ISSN 1817 - 2695

PUBLICATIONS OF
COLLEGE OF EDUCATION
UNIVERSITY OF BASRAH

JOURNAL OF BASRAH RESEARCHES
(Sciences)

Volume: 28
Number: 3

2002

J.Basrah Researches. Vol.28. part 3,136-145(2002)

Atom – Surface Interaction.

1- Analytic Formula for the Adatom Effective Charges Through out the Chemisorption Model.

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Abstract

Distance and temperature effects on the adatom's effective charge (i.e. the filling of the adatom levels) are studied within the frame work of the time dependent Anderson-Newns model. An analytical formula for the effective charge is developed where the repulsion of the two electrons of opposite spins in the adatom is taken in to account by means of the correlation energy. The Na/W (100) chemisorption system is investigated and discussed.

Introduction

There has been a considerable amount of work dealing with calculations in the chemisorption theory [1] and the theortical description of charge exchange process is often given on the basis of the time-dependent Newns Anderson model [2,3]. These studies had ben made for determinig the chemisorption parameters (energy and equilibrium distance of the bond) and thus are only dealing with the range around this equilibrium distance.

Recently, many techniques (the non-perturbative coupled angular mode (CAM), the wave packet propagation technique and time of light technique)have been used to study the charge exchange processes between the adparticle and solid surface [4] but the effective charge of the atomic level was not calculated.

Charge exchange [5,6] between a moving particle and a metal surface is one of the fundamental phenomeana in the dynamical process on the solid surface. The interaction gives rise to shifiting and broadening the ad-atom valence levels [7] and as a result of the interaction between the particle and the surface electrons, electrons can hop from the metal to particle and vice versa.

In the chemisorption theory, one considers the adatom levels (iionization Vi and affinity VA levels) to be interacting with the band of the metal, taking into account the intra-atomic Coulomb interaction amotting the spin indices in the model [8].

Our main goal is to develop an analytical formula to calculate all the chemisorption functions (i.e. the effective charges of the ad-atom levels, the corresponding energy positions, their half widths and the correlation function) as a function of distance and temperature.

In the next section, the treatment developed in this paper is presented and the appropriate time-dependence is given for the parameters in the model. The Na/W(100) chemisorption system is investigated, our calculations and discussions are carried out in section 3.

2-The Theoritical Model

The model, which we use in paper was sketched in fig (ib) in ref [9], where U is the intra-atomic Coulomb interaction for two electrons on the particle. This two electron Coulomb repulsive term is the complicated one in time dependent Anderson – Newns (TDAN) Hamiltonian [5], since a many electron approach should be used. The as-atom levels are broadened by the interaction with the states of energy Ek of metal band through the matrix elements

$$V_{ka} = \langle k|V|a\rangle \qquad \text{....... (1)}$$

Where denotes the atomic orbital and V is the perturbation due to the interaction between particle and the metal. Following simplifying assumptions, the dependence of Vak on k and S (distance from the solid surface) can be separated to [10]:

$$V_{ka}(E_k, S) = V_{ka}u(S) \qquad \text{....... (2)}$$

The energy dependence of the level width function can be neglected the instantaneous resonance wiodth can then given by [11]:

$$\Gamma(S) = \Gamma_o e^{-\alpha S} \qquad \text{....... (3)}$$

With Γ_o and α are adjustable parameters.

The repulsive term is treated as an average self energy and the position of the perturbed atomic level is [8]:

$$E_a^{\pm\sigma} = (\phi - V_i) + \Delta E(s) + Un_a^{\pm\sigma} \qquad \text{....... (4)}$$

With ΔE(s) is the electrostatic contribution to the interaction between atom and metal, which is given by [7]:

$$\Delta E(s)\frac{e^2}{4(s+s_o)} \qquad \text{....... (5)}$$

Where S_o is an adjustable parameter related to the screening length.

The density of states associated with each atomic level of spin σ (-σ) is a Lorentzian distribution [12] centered at $E_a^{\pm\sigma}$ $(E_a^{-\sigma})$ as:

$$\rho_a^{\sigma}(E) = \frac{1}{\pi}\frac{\Gamma(s)}{\left(E - E_a^{\sigma}\right)^2 + \Gamma^2(s)} \qquad \text{....... (6)}$$

Then, at any temperature T and distance S, the occupation is:

$$n_a^{\sigma} = \int_{u_o}^{\phi} \rho_a^{\sigma}(E) f(E,T)\, dE \qquad \text{....... (7)}$$

With $f(E,T)$ is Fermi distribution function, u_o is the bottom of the band and ϕ is the surface work function ($\phi = \phi_o - 1.6 \times 10^{-4}T$) [5].

The intra – atomic Coulomb interaction can be represented by an effective potential [8] :

$$U_{eff} = \frac{U}{1 + U\,\Phi(0)} \qquad \ldots\ldots. (8)$$

with,

$$\Phi(0) = \frac{1}{\pi\left(E_a^{+\sigma} + E_a^{-\sigma}\right)}\left[\tan^{-1}\frac{E_a^{+\sigma}}{\Gamma} + \tan^{-1}\frac{E_a^{-\sigma}}{\Gamma}\right] \qquad \ldots\ldots. (9)$$

with the condition [13], $U_{eff} \leq \dfrac{1}{\Phi(0)}$ ……. (10) and $U = V_i - V_A$

As we know, $\rho_a^{\sigma}(E)$ is sharply peaked at certain E especially at larg values of S which make the numerical solution uncorrect. So the analytical treatment will be preferred. Now,equation (7) can be approximated as:

$$n_a^{\sigma} = \int_{u_o}^{-kT} \rho_a^{\sigma}(E)dE + \int_{-kT}^{-kT} \rho_a^{\sigma}(E) f(E,T) dE` \qquad \ldots\ldots. (11)$$

An alternative expression for $f(E,T)$ in the second integral for the energy rang from – KT to KT with K is the Boltzman constant) is derived for any T from the best polynomial fitting as follows:

$$f(E) = a_o + a_1E + a_2E^2 + a_3E^3 \qquad \ldots\ldots. (12)$$

with $a_0 = 0.5$
$a_1 = 0.24949$
$a_2 = 7.35116 * 10^{-9}$
$a_3 = 0.0185601$

Then eq. (11) will be:

$$n_a^\sigma = \int_{u_o}^{-kT} \rho_a^\sigma(E)dE + \int_{-kT}^{-kT} (a_o + a_2 E^2)\rho_a^\sigma(E)dE \qquad \text{.......} (13)$$

The above equation can be solved analytically to be :

$$\pi n_a^\sigma = a_2\Gamma^2\left(\frac{2KT}{\Gamma}\right) - \tan^{-1}\frac{u_o - E_a^\sigma}{\Gamma} + a_2\Gamma\ln\left(\frac{(KT - E_a^\sigma)^2 + \Gamma^2}{(KT + E_a^\sigma)^2 + \Gamma^2}\right) + B_1^\sigma \tan^{-1}\frac{KT - E_a^\sigma}{\Gamma} + B_2^\sigma \tan^{-1}\frac{KT - E_a^\sigma}{\Gamma} \qquad \text{.......} (14)$$

where, $B_1^\sigma = 1 - a_o - a_2(E_a^\sigma)^2 - a_2\Gamma^2$,

$B_2^\sigma = 1 - a_o - a_2(E_a^\sigma)^2 + a_2\Gamma^2$,

Equations (8) and (14) are solved self-consistently getting two types of solutions magnetic $(n_a^{+\sigma} \neq n_a^{-\sigma})$ and non-magnetic $(n_a^{+\sigma} \neq n_a^{-\sigma})$, with the condition in eq.(10)is cheked to be satisfied for all S.

Finally, all energies are calculated with respect to Fermi level (E_F=0), the choice of spin's sing is arbitrary and for simplicity Γ (S) was written as Γ in the above equations.

Results and conclusions

Application to Na/W(100)

The spins up and down levels half width, that we calculate according to eq.(3) with Γo=0.8 eV and $\alpha = \sqrt{2|V_i|}$ a.u. are compasred with of the modified electric image model [14] both seem to have the same behavior, see figures (la) and (ib). At large distances Γ(S) is nearly zero and Lorentzian $\rho_a(E)$ tends to Dirac distribution.

The atom's effective charges are shown in fig.(2) as a function of the atom-surface separation for two different temperatures for Na/W (100) where $\phi_o = 4.58$ eV . A solution with the same occupation of the different levels (i.e nonmagnetic solution), corresponding to $n_a^\sigma \neq n_a^{-\sigma}$ is optained for $0 \le S \le 3.7$ A^{0} at T=300 K^{0} ($o \le S \le 2.1$ A^{o} at T = 2000 K^{o}). However it is of importance to underline that for $S > 3.7$ A^{o} at T=300 K^{o} ($S \le 2.1$ A^{o} at T=2000 K^{o}) solution with different occupations of different levels (i.e magnetic solution $n_a^{\sigma} \neq n_a^{-\sigma}$) is obtained. From wich one can conclude that the point where the solution changed, is determined by the temperature variation (i.e the work function variation). For both temperatures the solution at the surface is nonmagnetic. While n_a^{σ} and $n_a^{-\sigma}$ are more different when the temperature and the distance have larger values, this can be interpreted in terms of the strength of coupling. The effective charges close to the surface are small which reflects that the charge state of Na-adatom on W(100) is preferentially an ionic state. At temperature 2000 K^{o}, metal levels above Fermi levels will be populated by electrons, i.e. the metal levels that are in resonance or quasi-resonance with adatom levels will increase. Then the effective charge will increase as a function of temperature.

The corresponding energy position levels and the correlation energy are given as a function of temperature and distance in figs. (3) and (4), which show the effect of the correlation term $U_{eff} n_a^{+\sigma}$ in calculating $E_a^{-\sigma}$.

Another point of interest in fig. (3) that is the energy of the atomic level E_a^{σ} is weakly dependent on temperature, but $E_a^{-\sigma}$ being more sensitive to it.

It is overmentioned that at small distancethe state is nonmagnetic from which one can expect that the atom-metal coupling is strong enough to overcome the Coulomb repulsion between opposite spin electrons. To make this clear, U_{eff} and $\pi\Gamma(S)$ [8, 15] are shown in fig. (5) a function of distance. The distance where the coupling begins to be strong is about 0.3 A^{o} at T=300 K^{o} (0.5 A^{o} at T=2000 K^{o}). The increase of this distance with T is because of the increasing in the occupied metal levels above Fermi level or it may reflect the influence of the thermal excitation which reduces the correlation effects. This distance may changed with α and Γ_o keeping in mind that U_{eff} is T-dependent while $\Gamma(S)$ is not.

To show the importance of U_{eff} in determining the adatom charge state, another formula for U_{eff} is investigated given by the classical formula [12],

$$U_{eff}(S) = U - 2\,\Delta E(S) \qquad \text{.......} (15)$$

Which is function of distance only (see fig.(6)).

Our calculation are shown in figs. (7) and (8) for the occupation and the corresponding energies respectively. These figures show concide behavior to that of figures (2) and (3) in spite of U_{eff} in coincidence with that calculated from eq.(8) only at large distancees. The distance where the coupling begins to be strong (see fig.(6)) is about 2.8 A° keeping in mind that this distance may changed due to screening length S_o. Where increasing S_o in eq.(15) makes the point of changing from magnetic state S_{ch} to be more to surface.

The values of U_{eff} that calculated from eq.(8) are found (at S=0.0 and for all T) to be greater than KT. This means that forming negative ion is impossible [16]. Our model is then well adapted for describing all surface processes involving positive ions or/and neutral particles.

The correlation energies will be more investigated and discussed in our next step since the potential surfaces will be calculated for two types $\phi > V_i$ and $\phi < V_I$.

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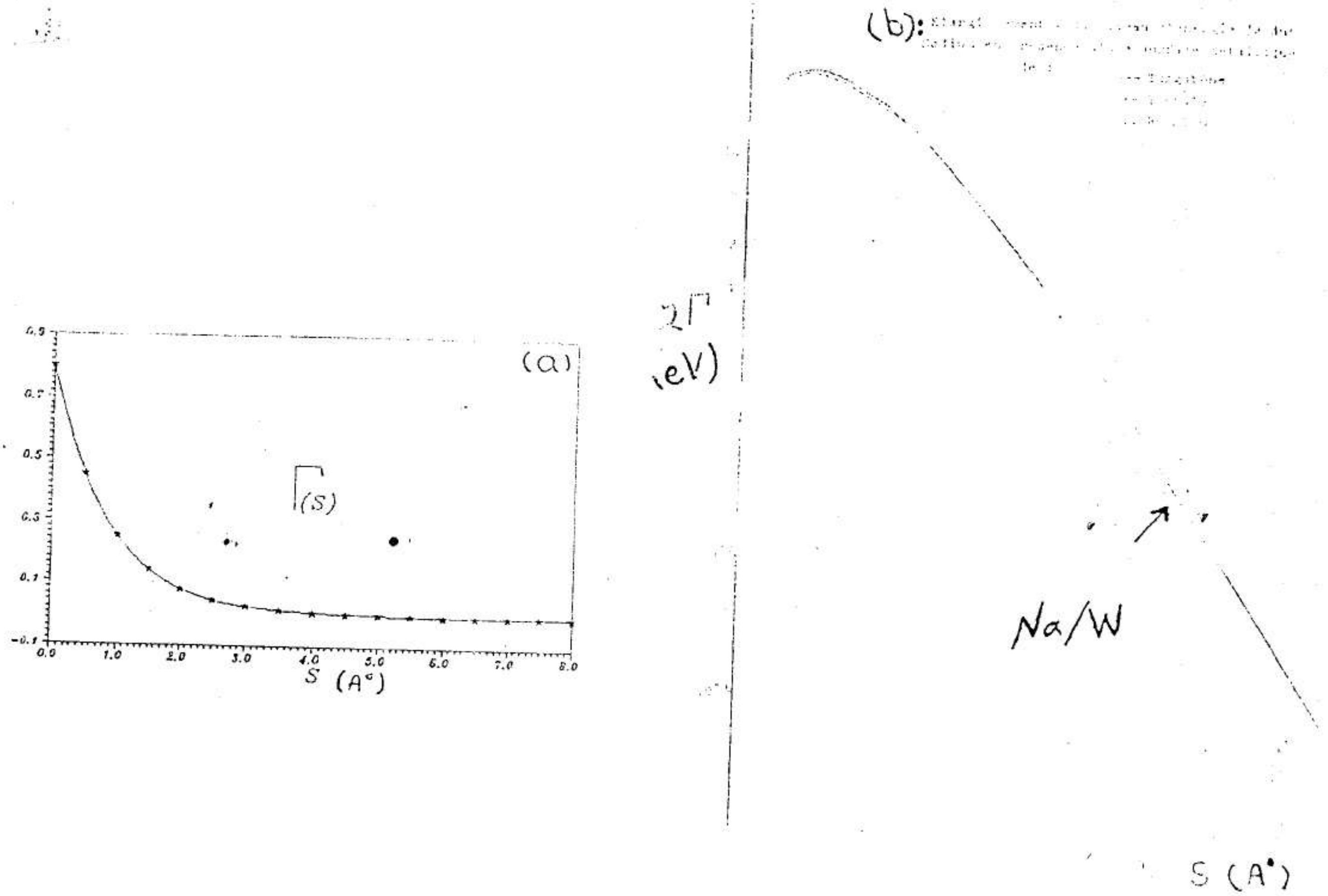

Fig. 1: The levels half width variations as a function of distance . a: our calculations , b: taken from Ref[13] for comparison.

$\Gamma_0 = 0.8$ eV , $\Gamma(S)$ in unit of eV.

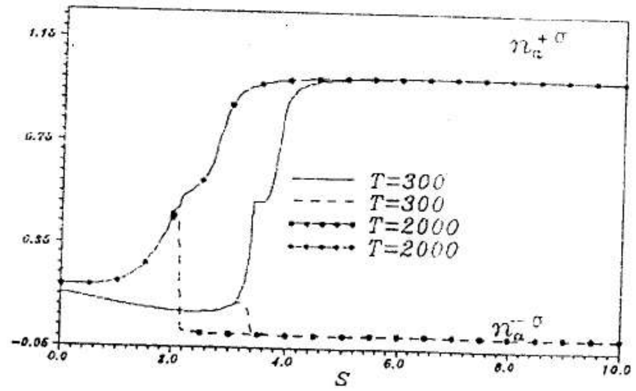

Fig. (2): The effective charges as a function of temperature and distance.

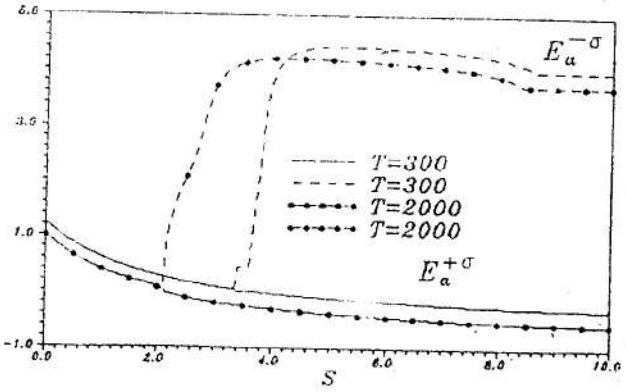

Fig. (3) E_a^{σ} and $E_a^{-\sigma}$ are shown as a function of T and S.

Ea in unit of eV .

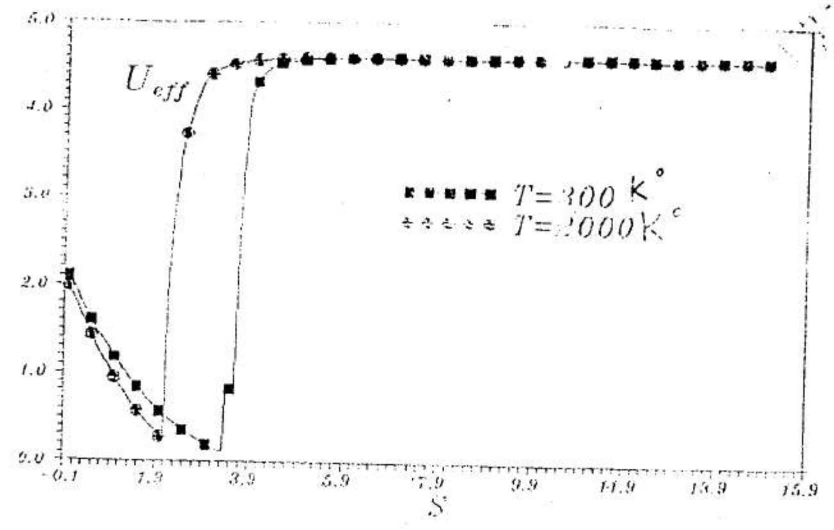

Fig. (4) U_{eff} is , shown as a function of T and S , calculated from eq. (8).

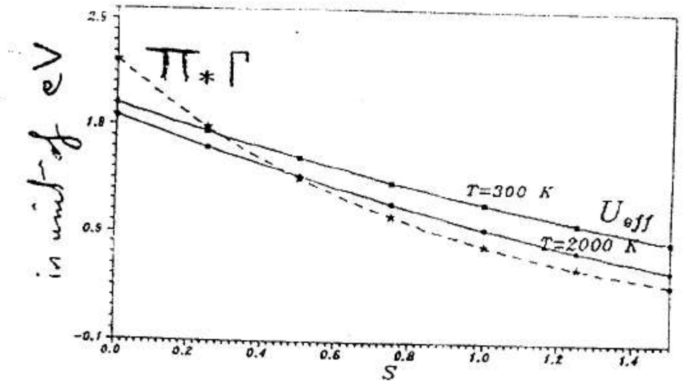

Fig. (5) U_{eff} and πΓ are shown as a function of S. and T .

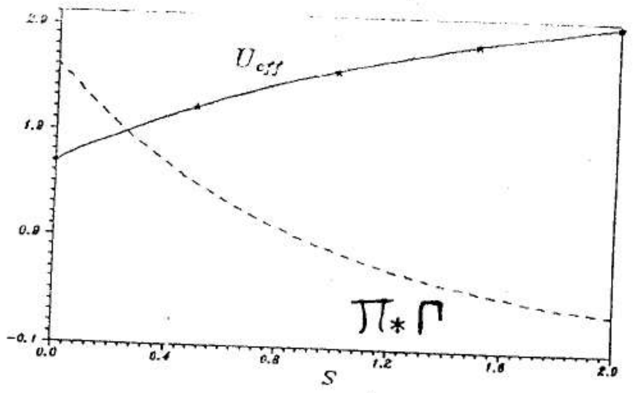

Fig. (6) The correlation is calculated using eq.(15) as a function of S with S_0=2.4 A^0.

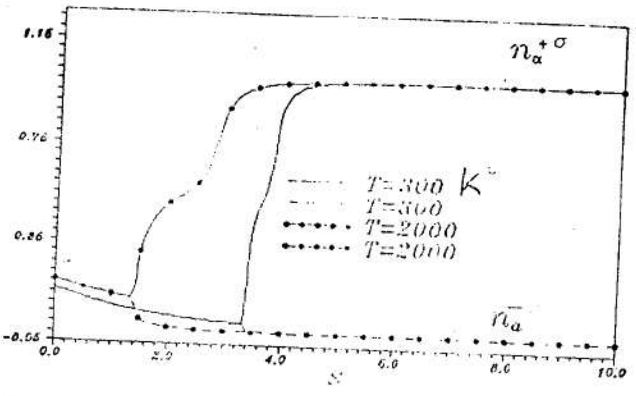

Fig. (7) The effective charges as a function of T and S with U_{eff} is calculated using eq.(15).

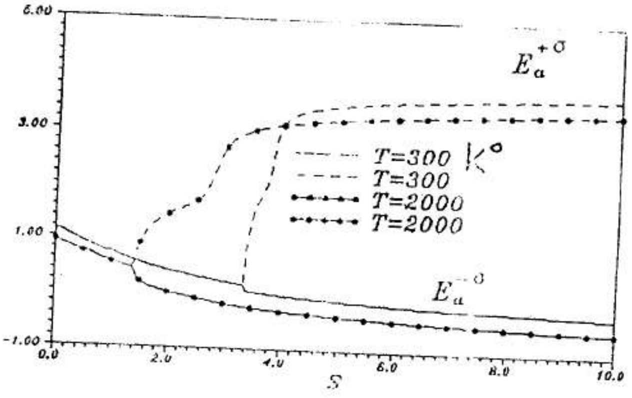

Fig. (8) E_a^{σ} and $E_a^{-\sigma}$ are shown as a function of T and S with U_{eff} is calculated using eq.(15).