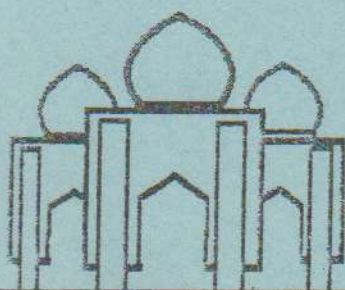


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The Chemisorption of Alkali ions on Ni surface

H.Q.AL-Edany

*Physics Department, College of Education, University of Basrah,
Basrah, Iraq.*

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Abstract:

The adatom's effective charges and chemisorption energies are calculated and investigated as a function of distance and surface temperature within the framework of previous papers [8,1], in which analytical formula were developed for the effective charges and chemisorption energy where the repulsion of the two electrons of opposite spins in the adatom was taken into account by means of the correlation energy. All the chemisorption functions (are considered as input data to calculate the effective charges and energies) are calculated and discussed. While the binding energies are calculated and showing a good agreement as it is compared with the experimental data.

Introduction:

The study of the interaction between adatoms and surface is considered as one of the most important subjects in surface physics, since it looks for calculating the adatom's binding energy and the potential energy dependence on the distance normal to the surface [1] during the adsorption and desorption processes.

As the atom approaches the surface, its atomic levels (Ionization level V_i and affinity level V_A) will be shifted due to image forces and broadened due to their interaction with the solid band levels. It is well known that as the atom chemisorbed on the surface, chemical bond is formed between the adatom and the surface will be compensating by redistribution and rearranging in the electronic surface density. The nature of this bond is restricted between the ionic bond and the covalent bond. It is possible to compute the chemisorption energy and study the factors that affect the chemisorption process throughout calculation potential energy curves or what is called "Potential Energy Surfaces" PES. These calculations are considered as a very important step in the chemisorption theory. The researchers offered many theoretical studies on chemisorption and one of the most important studies was awarded by Rasser and Remy [2] to explain the dependence of the charge exchange process on the normal distance to the surface and surface temperature, taking into account the image shift and the correlation effects. Gadzuk and others [3] offered a theory of chemisorption concern with the adsorption of alkali atoms on metal surfaces. The alkali chemisorption energy is proposed to consist of two parts, the metallic and the ionic parts. They concluded that the ionic bond is prevailing as the alkali ion chemisorbed on the transitional metal surface. Analytical formula was also derived by Kjollerstrom and others [4] to calculate the ground state energy for an impurity atom in a metal depending on Anderson's model [5] by using "low density approximation" taking into account the correlation effects. A method was derived to compute the chemisorption energy of atom on solid surface by Edwards and Newns [6] according to Anderson's model, in that method, the chemisorption energy was defined as the change of ground state energy when the interaction start between adatom and the surface. Researchers like Brivio [7] and others assured the importance of taking lattice structure into account in their studies to chemisorption using "Local Density Functional Approximation" and they discussed the effect of the bandwidth on adatom levels. Recently, analytical consequences of chemisorption theory are derived and discussed in part (2) of ref. [8]. Their realistic treatment was extended to large atom surface separation and the temperature effect was also introduced.

$$\begin{aligned} \pi n_a^\sigma = & 2a_2 k_B T \Gamma - \tan^{-1} \left(\frac{u_0 - E_a^\sigma}{\Gamma} \right) + a_2 \Gamma E_a^\sigma \ln \frac{(k_B T - E_a^\sigma)^2 + \Gamma^2}{(k_B T + E_a^\sigma)^2 + \Gamma^2} \\ & + B_1^\sigma \tan^{-1} \left(\frac{-k_B T - E_a^\sigma}{\Gamma} \right) + B_2^\sigma \tan^{-1} \left(\frac{k_B T - E_a^\sigma}{\Gamma} \right) \end{aligned} \quad \text{-----}(1)$$
$$E_a^{\pm\sigma} = \phi_o - V_i + \Delta E + U_{eff} n_a^{\mp\sigma} \quad \text{-----}(2)$$
$$E_M(S) = \frac{1}{\pi} \sum_{\sigma} \sum_{i=1}^5 C_i^{\sigma} g_i^{\sigma} - U_{eff} n_a^{\sigma} n_a^{-\sigma} \quad \text{-----}(3)$$
$$E_I(S) = -e^2 \int_S^\infty \frac{Z_{eff}^2(S') dS'}{4(S' + S_0)^2} \quad (4)$$
$$E_{CH}(S) = E_M(S) + E_I(S) \quad \text{-----}(5)$$
$$E_B = E_{CH}(S=0) - E_{CH}(S=\infty) \quad \text{-----}(6)$$

In this work, a complete treatment was got used to calculate the occupation numbers for the systems alkali atoms/Ni surface taking into account the effects of distance, temperature, screening length, image effects and correlation effects. Then the results of these calculations have been used to calculate the energies that are mentioned above. For more details, see the references [1,10].

Results and discussion:

In the chemisorption model; the work function is the surface discriminated factor (which was included in $E_a^{\pm\sigma}$ formula) and the discriminated factors of the adatom are represented by the ionization level (and affinity level) and the atomic radius which is included into the correlation energy formula (U_{eff}) and the half width ($\Gamma^{\pm\sigma}$) consequently.

All correlation interactions have been neglected except those that occur on the adatom, U_{eff} , which include the image shift effects. Worth mentioning, the screening effects influence clearly near the surface and determine the atomic level positions and ionic binding energy.

It is well known that the image shift depends on the particle position from the surface (S) and on the screening length (S_o) which is related to a type of surface and varies with the work function value (ϕ_o). That makes screening length should be varied with used face because its value (S_o) depends on the circumstances in which the preparation of that surface was accomplished for the experiment.

In this section, the following tables (from 1 to 5) will explain that the atom's kind and the surface face have a great effect on the binding energy calculation.

Firstly, the system Na/Ni (110) has been studied because it is one of the practically used system and it also represents the state between $\phi_o > V_i$ and $\phi_o < V_i$ states, i.e. one can get the two types of solutions (magnetic ($n_a^\sigma \neq n_a^{-\sigma}$) and non-magnetic ($n_a^\sigma = n_a^{-\sigma}$)). The occupation numbers $n_a^{\pm\sigma}$ calculation was done and the corresponding energy levels E_a with the screening length $S_o=0.9872 \text{ \AA}$ for two temperatures $T=300 \text{ }^\circ\text{K}$, $T=2000 \text{ }^\circ\text{K}$ for purpose to assure its general behavior as a function to the distance and temperature.

Figure (1) and (2) shows the following:

1. In the far distances, the magnetic solutions ($n_a^\sigma \neq n_a^{-\sigma}$) appear while the non-magnetic solutions ($n_a^\sigma = n_a^{-\sigma}$) appear near the surface.

2. The occupation numbers increase for all distance values as the temperature increases.

3. The point (S_{ch}) explains the region in which the solution changes from magnetic into non-magnetic solution whereas (S_{ch}) varies with the temperature.

The importance of this point is to limit the distance at which the solutions are non-magnetic, therefore limiting the system Charge State as a function of distance.

The surface crystallography was also studied and discussed. However, table (2) shows these calculations for different Ni faces and for different screening lengths.

Chemisorption energy calculation was also done to the two solutions, the magnetic and non-magnetic one, for the system Na/Ni as a function of temperature, distance and screening length (work function) where the results of occupation numbers calculations were used as input data to calculate chemisorption energy, see figure (3). For the case $\phi_o < V_i$, two states appear: the ionic (dashed line) and the atomic (connected line) which intersect in the point (S_c), this point has an importance in the desorption process because it assures that the ground state of the system is atomic state ($E_M > E_I$) when the atom is faraway from the surface while the ionic state is ($E_M < E_I$) as the atom approach to the surface.

The calculations for the case $\phi_o > V_i$ are shown in table (2), from which one can conclude that the ionic participation in the chemisorption energy E_{CH} (in the binding energy) is prevailing to all faces and this participation increases with ϕ_o (i.e. with S_o), on the contrary of the metallic participation. To study the temperature effect, the calculation of PES was done on the Na/Ni (110) system as a function of temperature as in figure (4) and table (6) which assure that the non-magnetic state does not change according to the temperature change otherwise it is near the surface on the contrary of the magnetic state whereas the temperature increases, S_c decrease. The theoretical and experimental values of the binding energies

mentioned in the previous tables which were taken from the references [3,11] are measured with respect to the ionic state, so it must be compared with E_{CH} values. The work function value of the face Ni(110) that is used in the reference [3] was equal to 4.72 eV and the S_o values were taken from reference [12]. The results that were obtained give a good agreement with the experimental data. Concerning the energy calculations, it was found that the work function and temperature have opposite effects with work function increasing

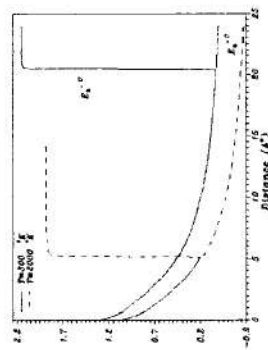


Figure (1): Shows the

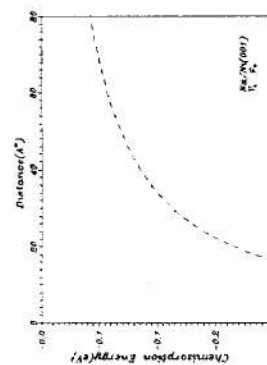


Figure (2 a). Shows the

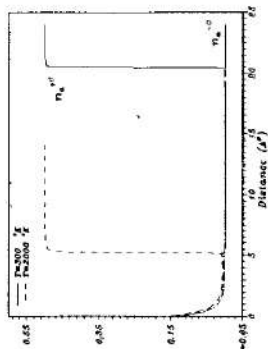


Figure (1): Shows the

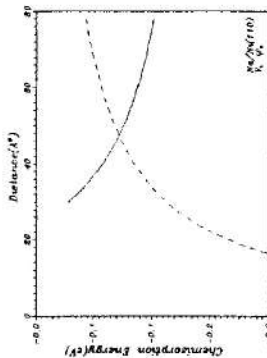


Figure (2 a). Shows the

Table (1):

Li/Ni, $V_f = 5.39 \text{ eV}$, $V_A = 0.62 \text{ eV}$, $r_f = 0.68 \text{ Å}$, $T = 300^\circ \text{K}$										
FAC	$\phi_o \text{ (eV)}$ [111]	$S_o(A'')$ [111]	n_a	$E_a \text{ (eV)}$	$U_{\text{eff}} \text{ (eV)}$	$\Gamma \text{ (eV)}$	$S_{\text{eff}}(A'')$	$E_f(S=0) \text{ (eV)}$	$E_{\text{CH}}(S=0) \text{ (eV)}$	$E_H \text{ (eV)}$
E										
110	5.04	0.8972	0.19896	1.3177	2.2233	1.2061	7.8	2.2850	0.94712	2.8821
001	5.22	1.1400	0.18892	1.4127	2.4247	1.2189	14.3	2.3304	0.91552	3.0759
111	5.35	1.2244	0.18032	1.5018	2.4875	1.2307	31.45	2.3676	0.88617	3.2138
										$S_C(A'')$
										17.5
										32.5
										80.0
										$E_H(\text{theor}) \text{ (eV)}$
										-
										-
										-

Table (2):

Na/Ni, $V_f = 5.14 \text{ eV}$, $V_A = 0.54 \text{ eV}$, $r_f = 0.97 \text{ Å}$, $T = 300^\circ \text{K}$										
FAC	$\phi_o \text{ (eV)}$ [111]	$S_o(A'')$ [111]	n_a	$E_a \text{ (eV)}$	$U_{\text{eff}} \text{ (eV)}$	$\Gamma \text{ (eV)}$	$S_{\text{eff}}(A'')$	$E_f(S=0) \text{ (eV)}$	$E_{\text{CH}}(S=0) \text{ (eV)}$	$E_H \text{ (eV)}$
E										
110	5.04	0.8972	0.12642	1.2964	2.2902	0.64094	20.35	2.0300	0.52521	2.4552
001	5.22	1.1400	0.11876	1.3952	2.4571	0.65105	-	2.0557	0.50594	2.6416
111	5.35	1.2244	0.11232	1.4891	2.5097	0.66054	-	2.0761	0.48932	2.7754
										$S_C(A'')$
										47
										-
										-
										-
										$E_H(\text{theor}) \text{ (eV)}$
										1.95
										[2]

Table (3):

K/Ni, $V_f = 4.34 \text{ eV}$, $V_A = 0.5 \text{ eV}$, $r_f = 1.33 \text{ Å}$, $T = 300^\circ \text{K}$										
FAC	$\phi_o \text{ (eV)}$ [111]	$S_o(A'')$ [111]	n_a	$E_a \text{ (eV)}$	$U_{\text{eff}} \text{ (eV)}$	$\Gamma \text{ (eV)}$	$S_{\text{eff}}(A'')$	$E_f(S=0) \text{ (eV)}$	$E_{\text{CH}}(S=0) \text{ (eV)}$	$E_H \text{ (eV)}$
E										
110	5.04	0.8972	0.05974	1.7930	1.7694	0.41177	-	1.7649	0.27669	2.7416
001	5.22	1.1400	0.05658	1.9075	1.9045	0.42026	-	1.7751	0.27121	2.9263
111	5.35	1.2244	0.05397	2.0134	1.9475	0.42802	-	1.7830	0.26758	3.0606
										$S_C(A'')$
										-
										-
										-
										$E_H(\text{theor}) \text{ (eV)}$
										1.90
										[2]

Table (4):

Rb/Ni , $V_i=4.18 \text{ eV}$, $V_A=0.42 \text{ eV}$, $r_i=1.48 \text{ Å}^0$, $T=300^\circ \text{K}$														
FAC E	$\varphi_o \text{ (eV)}$ [111]	$S_o(A^0)$ [111]	n_a	$E_a \text{ (eV)}$	$U_{\text{eff}} \text{ (eV)}$	$\Gamma \text{ (eV)}$	$S_{\text{ch}}(A^0)$	$E_i(S=0)$ (eV)	$E_M(S=0)$ (eV)	$E_{CH}(S=0)$ (eV)	E_R (eV)	S_C (A^0)	$E_R(\text{exp.})$ (eV)	$E_R(\text{theo.})$ r) (eV)
110	5.04	0.8972	0.04860	1.8908	1.7750	0.35409	-	1.6535	0.23188	1.8854	2.7454	-	-	1.8[2]
001	5.22	1.1400	0.04611	2.0098	1.8995	0.36205	-	1.6618	0.22838	1.8901	2.9301	-	-	-
111	5.35	1.2244	0.04408	2.1179	1.9392	0.36919	-	1.6680	0.22646	1.8945	3.0645	-	-	-

Table (5):

Cs/Ni , $V_i = 3.89 \text{ eV}$, $V_A = 0.39 \text{ eV}$, $r_i = 1.67 \text{ Å}$, $T = 300^\circ \text{K}$														
FAC E	$\phi_o(\text{eV})$ [111]	$S_o(A^\circ)$ [111]	n_a	$E_a(\text{eV})$	$U_{\text{eff}}(\text{eV})$	$\Gamma(\text{eV})$	$S_{\text{th}}(A^\circ)$	$E_i(S=0)$ (eV)	$E_M(S=0)$ (eV)	$E_{CH}(S=0)$ (eV)	E_R (eV)	S_C (A°)	$E_R(\text{exp.})$ (eV)	$E_R(\text{theor})$ (eV)
110	5.04	0.8972	0.03725	2.1052	1.6138	0.30654	-	1.5300	0.19217	1.7222	2.8722	-	1.87[8]	1.68[2]
001	5.22	1.1400	0.03548	2.2300	1.7266	0.31386	-	1.5363	0.19119	1.7274	3.0574	-	-	-
111	5.35	1.2244	0.03406	2.3406	1.7627	0.32027	-	1.5410	0.19143	1.7324	3.1924	-	-	-

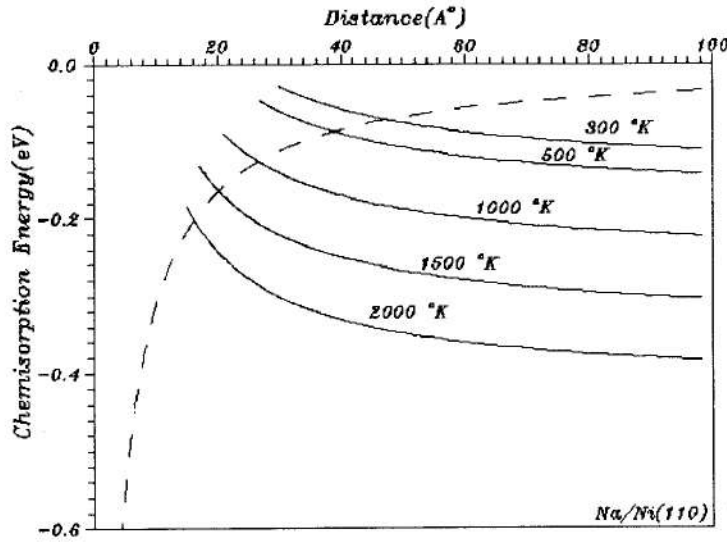


Figure (4): Shows the variation of PES as a function of temperature for the system Na/Ni (110).

Table (6): Characterizing the chemisorption functions, chemisorption energy (and it's contributions) and binding energy as a function of Temperature for the system Na/Ni (110).

Na/Ni(110), $V_i=5.14$ eV, $V_A=0.54$ eV, $r_i=0.97$ Å°, $\varphi_o=5.03$ eV, $S_o=0.8972$ Å°
 $U_{eff}=1.3302$ (eV), $S=0$ Å°

T (K)	$\Delta\varphi_o$ (eV)	n_a	E_a (eV)	Γ (eV)	E_I (eV)	E_M (eV)	E_{CH} (eV)	S_{ch} (Å°)	S_C (Å°)
00	4.992	0.08523	2.0803	0.71806	2.1233	0.45026	2.5736	20.35	47.0
00	4.960	0.08640	2.0498	0.71520	2.1198	0.45431	2.5741	15.75	39.0
700	4.880	0.08951	1.9739	0.70802	2.1106	0.46459	2.5752	9.90	26.5
500	4.800	0.09291	1.8985	0.70080	2.1009	0.47516	2.5761	7.00	20.0
000	4.720	0.09667	1.8235	0.69357	2.0905	0.48621	2.5767	5.20	16.0

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