellium	Ab initio[10]	Expt[1]
Be	hcp	1.88	Flat 0001	4.22 3.34	5.62	4.98
Mg	hcp	2.66	Flat 0001	3.34 3.25	3.86	3.66
Tl	hcp	2.48	Flat 0001	3.51 3.39		3.81
Sc	hcp	3.32	Flat 0001	2.88 2.58	3.74	3.5
Ti	hcp	1.92	Flat 0001	4.16 4.07	4.59	4.33
V	hcp	1.64	Flat 0001	4.63 4.57	5.2	4.3

Co	hcp	2.07	Flat 0001	3.96 3.88	5.81	5.0
Zn	hcp	2.31	Flat 0001	3.68 3.59		4.33 4.9
Y	hcp	2.61	Flat 0001	3.39 3.29	3.38	3.1
Zr	hcp	2.11	Flat 0001	3.90 3.79	4.15	4.05
Ru	hcp	1.93	Flat 0001	4.15 4.04	5.84	4.71
Cd	hcp	2.59	Flat 0001	3.40 3.31		4.22
Gd	hcp	2.99	Flat 0001	3.09 2.95		3.1
Tb	hcp	2.92	Flat 0001	3.14 3.00		3.0
Dy	hcp	2.94	Flat 0001	3.13 2.99		
Er	hcp	2.91	Flat 0001	3.15	3.01	
Tm	hcp	2.89	Flat 0001	3.16 3.02		
Lu	hcp	2.87	Flat 0001	3.18 3.04	3.57	3.3

References

- [1] Michaelson, H.B. (1977), The work function of the elements and its periodicity. *Journal of Applied Physics* Vol. 48, No.11, 4729-4733.
- [2] Hudson, J.B., (1992), *Surface Science: An Introduction*, Butterworth-Heinemann Publishers, USA, pp. 35 – 48.
- [3] Yoshitake, M. and Yoshihara, K., (1999), Measurement of work function change with surface segregation and substrate element on a deposited film. *Applied Surface Science* 144, 97 – 100.
- [4] Nishiyama, H. and Inoue, Y. (2006), PEEM Study of work function changes in Cu, Au, and Pd metal surfaces with surface acoustic wave propagation. *Surface Science*. 600, 2644- 2649.
- [5] Wigner, G. and Bardeen, J. (1935), Theory of the work function of monovalent metals *Physical Review* 48, 84 - 87.
- [6] Smith, J. R. (1969), Self-consistent many electron-electron theory of work function and surface potential characteristics for selected metals. *Physical Review B* Vol.181, No.2, 522 – 528.
- [7] Lang, N.D. and Kohn, W. (1971), Theory of metal Surfaces: Work function *Physical Review B*, Vol. 3, 1215 – 1223.
- [8] Mahan, G. D. and Schaich W. L. (1974), Comment on the theory of work function, *Physical Review B*, Vol.10, No.6, 2647 -2651.
- [9] Monnier, R., Perdew, J. P., Langreth, D.C. and Wilkin, J. W., (1978), Change-in-self- consistent-field theory of the work function. *Physical Review B*, Vol.13, N0.2, 656 – 666.
- [10] Skriver, H. L. and Rosengard, N. M. (1992), Surface energy and work function of elemental metals. *Physical Review B*, Vol.46, N0.11, 7157 – 7167.
- [11] Perdew, J.P. Tran, H. Q. and Smith, D. E. (1990), Stabilized jellium: Structureless pseudopotential model for the cohesive and surface properties of metals. *Physical Review B*, Vol. 42, No. 18, 11627 -11636.
- [12] Monnier, R. and Perdew, J. P. (1978), Surfaces of real metals by the variational self-consistent method. *Physical Review B*, Vol. 17, No.6, 2595 -2611.
- [13] Fiolhais, C. Henriques, C. Sarria, I. and Pitsrke, J. M. (2001), Metallic slabs: Perturbative treatments based on jellium. *Progress in surface Science* Vol. 67, 285-298.
- [14] Sarrina, L., Henriques, C, Fiolhais, C. and Pitarke, J. M. (2001), Slabs of stabilized jellium. Quantum – size and self compression effects. *Physical Review B*, Vol. 62, N0.3, 1669 – 1705.
- [15] Seidl, M., Perdew, J. P, Brajczewska, M. and Fiolhais, C. Ionization energy and electron affinity of a metal cluster in the stabilized jellium model: Size effect and charging limit. *Journal of chemical Physics* Vol. 108, No. 19, 8182 -8189.

- [16] Wojciechowski, K. F. (1995), Bulk properties of stabilized uniform interstitial electron gas in metals. *Physical Review B*, Vol. 51, B0. 4, 2563 - 2565. .
- [17] Perdew, J. and Zunger, A. (1981) Self-interaction correction to density functional approximation for many electron system . *Physical Review B*, Vol. 23, No. 10, 5075 – 5076.
- [18] Kiejna, A (1993) Surface properties of simple metals in a structureless pseudopotential *Physical Review B*, Vol. 47, No. 12, 7361 – 7364.
- [19] Serena, P. A., Sover, J. M and Garcia, N. (1998), Work function and image-plane position of metal surfaces. *Physical Review B*, Vol. 37, No.15, 8701 – 8706.