

**ON THE ROLE OF IMAGE FORCES IN CHEMISORPTION THEORY****O.M. BRAUN***Institute of Physics, Ukrainian Academy of Sciences, Kiev 28 GSP, 252650 USSR*

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The Extended Anderson Hamiltonian is used to study the effect of fluctuations of an adatom charge  $Q$  on the ionic part of the chemisorption energy. It is shown that dynamical effects essentially modify the classical expression  $E = -\varphi Q^2$  for the energy of interaction between a static charge  $Q$  and a metal ( $\varphi$  is the interaction energy for a unit charge). The exact solution for the one-electron two-level model as well as a variational solution for the Extended Anderson Hamiltonian model are given. Validity conditions for a variety of approximate schemes are studied. The results are presented for the Extended Anderson Hamiltonian model parameterized so as to describe some aspects of the Li/W and Li/Mo chemisorption systems.

**1. Introduction**

The expression for chemisorption energy involves the ionic and metallic contributions. The metallic contribution is caused by hybridization of the metal states  $|k\rangle$  and the adatom state  $|A\rangle$ , while the ionic contribution is caused by the screening effects. It is well known that the energy of interaction between a static point charge  $Q$  and a metal is given by

$$E_{\text{image}} = -\varphi Q^2, \quad (1)$$

where  $\varphi$  is the interaction energy for a unit charge. However, expression (1) does not take into account the adatom charge fluctuations.

Let us denote the frequency of adatom charge fluctuations by  $\omega_f = \tau_f^{-1}$  and that of nondispersive surface plasmons by  $\omega_0$ . As it was shown by Hewson and Newns [1], the value  $\tau_0 = \omega_0^{-1}$  determines the relaxation time of a plasmon subsystem. When the fluctuations are fast,  $\tau_f \ll \tau_0$ , the plasmon subsystem has no time to adjust to adatom charge changes and remains in a displaced but a static position determined by the adatom mean charge  $\langle \hat{Q} \rangle$ . In this case

(adiabatic limit) one can expect the expression (1) to be valid if we replace  $Q$  by  $\langle \hat{Q} \rangle$ , the average being taken over the ground state.

In the opposite case,  $\tau_f \gg \tau_0$ , the plasmon subsystem instantaneously follows the adatom charge fluctuations. Let us consider an adatom with a single nondegenerate electron level  $\epsilon_A$ . If the level is occupied by one electron, the adatom is neutral. The ionic part of chemisorption energy is equal to

$$E_{\text{ion}} = -\varphi P_2 - \varphi P_0 = -\varphi \langle \hat{Q}^2 \rangle, \quad (2)$$

where  $P_2 = \langle \hat{n}_{A\sigma} \hat{n}_{A-\sigma} \rangle$  is the probability for the adatom to have two electrons and  $P_0 = \langle (1 - \hat{n}_{A\sigma})(1 - \hat{n}_{A-\sigma}) \rangle$  is that for no electrons,

$$\hat{Q} = 1 - \hat{n}_A, \quad \hat{n}_A = \hat{n}_{A\sigma} + \hat{n}_{A-\sigma}, \quad (3a)$$

$$\langle \hat{Q}^2 \rangle = 1 - \langle \hat{n}_A \rangle + 2\langle \hat{n}_{A\sigma} \hat{n}_{A-\sigma} \rangle, \quad (3b)$$

$\hat{n}_{A\sigma}$  is the number operator for an electron with spin  $\sigma$  in the localized adatom state  $|A\rangle$ . If  $\epsilon_A - \epsilon_F \gg \Delta$  ( $\epsilon_F$  is the Fermi level and  $\Delta$  the half-width of the adatom level), then  $P_2 \approx 0$ ,  $\langle \hat{Q}^2 \rangle \approx \langle \hat{Q} \rangle$  and  $E_{\text{ion}} \approx -\varphi \langle \hat{Q} \rangle$ . Similarly, if  $\epsilon_F - \epsilon_A \gg \Delta$ , then  $E_{\text{ion}} \approx +\varphi \langle \hat{Q} \rangle$ . In general, if the adatom level is situated far enough from the Fermi level, one obtains

$$E_{\text{ion}} \approx -\varphi |Q|.$$

If  $|\epsilon_A - \epsilon_F| \ll \Delta$ , then  $Q \approx 0$  and

$$E_{\text{ion}} \approx -2\varphi P_2 \neq 0.$$

Therefore, in this case (inverse adiabatic limit) the adatom charge fluctuations essentially modify the classical expression (1).

According to Tomonaga [2] and Haldane [3], the interaction of a local charge with the metal electrons may be considered as the one with the electron density fluctuations represented by a boson field. In the case of chemisorption these bosons are the surface plasmons (see ref. [4]). Thus the electrostatic image forces can be treated in terms of the Extended Anderson Hamiltonian (EAH model)

$$H = \epsilon_A n_A + U n_{A\sigma} n_{A-\sigma} + \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{k\sigma} (V_{Ak} \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + \text{h.c.}) + \omega_0 \hat{a}^* \hat{a} + \sqrt{\varphi \omega_0} (\hat{n}_A - 1) (\hat{a} + \hat{a}^*). \quad (4)$$

Here  $U$  is the energy of Coulomb repulsion between two adatom electrons with opposite spins,  $V_{Ak}$  is the matrix element of mixing between the  $|A\rangle$  and  $|k\rangle$  states; the operator  $\hat{c}_{k\sigma}^*$  creates an electron in the  $|k\rangle$  state with energy  $\epsilon_k$  and spin  $\sigma$ ,  $\hat{n}_{k\sigma} = \hat{c}_{k\sigma}^* \hat{c}_{k\sigma}$ ;  $\hat{a}^*$  is the creation operator for a surface plasmon.

The EAH model (4), originally proposed by Hewson and Newns [1], has been applied by many authors [5–8] to study the spectral properties of valence and core levels of the adatom. It was shown that under certain conditions the Coulomb repulsion  $U$ , the resonance half-width  $\Delta$  and the position of the

adatom level  $\epsilon_A$  are renormalized, and new resonances appear in the density of states. In the one-electron case the exact result for the density of states was obtained by Hewson and Newns [6]. They used the exact recurrence relations for the adatom Green function derived by Swain [9]. The EAH model was also used by Khomskii [10] and Hewson and Newns [11] for mixed valence systems. The main question of interest was whether the polaronic effects can stabilize the intermediate valence state.

The purpose of this work is to study the effect of coupling between surface plasmons and an adatom charge on chemisorption energy. The simplified EAH model proposed by Khomskii [10] is considered in section 2. We find the exact solution for this model and determine the validity conditions of the adiabatic approximation, the inverse adiabatic approximation and the Khomskii variational method. In section 3, we analyze the EAH model (4) in the adiabatic and the inverse adiabatic limits. The interpolation between these limits is performed by the variational method which is an extension of the Khomskii method. The numerical results for the EAH model parameterized so as to describe some aspects of the Li/W and Li/Mo chemisorption systems show the importance of the correct calculation of the ionic contribution to chemisorption energy.

## 2. The exact solution of the one-electron two-level model

In order to investigate the validity conditions of various approximate schemes, we obtain in this section the exact results for the simplified EAH model with a single electron and two levels. The model Hamiltonian is

$$H = \epsilon_A \hat{n}_A + \epsilon_B \hat{n}_B + (V \hat{c}_A^* \hat{c}_B + \text{h.c.}) + \omega_0 \hat{a}^* \hat{a} + \sqrt{\varphi \omega_0} \hat{n}_A (\hat{a} + \hat{a}^*). \quad (5)$$

This model was previously considered by Khomskii [10] in the generalized mean field approximation. The wave function was written in the form

$$|\psi\rangle = (u \hat{c}_A^* |\alpha\rangle + v \hat{c}_B^* |\beta\rangle) |0\rangle,$$

where  $|\alpha\rangle$  is the coherent boson state,  $\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$ , and  $|0\rangle$  is the vacuum state for an electron subsystem. Different types of the dependence of the occupation number  $n_A$  ( $n_A = \langle \hat{n}_A \rangle$  is the measure of valence) on the level position  $\epsilon_A$  are given in fig. 1. One can see that for a certain range of model parameters, a jumplike transition between the integral-valence states (see curves 2 and 3 in fig. 1) as well as a transition from the integral-valence state to the intermediate-valence state (see curve 4 in fig. 1) are possible.

In the present work we give the exact solution of the model (5). Let us represent the wave function in the following way:

$$|\psi\rangle = [\hat{c}_A^* f_A(\hat{a}^*) + \hat{c}_B^* f_B(\hat{a}^*)] |\text{vacuum}\rangle, \quad (6)$$

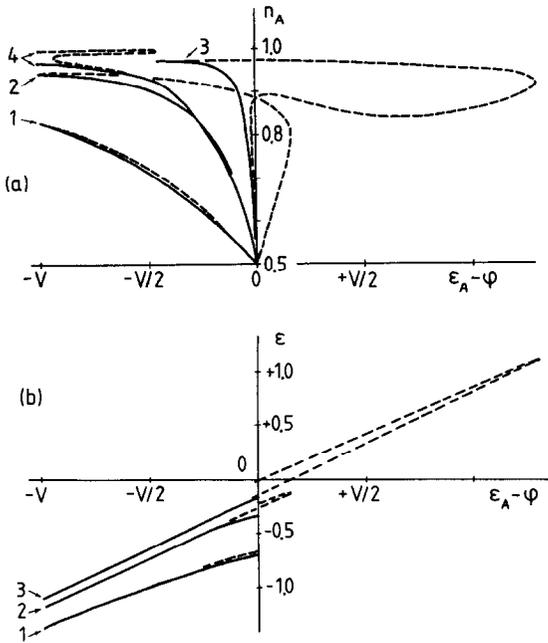


Fig. 1. (a) The occupation number  $n_A$  and (b) the ground state energy  $\epsilon$  versus the adatom level position  $\epsilon_A$ . The full curve is for the exact solution and the dashed curve for the variational solution: (1)  $\varphi = 2, V = 1$ ; (2)  $\varphi = 5, V = 1$ ; (3)  $\varphi = 8, V = 1$ ; (4)  $\varphi = 3.8025, V = 0.1$ .

$$f_A(x) = \sum_{n=0}^{\infty} a_n x^n, \quad f_B(x) = \sum_{n=0}^{\infty} b_n x^n, \quad (7)$$

$$\sum_{n=0}^{\infty} (|a_n|^2 + |b_n|^2) n! = 1. \quad (8)$$

If we substitute this wave function to the Schrödinger equation and use the commutation relation  $[\hat{a}, f(\hat{a}^*)] = f'(\hat{a}^*)$ , it is easy to show that  $f_A$  and  $f_B$  obey the system of differential equations ( $\omega_0 = 1, \epsilon_B = 0$ ):

$$Vf_B + (x + \sqrt{\varphi})f'_A = (\epsilon - \epsilon_A - x\sqrt{\varphi})f_A, \quad (9a)$$

$$Vf_A + xf'_B = \epsilon f_B. \quad (b)$$

If we exclude  $f_B$  from eq. (9) we obtain the differential equation for  $f_A$ :

$$x(x + \sqrt{\varphi})f''_A + [x^2\sqrt{\varphi} + x(1 + \epsilon_A - 2\epsilon) - \epsilon\sqrt{\varphi}]f'_A + [x(1 - \epsilon)\sqrt{\varphi} + \epsilon(\epsilon - \epsilon_A) - V^2]f_A = 0. \quad (10)$$

From the normalization condition (8) one can see that in the limit  $n \rightarrow \infty$  the

coefficients  $a_n$  and  $b_n$  tend to zero faster than  $1/\sqrt{n!}$ . Therefore,  $f_A$  and  $f_B$  must be integral functions, i.e. analytical in the whole complex plane  $|z| < \infty$ . The analytical solution of the system (9) or, similarly, of eq. (10) exists only for certain values of  $\epsilon$  which are eigenvalues of the Hamiltonian (5).

The system (9) has a simple solution if  $V = 0$  or  $\varphi = 0$ . If  $V = 0$ ,

$$f_A \sim (x + \sqrt{\varphi})^n \exp(-x\sqrt{\varphi}), \quad f_B = 0, \quad \epsilon = \epsilon_A - \varphi + n,$$

or

$$f_A = 0, \quad f_B \sim x^n, \quad \epsilon = n.$$

In the case of  $\varphi = 0$ ,

$$f_A \sim x^n, \quad f_B \sim x^n,$$

and the eigenvalues are the roots of the equation

$$(\epsilon - \epsilon_A - n)(\epsilon - n) - V^2 = 0.$$

Let us consider the limiting cases. From eq. (9b) we can obtain

$$f_B(x) = V \sum_{n=0}^{\infty} \frac{a_n x^n}{\epsilon - n}. \quad (11)$$

In the case of

$$|\epsilon| \gg 1, \quad (12)$$

we can obtain from (11):

$$f_B \approx V f_A / \epsilon. \quad (13)$$

If we substitute (13) to (9a) and solve the resulting equation, we can obtain

$$f_A(x) \sim \exp(-x\sqrt{\varphi}).$$

The eigenvalues are the roots of the equation

$$\epsilon(\epsilon - \epsilon_A + \varphi) - V^2 = 0.$$

This case corresponds to the adiabatic limit. The conditions for its validity are determined by eq. (12), i.e.  $|\epsilon_A - \varphi| \gg 1$  or  $V \gg 1$ .

In the case of

$$|\epsilon| \ll 1, \quad (14)$$

we obtain from (11):  $f_B \approx V a_0 / \epsilon$ . Analogously to the previous case, we can obtain

$$f_A(x) \approx V^2 \frac{a_0}{\epsilon} e^{-\varphi} e^{-x\sqrt{\varphi}} \frac{1}{\epsilon - \epsilon_A + \varphi}. \quad (15)$$

A comparison of (15) and (18) leads to the equation for the eigenvalues

$$\epsilon(\epsilon - \epsilon_A + \varphi) - V^2 e^{-\varphi} = 0.$$

This case corresponds to the inverse adiabatic limit. Its validity conditions are determined by eq. (14), i.e.  $|\epsilon_A - \varphi| \ll 1$ ,  $V \ll 1$  and  $\varphi \ll 1/|\epsilon_A - \varphi|$ .

Let us consider now the exact solution of eq. (10). The substitution of (7) into (10) leads to the recurrence relations

$$\sqrt{\varphi}(n+1)a_{n+1} - \left( \epsilon - \epsilon_A - n - \frac{V^2}{\epsilon - n} \right) a_n + \sqrt{\varphi}a_{n-1} = 0. \quad (16)$$

The solution of these relations gives the function  $f_A(z)$  which is analytical in the circle  $|z| < \sqrt{\varphi}$ . In the vicinity of the point  $x = -\sqrt{\varphi}$ , eq. (10) has two independent solutions; only one of them is analytical. We express it in the form

$$\tilde{f}_A(x) = \sum_{n=0}^{\infty} c_n (x + \sqrt{\varphi})^n. \quad (17)$$

The coefficients  $c_n$  are determined by the recurrence relations

$$\begin{aligned} & \sqrt{\varphi}(n+1)(\epsilon - \epsilon_A + \varphi - n - 1)c_{n+1} \\ & + [(\epsilon - n)(\epsilon - \epsilon_A + \varphi - n) - \varphi(n+1) - V^2]c_n \\ & - \sqrt{\varphi}(\epsilon - n)c_{n-1} = 0. \end{aligned} \quad (18)$$

The function  $\tilde{f}_A$  determined by (17) and (18) is analytical in the circle  $|z + \sqrt{\varphi}| < \sqrt{\varphi}$ . In order to make the function  $f_A$  and its derivative continuous, it is sufficient to require that

$$f'_A(x_0)/f_A(x_0) = \tilde{f}'_A(x_0)/\tilde{f}_A(x_0), \quad (19)$$

where  $x_0$  ( $\neq 0$  or  $-\sqrt{\varphi}$ ) is an arbitrary point. Thus, we obtain the analytical solution in the whole complex plane  $|z| < \infty$ . The continuity condition (19) determines the eigenvalues of the Hamiltonian (5).

The numerical data for the occupation number  $n_A$  and the ground state energy  $\epsilon$  versus the adatom level energy  $\epsilon_A$  for different values of  $\varphi$  and  $V$  are given in fig. 1. A comparison of the exact and the variational solutions leads to the conclusion about the good accuracy of the variational method for the calculation of the ground state energy if the states on the "loops" are not taken into account. At  $\varphi \leq 3$  (this condition is valid for chemisorption systems) there is a qualitative agreement between the dependences  $n_A(\epsilon_A)$  obtained by both methods. In connection with the theory of mixed-valence systems, it is interesting to point out that for the definite range of parameters ( $\varphi > 27/8$ ,  $V \sim 0.1$ ) the variational method predicts a discontinuous transition from the integral-valence state to the intermediate-valence state (curve 4 in fig. 1). However, the exact solution shows that only the continuous transitions between the integral-valence states may occur.

### 3. The variational method

As was shown in section 2, the variational method gives with good accuracy the occupation number and the ground state energy for chemisorption systems. Now we obtain the variational solution for the initial EAH model (4). Let us first consider the limiting cases.

From (4) we obtain

$$dE/d\varphi = \langle \partial H / \partial \varphi \rangle = \frac{1}{2} (\omega_0 / \varphi)^{1/2} \langle (\hat{n}_A - 1)(\hat{a} + \hat{a}^*) \rangle.$$

Haldane [12] has shown that in the adiabatic approximation (mean field approximation) the averages over the plasmon and electron subsystems are taken independently. In this case we have

$$dE/d\varphi = -\frac{1}{2} (\omega_0 / \varphi)^{1/2} Q \langle \hat{a} + \hat{a}^* \rangle. \quad (20)$$

If we take into account that in the mean field approximation

$$\langle \hat{a} \rangle = \langle \hat{a}^* \rangle = Q (\varphi / \omega_0)^{1/2},$$

then we obtain from (20):

$$dE/d\varphi = -Q^2.$$

For small  $\varphi$  we obtain

$$E_{\text{ion}} \approx -\varphi Q^2,$$

i.e. in the adiabatic limit the ionic part of chemisorption energy is defined by the same expression as the energy of interaction between a static point charge  $Q$  and a metal.

In the inverse adiabatic limit, the ground state wave function can be represented by

$$|\psi\rangle = (|0\rangle \hat{P}_0 + |1\rangle \hat{P}_1 + |2\rangle \hat{P}_2) |\psi_e\rangle, \quad (21)$$

where the projection operators are determined by

$$\hat{P}_0 = (1 - \hat{n}_{A\sigma})(1 - \hat{n}_{A-\sigma}), \quad (22a)$$

$$\hat{P}_1 = \hat{n}_{A\sigma}(1 - \hat{n}_{A-\sigma}) + \hat{n}_{A-\sigma}(1 - \hat{n}_{A\sigma}), \quad (22b)$$

$$\hat{P}_2 = \hat{n}_{A\sigma} \hat{n}_{A-\sigma}, \quad (22c)$$

$|\psi_e\rangle$  is a many-electron wave function, and the coherent boson states  $|0\rangle$ ,  $|1\rangle$  and  $|2\rangle$  are determined by

$$|\gamma\rangle = \exp\left[(\varphi / \omega_0)^{1/2} (1 - \gamma)(\hat{a}^* - \hat{a})\right] |\text{vacuum}\rangle. \quad (23)$$

By taking the average in eq. (4) over the plasmon subsystem with the help of

the wavefunction (21), we obtain the effective electron Hamiltonian

$$H_{1A} = (\epsilon_A + \varphi) \hat{n}_A + (U - 2\varphi) \hat{n}_{A\sigma} \hat{n}_{A-\sigma} + \sum_{k\sigma} \epsilon_k \hat{n}_{k\sigma} + \sum_{k\sigma} (V_{Ak} e^{-\varphi/2\omega_0} \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + \text{h.c.}) - \varphi. \quad (24)$$

From (24) we obtain

$$dE/d\varphi = \langle \partial H_{1A} / \partial \varphi \rangle = -\langle \hat{Q}^2 \rangle + O(m/\omega_0), \quad (25)$$

where

$$m = \left\langle \sum_{k\sigma} V_{Ak} e^{-\varphi/2\omega_0} \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + \text{h.c.} \right\rangle \approx \frac{V^2 e^{-\varphi/\omega_0}}{|\epsilon_A - \epsilon_F|}.$$

Neglecting the terms of the order  $m/\omega_0$  in (25), we obtain the results derived in section 1 in a qualitative way.

The interpolation between the limiting cases can be realized with the help of the variational wave function

$$|\psi\rangle = (|\gamma_0\rangle \hat{P}_0 + |\gamma_1\rangle \hat{P}_1 + |\gamma_2\rangle \hat{P}_2) |\psi_e\rangle, \quad (26)$$

where  $\gamma_0$ ,  $\gamma_1$  and  $\gamma_2$  are variational parameters. Taking the average in eq. (4) over the plasmon subsystem with the help of the wave function (26), one obtains the effective electron Hamiltonian

$$H_{\text{var}} = (\epsilon_A + 2\varphi) \hat{n}_A + \sum_{k\sigma} \epsilon_k \hat{n}_{k\sigma} + \sum_{k\sigma} \left\{ V_{Ak} \exp\left[-\frac{\varphi}{2\omega_0} (\gamma_1 - \gamma_0)^2\right] (1 - \hat{n}_{A-\sigma}) \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + V_{Ak} \exp\left[-\frac{\varphi}{2\omega_0} (\gamma_2 - \gamma_1)^2\right] \hat{n}_{A-\sigma} \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + \text{h.c.} \right\} + \varphi \gamma_0^2 \hat{P}_0 + \varphi \gamma_1 (\gamma_1 - 2) \hat{P}_1 + [U + \varphi \gamma_2 (\gamma_2 - 4)] \hat{P}_2 - \varphi. \quad (27)$$

The following arguments bring about an essential simplification of this Hamiltonian. In the symmetric case,  $\epsilon_A = -\frac{1}{2}U$ , the symmetry leads to

$$\gamma_1 = 0, \quad \gamma_0 = -\beta, \quad \gamma_2 = +\beta.$$

In the non-symmetric case it is reasonable to put

$$\gamma_1 = \alpha, \quad \gamma_0 = \alpha - \beta, \quad \gamma_2 = \alpha + \beta. \quad (28)$$

Then the Hamiltonian (27) takes the following form:

$$H_{\text{var}} = \tilde{\epsilon}_A \hat{n}_A + \tilde{U} \hat{n}_{A\sigma} \hat{n}_{A-\sigma} + \sum_{k\sigma} \epsilon_k \hat{n}_{k\sigma} + \sum_{k\sigma} (\tilde{V}_{Ak} \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + \text{h.c.}) + \varphi (\alpha - \beta)^2 - \varphi, \quad (29)$$

where

$$\tilde{\epsilon}_A = \epsilon_A + 2\varphi - \varphi\beta^2 + 2\varphi\alpha(\beta - 1),$$

$$\tilde{U} = U - 2\varphi + 2\varphi(\beta - 1)^2,$$

$$\tilde{V}_{Ak} = V_{Ak} \exp(-\beta^2\varphi/2\omega_0). \quad (30)$$

Minimization of the Hartree-Fock ground state energy with respect to  $\alpha$  and  $\beta$  yields the system of coupled equations

$$\partial E/\partial\alpha = \langle \partial H_{\text{var}}/\partial\alpha \rangle = 2\gamma(\alpha - \beta) + 2\varphi(\beta - 1)n_A = 0, \quad (31a)$$

$$\partial E/\partial\beta = -2\varphi(1 - n_A)(\alpha - \beta) - \beta\varphi m/\omega_0 + 4\varphi(\beta - 1)n_{A\sigma}n_{A-\sigma} = 0, \quad (31b)$$

where it is taken into account that

$$\partial E/\partial\epsilon_\sigma = n_{A\sigma}, \quad \epsilon_\sigma = \tilde{\epsilon}_A + \tilde{U}n_{A-\sigma},$$

$$m = \left\langle \sum_{k\sigma} \tilde{V}_{Ak} \hat{c}_{A\sigma}^* \hat{c}_{k\sigma} + \text{h.c.} \right\rangle = \tilde{V} \partial E/\partial \tilde{V},$$

$$\tilde{V} = \left( \sum_k |\tilde{V}_{Ak}|^2 \right)^{1/2}.$$

Solving the system (31), we can obtain

$$\alpha = \frac{1 + An_A}{1 + A}, \quad \beta = \frac{1}{1 + A}, \quad A = \frac{\omega_f}{\omega_0}, \quad (32)$$

where

$$\omega_f = -\frac{1}{2} \frac{m}{n_{A\sigma}(1 - n_{A\sigma}) + n_{A-\sigma}(1 - n_{A-\sigma})}. \quad (33)$$

From (32) we can see that the adiabatic approximation is valid at  $\omega_f \gg \omega_0$ ; then  $\alpha \approx n_A$  and  $\beta \approx \omega_0/\omega_f \ll 1$ . The inverse adiabatic approximation is valid at  $\omega_f \ll \omega_0$  and then  $\alpha \approx \beta \approx 1$ .

Note that the difference between the values  $E_{\text{ion}}$  calculated in the inverse adiabatic and the adiabatic approximations is proportional to  $\langle \hat{Q}^2 \rangle - \langle \hat{Q} \rangle^2$ . If there are no fluctuations (for example, if  $V \rightarrow 0$  or if  $|\epsilon_A - \epsilon_F|, |\epsilon_A + U - \epsilon_F| \rightarrow \infty$ ) this difference tends to zero, so both approximations give the same result.

To compute  $\omega_f$ , we use Newns model [13] where the local density of states has a semi-elliptical form and the Fermi level is situated in the middle of the metal band. In the special cases we obtain the following results:

- (a) if  $|\tilde{\epsilon}_A - \epsilon_F|, |\tilde{\epsilon}_A + \tilde{U} - \epsilon_F| \gg \tilde{\Delta}$ ,  
 $\omega_f \sim \min[|\tilde{\epsilon}_A - \epsilon_F|, |\tilde{\epsilon}_A + \tilde{U} - \epsilon_F|];$
- (b) if  $\min[|\tilde{\epsilon}_A - \epsilon_F|, |\tilde{\epsilon}_A + \tilde{U} - \epsilon_F|] \ll \tilde{\Delta}$ ,  
 $\omega_f \sim \tilde{\Delta};$
- (c) if  $\tilde{V} \gg W$ ,  
 $\omega_f \sim 2\tilde{V}.$

These cases can be described on the base of the following time-scale arguments. In case (a) the adatom level is situated far from the Fermi level,  $n_{A\sigma} \approx 0$  or 1. In the main the system is found in the state with the lowest energy, whereas in the excited state the system is for the time  $\tau_f \sim |\epsilon_A - \epsilon_F|^{-1}$ . In cases (b) and (c) the states with different occupations of the adatom levels have approximately the same total energy. In this quasi-degenerate case the period of charge fluctuations  $\tau_f$  is determined by the tunnelling between these states and, thus, it is  $\sim 1/\Delta$  (in case (b)) or  $\sim 1/V$  (in case (c)).

The dependences of the chemisorption energy  $D$  on  $\omega_0$  for various parameters  $\epsilon_A$ ,  $U$  and  $V$  are shown in fig. 2. One can see that in the inverse adiabatic limit this dependence is strong enough. The dependences  $dE/d\varphi$  versus  $Q$  are given in fig. 3. They demonstrate that  $dE/d\varphi \rightarrow Q^2$ , as  $\omega_0$  decreases. If  $Q \approx 0.3$ , the chemisorption energy  $D \approx 3$  eV and the EAH model describe some aspects of the Li/W and Li/Mo chemisorption systems. From fig. 3 one can see that for the same values of  $\varphi$  and  $Q$ , the difference in  $\omega_0$  for tungsten ( $\omega_0 = 21$  eV [14]) and molybdenum ( $\omega_0 = 1.35$  eV [15]) leads to a difference of more than twice in the ionic part of chemisorption energy.

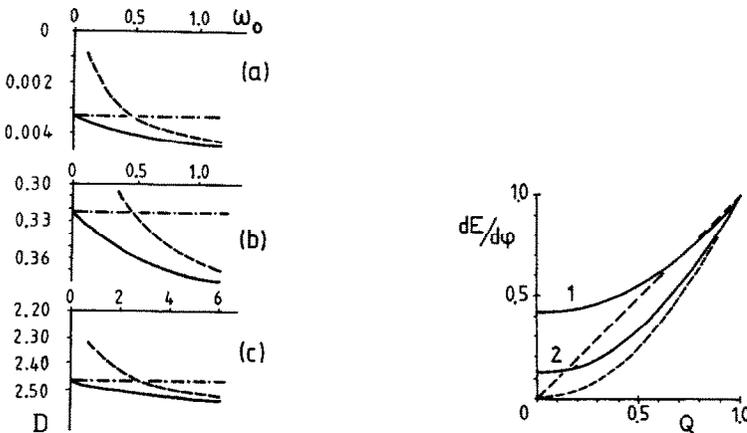


Fig. 2. The chemisorption energy  $D$  versus the surface plasmon frequency  $\omega_0$ . Curves are for  $\varphi = 0.2$ ,  $W = 2$  ( $W$  is the metal band width). Full line: the variational solution; dashed line: the inverse adiabatic approximation; dash-dotted line: the adiabatic approximation; (a)  $\epsilon_A = -0.35$ ,  $U = 0.80$ ,  $V = 0.05$ ; (b)  $\epsilon_A = -0.02$ ,  $U = 0.05$ ,  $V = 0.30$ ; (c)  $\epsilon_A = -0.02$ ,  $U = 0.95$ ,  $V = 1.50$ .

Fig. 3.  $dE/d\varphi$  versus the adatom charge  $Q$  for the EAH model for  $\omega_0 = 4.20$  (curve 1) and  $\omega_0 = 0.27$  (curve 2). Curves are for  $W = 2$ ,  $\varphi = 0.2$ ,  $U = 0.95$  and  $V = 0.5$ . At  $Q \approx 0.3$ , the parameters of the model correspond to the Li/W and Li/Mo chemisorption systems.

#### 4. Conclusion

In this work the effect of the dynamical nature of the adatom charge on the ionic part of the chemisorption energy is studied. It is shown that the charge fluctuations significantly modify the classical expression for the ionic part of the chemisorption energy. On the base of the time-scale arguments one can determine various regimes for which, due to differences in physics, different theoretical methods must be used to compute the chemisorption energy. We have computed the adatom charge fluctuation frequency  $\omega_f$  using the Khomskii variational method. A comparison of the exact solution with the variational one shows a very good accuracy of the variational method for chemisorption systems when  $\varphi \lesssim 3\omega_0$ .

We also point out that in the case of two adatoms, their charge fluctuations are independent. Thus, the dynamical effects of screening do not affect the interaction of these adatoms. As it was shown by Braun et al. [8], the energy of the electrostatic interaction between two chemisorbed atoms is equal to that of two static point charges  $\langle \hat{Q} \rangle$ .

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