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Electron Density Profiles In Metallic Surfaces

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Abstract:- This paper takes a look at the properties of electron density profiles at the metal surfaces; this was done by calculating the properties in the bulk, at the surface and just outside the metal surface using the equations proposed by Kiejna and Wojciechowski. The results obtained shows that; in the bulk of metals, electron density profile depends inversely on the concentration of the electrons and also on the binding energy of the metal as binding energy per electron exhibit the same trend. It decays and saturates exponentially towards the bulk.

Keyword: Electron density profile, metallic surfaces.

I. INTRODUCTION AND METHODOLOGY

A positive charge of density $\rho(r)$ is superimposed on an electron gas of concentration $n_0 e$ where e is the electronic charge, the positive charge will give rise to an electrostatic potential $\phi(r)$. If $V(r)$ is the potential established as a result of the movement of the charge density, then the total $U(r)$ is

$$U(r) = \phi(r) + V(r) \qquad (1)$$

This is connected with one electron wave function $\psi_i(r)$ the sum over take the psi to right place occupied states

$$n(r) = \sum_{i=1} \psi_i^{*}(r)\psi_i(r) \qquad (2)$$

The function ψ_i satisfy one-electron Schrödinger wave equation

$$H\psi_i = \varepsilon_i \psi_i \qquad (3)$$

with the Hamiltonian;

$$H = -\frac{1}{2}\nabla^2 + V(r) \qquad (4)$$

since

$$t_s[n] = \frac{3}{10}\left(3\pi^2\right)^{\frac{2}{3}} n^{\frac{5}{3}}(r) \qquad (5)$$

$t_s[n]$ is the kinetic energy while $V(r)$ is the potential energy with which the electron moves. The total kinetic energy is given by

$$T_0 = \int t_s[n]dr = \frac{3}{10}\left(3\pi^2\right)^{\frac{2}{3}} \int n^{\frac{5}{3}}(r)dr \qquad (6)$$

denotes that t_s is a functional of $n(r)$. $V_e(r)$ and $V_a(r)$ are the coulomb's repulsive potential energy and the external ionic potential energy respectively.

$$V_e = \int \frac{n(r')}{|r - r'|}dr \qquad (7)$$

thus the total energy expressed in terms of electron density is given by;

$$E[n] = \int n(r)V_a(r)dr + \frac{1}{2}\int \frac{n(r)n(r')}{|r - r'|}drdr' = \frac{3}{10}\left(3\pi^2\right)^{\frac{2}{3}} \int n^{\frac{5}{3}}(r)dr \qquad (8)$$

it should be noted that the total electron number is the same in this condition i.e. $\int n(r)dr = N$ The ground state density n(r) can be determined variationally and the variation calculation gives the Euler $\delta\left\{E\left[n(r)\right]-\lambda\int n(r)dr\right\}$ and replacing the langrangian multiplier $\lambda = \mu$ in the above equation gives;

$$\int\left[V_a(r)+\int\frac{n(r')}{|r-r'|}dr'+\frac{1}{2}\left(3\pi^2\right)^{\frac{2}{3}}-\mu\right]\delta n\delta r \qquad (9)$$

where $\lambda=\frac{\delta E[n]}{dn}=\mu$ which is the chemical potential and

$$V_a(r)+\int\frac{n(r')}{|r-r'|}dr'+\frac{1}{2}\left(3\pi^2\right)^{\frac{2}{3}}-\mu=0 \qquad (10)$$

The total electrostatic potential is; $\phi(r)=V_a(r)+\int\frac{n(r')}{|r-r'|}dr'$ replacing this in (1) gives

$$\phi(r)+\frac{1}{2}\left(3\pi^2\right)^{\frac{2}{3}}[n(r)]^{\frac{2}{3}}=\mu \qquad (11)$$

Making n(r) the subject of formula gives

$$n(r)=\frac{1}{3\pi^2}[2(\mu-\phi(r)]^{\frac{3}{2}} \qquad (12)$$

this is the Thomas-Fermi equation which when in the semi infinite methods takes the form;

$$n(x)=\frac{1}{3\pi^2}[2(\mu-\phi(r)]^{\frac{3}{2}} \qquad (13)$$

The electrostatic potential obeys Poisson's equation

$$\frac{d^2\phi_{(x)}}{dx^2}=-4\pi\left[n(x)\,n\theta(-x)\right] \qquad (14)$$

hence,

$$\phi_{(X)}=-\frac{1}{2}\left[3\pi^2 n(x)\right]^{\frac{3}{2}}+\mu \qquad (15)$$

Using the Poisson equation (15) gives

$$\frac{1}{2}(3\pi^2)^{\frac{2}{3}}\left[\frac{dn^{\frac{2}{3}}(x)}{dx^2}\right]d\left[\frac{dn^{\frac{2}{3}}(x)}{dx^2}\right]=4\pi\left[n(x)-n(-x)\right]dn^{\frac{2}{3}}(x) \qquad (16)$$

Integrating for x less than zero which is the boundary condition inside the positive background $n(x)\to\bar{n}$ and $\frac{dn(x)}{dx}\to 0$.

For, $x\to-\infty$,

$$\frac{1}{4}(3\pi^2)^{\frac{2}{3}}\left[\frac{dn^{\frac{2}{3}}(x)}{dx^2}\right]=4\pi\left[\frac{2}{5}n^{\frac{5}{3}}(x)-n\bar{n}^{\frac{2}{3}}(x)+\frac{3}{5}\bar{n}^{\frac{5}{3}}\right] \qquad (17)$$

Integrating along the boundary condition $X>0$, $X\to\infty$ and $n(x)\to 0$. Then;

$$\frac{1}{4}(3\pi^2)^{\frac{2}{3}}\left[\frac{dn^{\frac{2}{3}}(x)}{dx^2}\right]^2 = \frac{8\pi}{5}n^{\frac{5}{3}}(x) \qquad (18)$$

and for $X \to 0$ we obtain;

$$n^{\frac{2}{3}}(0) = \frac{3}{5}n^{-\frac{2}{3}} \qquad (19)$$

$\bar{x} \equiv \frac{x}{\lambda_{TF}}$ and $\bar{n} \equiv \frac{n}{\bar{n}}$ where λ_{TF} is the Thomas-Fermi screening length

$$\frac{x}{\lambda_{TF}} = \left(\frac{4K_F}{\pi a_o}\right)^{\frac{1}{2}} \qquad (20)$$

$$\lambda_{TF} = \frac{1}{K_{TF}} = \frac{r_s^{\frac{1}{2}}}{3\alpha}a_o \qquad (21)$$

$$a_0 = \frac{\hbar^2}{me^2}$$

$\alpha = 0.52106$

In the bulk, at $X \to -\infty$ the solution to the equation now becomes:-

$$V_{(x)} = \frac{n(x)}{\bar{n}} \approx 1 - 0.621\left(\frac{x}{\lambda_{TF}}\right) \qquad (22)$$

At the surface $X = 0$

$$V(r_s) = 0.503006 - 0.0265357\ r_s + 0.000535743\ r_s \qquad (23)$$

Away from the jellium surface X>0

$$V_{(x)} = 27000\left(\frac{x}{\lambda_{TF}} + a\right)^{-6} \qquad (24)$$

Necessary equations derived in this chapter were used to compute different electronic properties of metallic surfaces.

II. RESULTS AND DISCUSSION

Table 1.0 gives the electron density profile for group one and group two metals. The electron density profiles in Figure 1.0 to figure 5.0 shows that the variation of electron density profile with distance. The figures revealed that the electron density profiles decreases exponentially from the surface into the bulk of the metals. At the surface, i.e when x > 0 equation 24, all the metals have the same value of the electron density profile, but as we proceed into the bulk, the electron density profile of the metals begins to vary. As shown in the Figure 1.0 , Be is highest for the group two metals; this is followed by Mg, then Ca, Sr and finally Ba. This seems to suggest that electron density profile depends inversely on the concentration of the electrons on the bulk of the metals and also on the binding energy per electron of the metal as the binding energy per electron of the metals exhibit the same trend. The same trend is seen in othr groups as seen in figures 2.0 to 5.0 confirming this trend.

Figure 6.0 to 10.0 shows the variation of electron density profiles for the group one and two and three at x < 0. The figure was obtained using the (equation 22), at it reveals that the electron density profile decays with inverse sixth power of the energy distribution, while inside the bulk, the electron density profile saturates exponentially towards the bulk. The observed phenomenon is due to the electronic concentration of the metals. The high electron density profile at near the metallic surfaces may be due to the formation of electron clouds at the metallic surfaces. This may also be due to the high value or valence electrons at the metallic surfaces.

Figure 11 shows the variation of electron density variation at x = 0 (equation 23) for different metallic surfaces. The figure reveals that metal in the high density limit, they have low values of the electron density profile, metals in the high density limit have low electronic density concentration while metals in the low density limit

has high electronic density concentration. This may be due to the fact that the same group exhibit similar electronic properties as their surfaces.

Table 1.0 Electron density profiles for group one metals

Separating distance	Li	Na	K	Rb	Cs
-2	0.87265	0.8524	0.8288	0.8229	0.8147
-1.9	0.86215	0.8412	0.8174	0.8115	0.8031
-1.8	0.8508	0.8296	0.8052	0.7992	0.791
-1.7	0.8385	0.8169	0.7923	0.7862	0.7778
-1.6	0.8252	0.8032	0.7785	0.7724	0.764
-1.5	0.8107	0.7886	0.7637	0.7577	0.7493
-1.4	0.7952	0.7728	0.748	0.742	0.7337
-1.3	0.7783	0.7559	0.7312	0.7253	0.7171
-1.2	0.76	0.7377	0.7133	0.7075	0.6994
-1.1	0.7402	0.7182	0.6942	0.6886	0.681
-0.9999	0.7188	0.6972	0.674	0.6684	0.661
-0.8999	0.6956	0.6747	0.6522	0.6469	0.64
-0.7999	0.6705	0.6504	0.629	0.6241	0.6172
-0.6999	0.6433	0.6244	0.6044	0.5997	0.5933
-0.5999	0.6139	0.5964	0.5781	0.5738	0.568
-0.4999	0.5821	0.5664	0.55	0.5462	0.541
-0.3999	0.5477	0.5341	0.52	0.5168	0.5124
-0.2999	0.5104	0.4994	0.4881	0.4855	0.482
-0.1999	0.467	0.4621	0.4541	0.4522	0.4497
-0.0999	0.4263	0.422	0.4177	0.4168	0.4154
0	0.379	0.379	0.379	0.38	0.379
0.1	0.3278	0.3328	0.3377	0.3388	0.3403
0.2	0.2724	0.2831	0.2936	0.296	--
0.3	0.2124	0.2297	0.2466	0.2504	0.2555
0.4	0.1475	0.1723	0.1965	0.2019	0.2091
0.5	0.0772	0.1107	0.143	0.1502	0.1598
0.6	0.0011	0.0445	0.086	0.0951	0.1074
0.7	-0.0812	-0.0267	0.0252	0.0366	0
0.8	-0.1704	-0.1031	-0.0397	-0.0258	-0.0073
0.9	-0.2669	-0.1853	-0.1089	-0.0922	-0.0701

Table 2.0 Electron density profiles for group two metals

Separating distane (au)	Be=1.87	Mg = 2.65	Ca= 3.27a	Sr= 3.57	Ba= 3.71
-2	0.9238	0.8934	0.8729	0.8639	0.8600
-1.9	0.9154	0.8836	0.8625	0.8533	0.8492
-1.8	0.906	0.8729	0.8511	0.8417	0.8376
-1.7	0.8957	0.8612	0.8388	0.8292	0.8249
-1.6	0.8841	0.8484	0.8255	0.8157	0.8114
-1.5	0.8713	0.8344	0.8111	0.8012	0.7968
-1.4	0.8571	0.8192	0.7955	0.7855	0.7811
-1.3	0.8412	0.8025	0.7786	0.7686	0.7642
-1.2	0.8237	0.7843	0.7603	0.7503	0.7459
-1.1	0.8042	0.7644	0.7405	0.7306	0.7263
-0.9999	0.7825	0.7428	0.7191	0.7094	0.7052
-0.8999	0.7585	0.7191	0.6959	0.6865	0.6824
-0.7999	0.7312	0.6932	0.6708	0.6617	0.6578
-0.6999	0.7021	0.6649	0.6436	0.6350	0.6313
-0.5999	0.6691	0.6340	0.6142	0.6062	0.6028

-0.4999	0.6325	0.6003	0.5824	0.5752	0.5721
-0.3999	0.5912	0.5635	0.5479	0.5417	0.5390
-0.2999	0.5467	0.5233	0.5105	0.5055	0.5034
-0.1999	0.4965	0.4794	0.4701	0.4665	0.4649
-0.0999	0.4409	0.4314	0.4264	0.4244	0.4236
0	0.379	0.3789	0.3789	0.3789	0.3789
0.1	0.3103	0.3218	0.3277	0.3300	0.3309
0.2	0.234	0.2593	0.2722	0.2772	0.2792
0.3	0.1491	0.1910	0.2121	0.2201	0.2235
0.4	0.0552	0.1165	0.1471	0.1586	0.1635
0.5	-0.0493	0.0351	0.0766	0.0292	0.0988
0.6	-0.165	-0.0538	0.0004	0.0206	0.0291
0.7	-0.2943	-0.1509	-0.0822	-0.0567	-0.0460
0.8	-0.4375	-0.2569	-0.1715	-0.1400	-0.1269
0.9	-0.5965	-0.3727	-0.2682	-0.2299	-0.2140

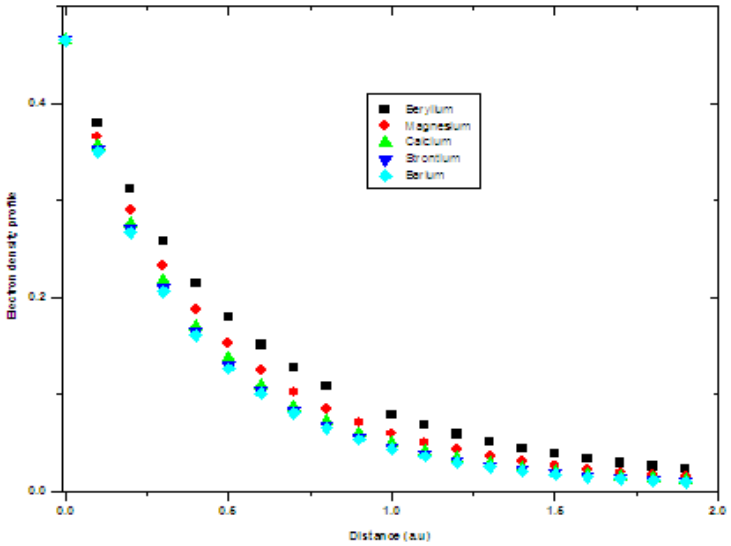

Figure 1.0 electron density profile outside the bulk x>0 for group 2 metals

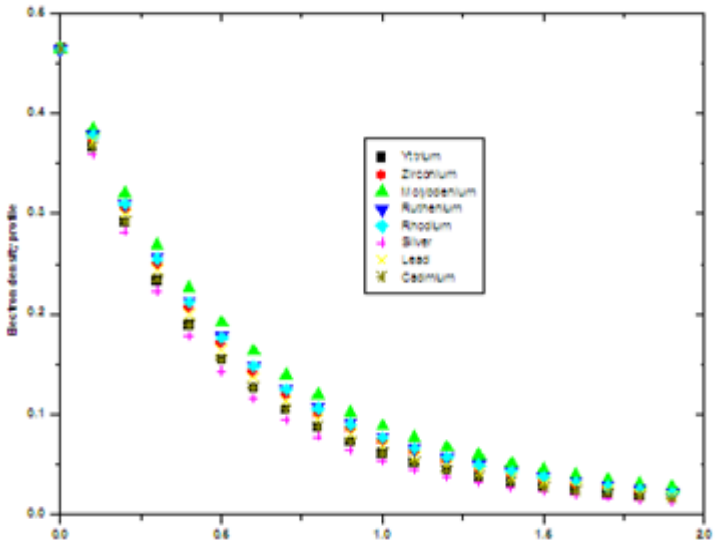

Figure 2.0 electron density profile outside the bulk x>0 for metals

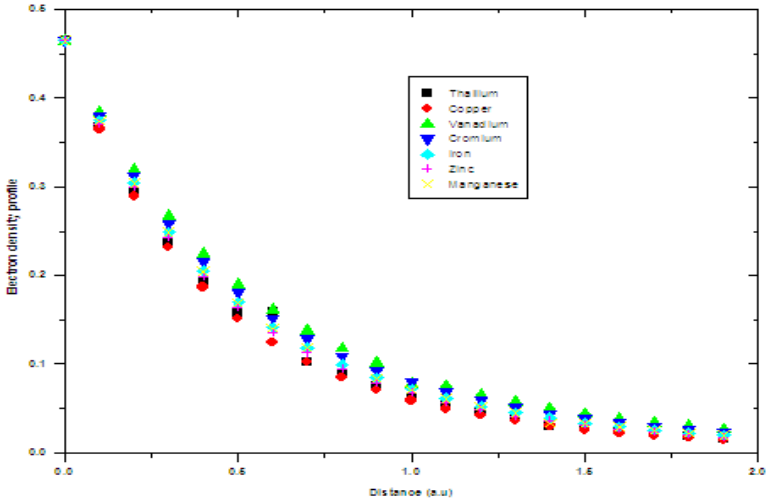

Figure 3.0 electron density profile outside the bulk x>0 for metals

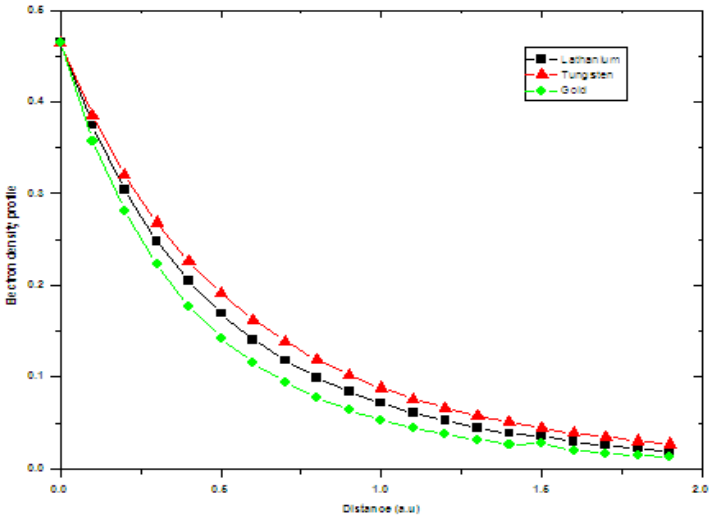

Figure 4.0 electron density profile outside the bulk x>0 for metals

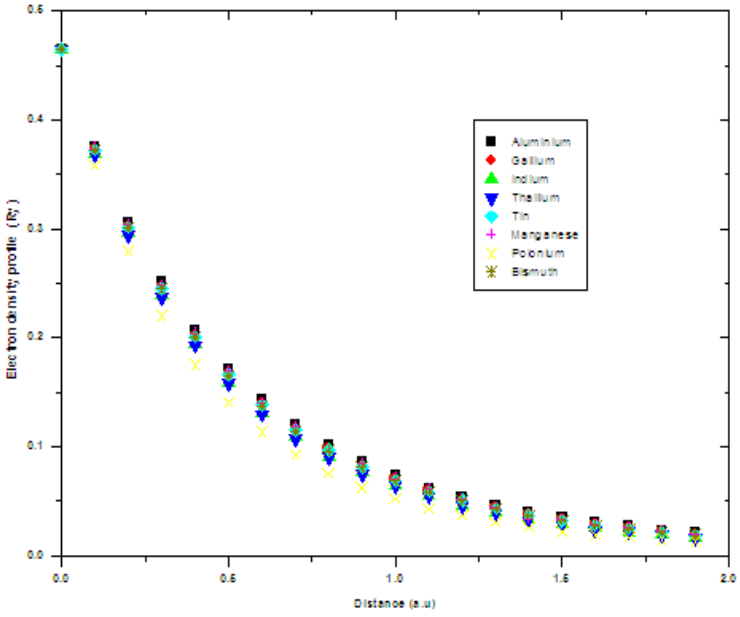

Figure 5.0 electron density profile outside the bulk x>0 for metals

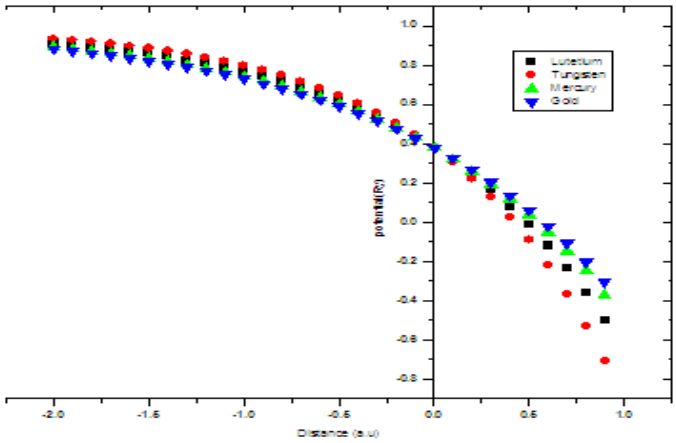

Figure 6.0 electron density profile inside the bulk x<0 for group 2 metals

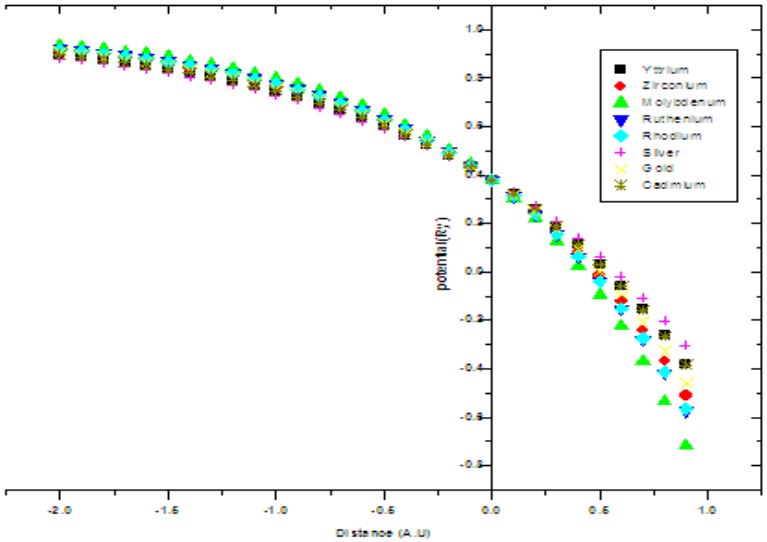

Figure 7.0 electron density profile inside the bulk x<0 for some selected metals

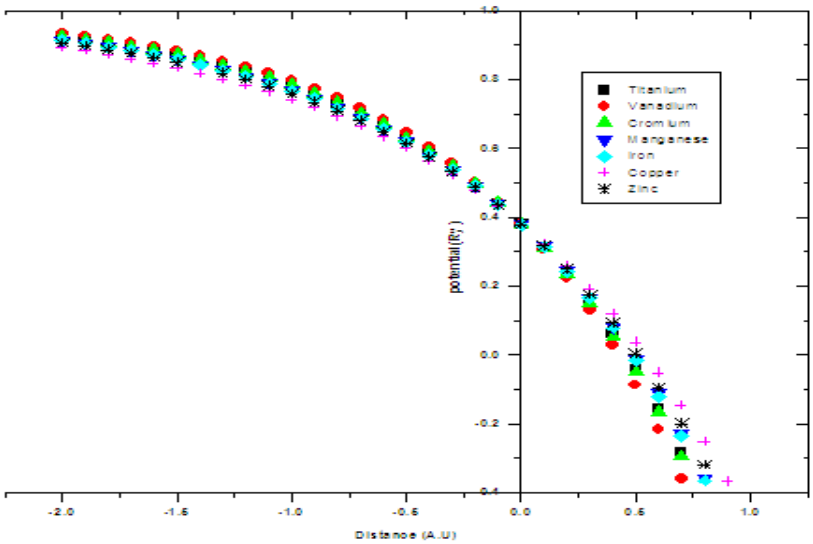

Figure 8.0 electron density profile inside the bulk x<0 for some selected metals

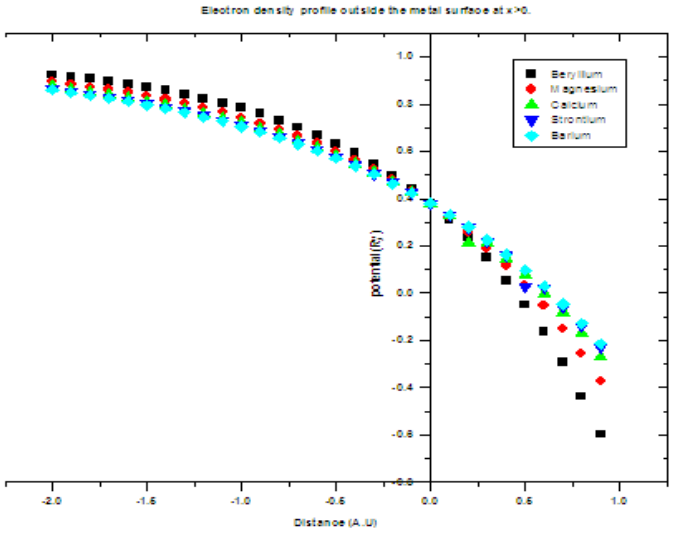

Figure 9.0 electron density profile inside the bulk x<0 for some selected metals

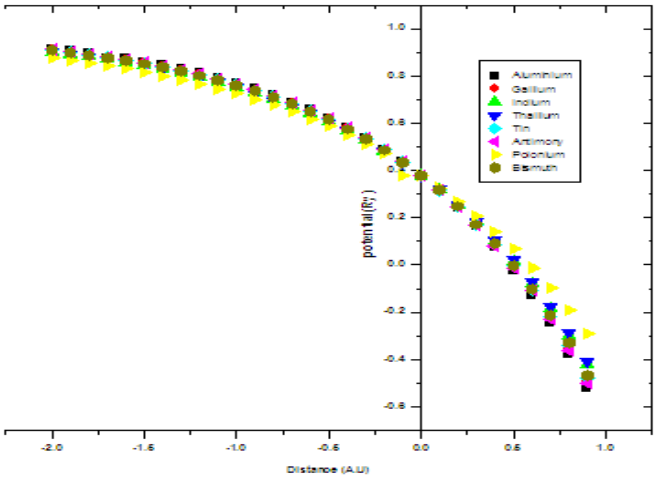

Figure 10.0 electron density profile inside the bulk x<0 for some selected metals

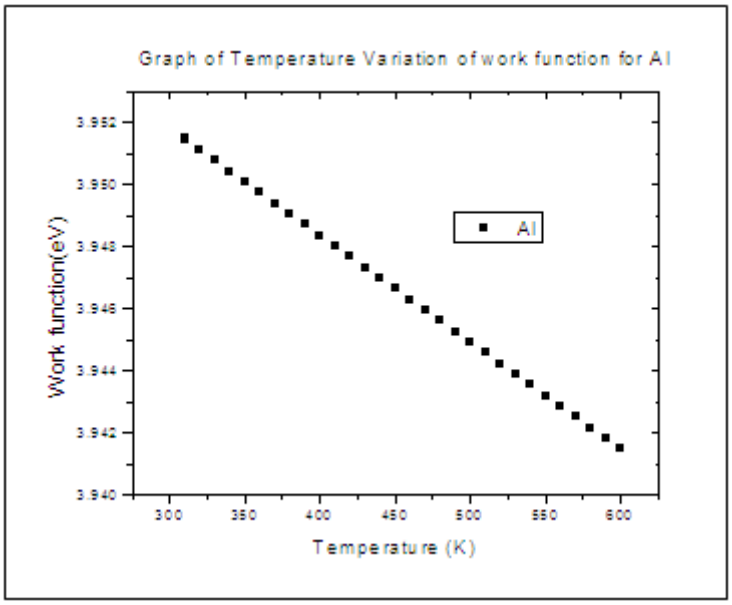

Figure 11.0 electron density profile sat the surface x=0 for metal surfaces using copper as reference point

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