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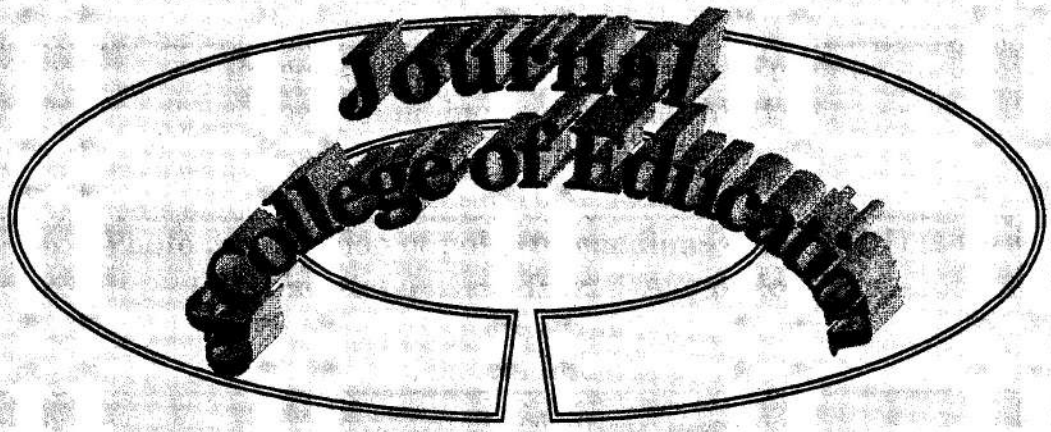

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The Electric Field effects on the charge state and the Potential Energy Surfaces of the system Na/Ni (110)

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Abstract:

Distance and screening effects on the adatom's effective charge are studied within the framework of the time – dependent Anderson – Newns model throughout the chemisorption theory. An analytical formula for the effective charges is used and developed where the repulsion of the two electrons of opposite spins in the adatom is taken into account by means of the correlation energy.

An analytical formulation for the metallic chemisorption energy [1] is also used and developed while the ionic contribution to the chemisorption energy is solved numerically. The chemisorption energies are calculated as a function of distance, screening length and applied electric field. The comparison with the behavior of the experimental data gives good agreement.

الملخص:

لقد تمت دراسة تاثيرات الحجب والمسافة على الشحنة المؤثرة للذرة الملتصقة حسب نموذج اندرسون – نيونز المعتمد على الزمن من خلال نظرية الالتصاق الكيميائي. تم استخدام وتعديل صيغة تحليلية للشحنات المؤثرة تاخذ بنظر الاعتبار التنافر الكولومي للالكترونات المتعاكسة البرم للذرة الملتصقة باستخدام بمفهوم طاقة الترابط.

تم ايضاً استخدام وتعديل صيغة تحليلية للجزء المعدني لطاقة الالتصاق الكيميائي [1] بينما تم حل اسهام الجزء الايوني لطاقة الالتصاق الكيميائي حلاً عددياً. طاقات الالتصاق الكيميائي حسبت كدالة للمسافة وطول الحجب المجال الكهربائي المسلط. وتم الحصول على تقارب جيد من خلال مقارنة التصرف العام لنتائج هذا العمل مع البيانات العملية المتوفرة.

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 Vi 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.

Researchers like Brivio [4] 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. [5]. Their realistic treatment was extended to large atom surface separation and the temperature effect was also introduced. Including the Coulomb repulsion between opposite spin electrons provided us with a qualitatively correct physical description to the atom – metal interaction. Calculations of the atomic level's position, half width and occupation as well as the effective Coulomb term were used to calculate the binding energies for different alkali types and substrates crystallography which give good quantitative agreement with experimental data (see also ref. [7]). Alkali atom is chemisorbed on the surface of transitional metal as a positive ion [6].

As the practical studies of the phenomena which occur on the surface (such as Diffusion, Crystal growth, Field Ion Microscope, Field Emission, Field Evaporation, field Desorption and others) are originally focusing on the binding energy and dependence of potential energy on the distance, this research will concentrate on the interaction between the adatom and the surface, where the calculations of the chemisorption energy (binding energy) as a function of distance which means to find the potential energy surfaces (PES), which is considered a very important step in those calculations, furthermore, the most important matter is that represents the charge state on the surface during the adsorption process.

In this work, a complete treatment was used to calculate the occupation numbers for the system Na/Ni(110) taking into account the effects of distance, applied electrical field, screening length, image effects and correlation effects. Then the results of these calculations have been used to calculate the energies that are mentioned above.

Theoretical considerations:

In regard to subject of this work, an analytical formula was derived for the occupation numbers of the adatom's levels (valance level with spin $+\sigma$ and affinity level with spin $-\sigma$) is given at any temperature by the following [1, 6]:

$$n_a^\sigma = 2a_2 k_B T\Gamma - \tan^{-1}\left(\frac{u_0 - E_a^\sigma}{\Gamma}\right) + a_2\Gamma E_a^\sigma \ln\frac{(k_B T - E_a^\sigma)^2 + \Gamma^2}{(k_B T + E_a^\sigma)^2 + \Gamma^2} + B_1^\sigma \tan^{-1}\left(\frac{-k_B T - E_a^\sigma}{\Gamma}\right) + B_2^\sigma \tan^{-1}\left(\frac{k_B T - E_a^\sigma}{\Gamma}\right) \quad \text{----------(1)}$$

where

$B_1^\sigma + B_2^\sigma = 1$

$B_2^\sigma = a_0 + a_2 (E_a^\sigma)^2 + a_2\Gamma^2$

a_o, a_1 *and* a_2 are constants, k_B is the Boltezman constant, T is the temperature of the surface, u_o is the band with of conduction band and Γ represents the half width (the broadening) of the adatom energy level. Taking into account the image shift $\Delta E(S)$ and correlation effects U_{eff} the corresponding energy levels positions are given by [1,6]:

$$E_a^{\pm\sigma} = \phi_o - V_i + \Delta E + U_{eff} n_a^{+\sigma} \quad \text{----------(2)}$$

where ϕ_o is surface work function.

Equation (1) and (2) are solved consistently getting two types of solutions, magnetic $(n_a^\sigma \neq n_a^{-\sigma})$ and non-magnetic $(n_a^\sigma = n_a^{-\sigma})$. The naming magnetic or non-magnetic refers to the net spin on the adatom whereas the

occupation numbers $n_a^{\pm\sigma}$, the positions of the atomic levels $E_a^{+\sigma}$ and the atomic half width $\Gamma^{\pm\sigma}$ are functions of spin.

When the adatom approaches to the surface, a strong coupling occur which leads to charge transfer from the adatom to the surface. That mean the non-magnetic solutions $(n_a^{\sigma} = n_a^{-\sigma})$ appear on the surface. Where the occupation numbers $(n_a^{\pm\sigma})$ represents a standard to the charge state on the adatom.

The density of electronic states of the adatom $(\rho_a^{\pm\sigma}(E))$ given by [2]:

$$\rho_a^{\pm\sigma}(E) = \frac{1}{\pi} \frac{\Gamma^{\pm\sigma}(S)}{(E - E_a^{\pm\sigma}(S))^2 + (\Gamma^{\pm\sigma}(S))^2} \qquad \text{----------(3)}$$

Whereas $\Gamma^{\pm\sigma}(S)$ is the half width of the adatom energy level which is given by[7]:

$$\Gamma^{\pm\sigma}(S) = \frac{(q_a^{\pm\sigma})^2}{16V_o(S + r_i)} \sqrt{2V_o - (q_a^{\pm\sigma})^2} \left(1 + \frac{1}{2(S + r_i)q_a^{\pm\sigma}}\right) e^{-2Sq_a^{\pm\sigma}} \qquad \text{----------(4)}$$

r_i represents the ionic radius and $V_o = \emptyset + |u_o|$, whereas $|u_o|$ is the metal band width and $q_a^{\pm\sigma}$ is given b:

$$q_a^{\pm\sigma} = \sqrt{2E_a^{\pm\sigma}} \qquad \text{----------(5)}$$

An analytical formula was also derived for the metallic binding energy that is given by the following:

$$E_M(S) = \frac{1}{\pi} \sum_{\sigma} \sum_{i=1}^{5} C_i^{\sigma} g_i^{\sigma} - U_{eff} n_a^{\sigma} n_a^{-\sigma} \qquad \text{----------(6)}$$

Whereas the functions C_i and g_i are well known in the reference [1].

However, the ionic energy part is given by the following relation [3] that has been solved numerically:

$$E_I(S) = -e^2 \int_S^{\infty} \frac{Z_{eff}^2(S')dS'}{4(S' + S_o)^2} \qquad \text{----------(7)}$$

S_o represents the screening length and $Z_{eff}(S)$ is the effective charge that concentrated on the adatom. Accordingly, the total chemisorption energy is given by:

$$E_{CH}(S) = E_M(S) + E_I(S) \qquad \text{----------(8)}$$

From equation (8), it would be possible to find the potential energy surfaces PES that represents the system energy states whether it is in the magnetic state (atomic) or in the non-magnetic state (ionic) especially near the surface. And the binding energy was calculated as follows:

$$E_B = E_{CH}(S = 0) - E_{CH}(S = \infty) \qquad \text{----------(9)}$$

By applying external electrical field of strength F on the system of adatom – surface, thus its affect is added to the surface of the adatom energy level that will be shifted by (eFS_o)[8], whereas S_o represents the

screening length. Then, the chemisorption energy of the non-magnetic state as a function of distance(S) and the applied field (F) given by [9]:

$$E_{CH}(S,F) = E_M(S,F) + E_I(S,F) + E_{IF}(S,F) - \frac{1}{2}\alpha_i F^2 \qquad \text{----------(10)}$$

Where $E_m(S,F)$ and $E_I(S,F)$ are calculated according to eq.s(6,7) with the applied field. The third term of eq.(10) amount of the energy which associated with the brings of the effective charge $|e|Z_{eff}(S,F)$ from S=0 to the applied field zone at the distance S from the surface and it is given by [9]:

$$E_{IF}(S,F) = eF \int_{S+S_o}^{0} Z_{eff}(S',F)dS' \qquad \text{----------(11)}$$

The fourth term of eq.(10) represents the ion polarization energy and α_i is a polarization factor of the electric dipole of ion.

The chemisorption energy of the magnetic state as a function of distance(S) and the applied field (F) is given by a similar formula to eq.(10) but by changing α_A instead of α_i (whereas α_A is a polarization factor of the electric dipole of atom).

Results and discussion:

In the chemisorption model; the band width(u_o) and the work function (which was included in $E_a^{+\sigma}$ formula) are the surface discriminated factor and the discriminated factors of the adatom are represented by the ionization level (V_i and affinity level V_A) and the atomic radius (r_i) 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.

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 $E_a^{+\sigma}$ with the screening length S_o=0.9872 A° for various values of applied electric field, for purpose to assure its general behavior as a function of distance and applied external field.

Table(1) shows the following:

1. The occupation numbers $n_a^{\pm\sigma}$ (the position of adatom energy level $E_a^{\mp\sigma}$) decrease (increase) for all distance values, especially at the surface, as the applied field increases.
2. The point (S_{ch}) explains the region in which the solution changes from magnetic into non-magnetic solution whereas (S_{ch}) varies with the applied field.

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.

3. The adatom energy levels are sited above the Fermi energy level, as shown in figure (1). However, the value of density of states on adatom decrease with the applied field increases at the surface where the solutions are non-magnetic ($n_a^{\sigma} = n_a^{-\sigma}$) either the filed was existed or not existed.

While figure (2) shows the density of states calculations at distance S=30 A° from the surface, to compare it with those at the surface (S=0). The $E_a^{-\sigma}$ site above ($E_a^{+\sigma}$ nearly fitting at) Fermi level (E_F=0) either the filed was existed or not existed. Where $\Gamma^{+\sigma} >> \Gamma^{-\sigma}$ and $n_a^{+\sigma} >> n_a^{-\sigma}$, so, the solutions are magnetic state because the acting of correlation effects and image force effects.

4. Chemisorption energy calculation was also done to the two solutions, the magnetic and non-magnetic one, for the system Na/Ni(110) as a function of distance and applied field 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 (connected line) and the atomic (dashed 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. These calculations 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 values of the applied field and this participation increases with the applied field increases, on the contrary of the metallic participation.

The theoretical and experimental values of the binding energies mentioned in table (2) which where taken from the references [3,10] are measured with respect to the ionic state, so it must be compared with E_{CH}

value. The results that were obtained give a good agreement with experimental data.

5. To study the external electric field effect, the calculation of PES was done on the Na/Ni (110) system as a function of applied field. By applying an external electrical field F , which should be greater than the local field causes by the induced image at the surface on the ion that is wanted to be desorbed. The adatom energy level will shift up to Fermi level by($|e|FS_o$). As a result, the local electronic charge near the adatom will be greatly decreased (especially to the stronger fields), because the trails of the adatom Lorentizian shape will be intersected with levels of the metal energy band. Then, the increases of the broadening Γ of the adatom energy level that leads to decreasing of the electronic charge n_a which was localized near the adatom.

Figure(4) shows the magnetic solution (dashed line) is not affected by the weak applied field but the effect of the applied field is added of this kind of solutions as a shifting with amount $\frac{1}{2}\alpha_A F^2$ matching with the case of F=0. While for the stronger applied field there is no magnetic state, because the adatom energy level will shifted up to Fermi level then, the non-magnetic state was dominated starting from the effective charges (occupation numbers) and ending with the chemisorption energy.

The non-magnetic solution (connecting line) is being curved with respect to strength of the applied field F, comparing with the case of F=0 which was shown in the previous figure (3). The intersect of these curves (magnetic and non-magnetic curves) depend on the strength of applied field. Figure(4) shows the mechanism of desorption process, where adatom is been desorbed as a positive ion through the ground state G.S. of the system, which is an ionic state without intersecting with the magnetic state (atom) curve, i.e. the crossing point S_C is vanish.

Conclusion:

A model derived from the chemisorption theory, which determines the effective charges of an alkali atom adsorbed on a metallic surface. It has explained that the effective charge and the chemisorption energy are very sensitive to the atom – surface distance and strength of the applied electric field, especially at the distances larger than $5a_o$. This is of a great interest for various atoms –surface interaction processes involving external electric field.

By applying an external electrical field F , the adatom energy level will shift up to Fermi level by($|e|FS_o$). As a result, the local electronic

charge near the adatom will be greatly decreased especially to the stronger fields.

The magnetic solution is not affected by the weak applied field but the effect of the applied field is added of this kind of solutions as a shifting with amount $\frac{1}{2}\alpha_A F^2$ and for the stronger applied field there is no magnetic state. The non-magnetic state was dominated starting from the effective charges (occupation numbers) and ending with the chemisorption energy. The non-magnetic solution is being curved with respect to strength of the applied field F, while the intersecting of the magnetic and non-magnetic curves depends on the strength of applied field.

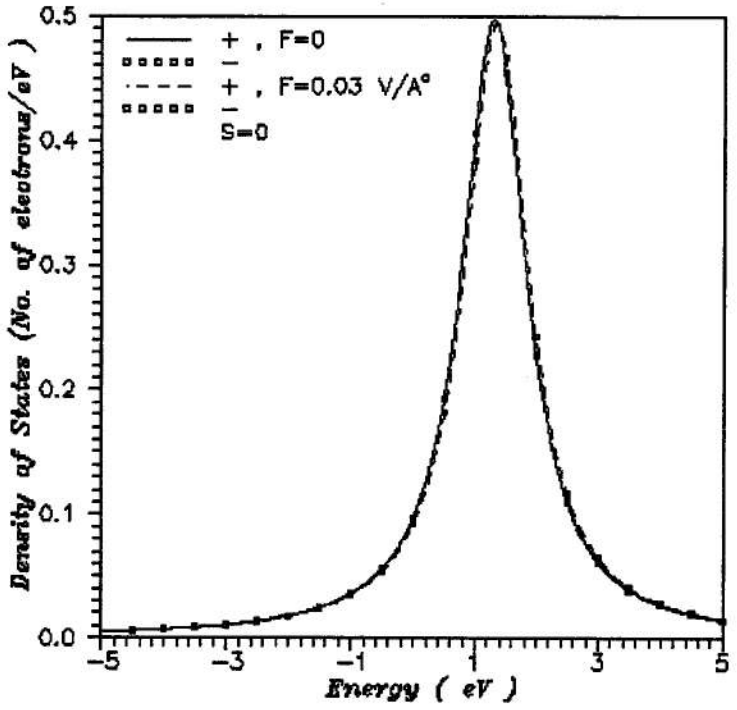

Figure (1): The density of states on the adatom at the surface

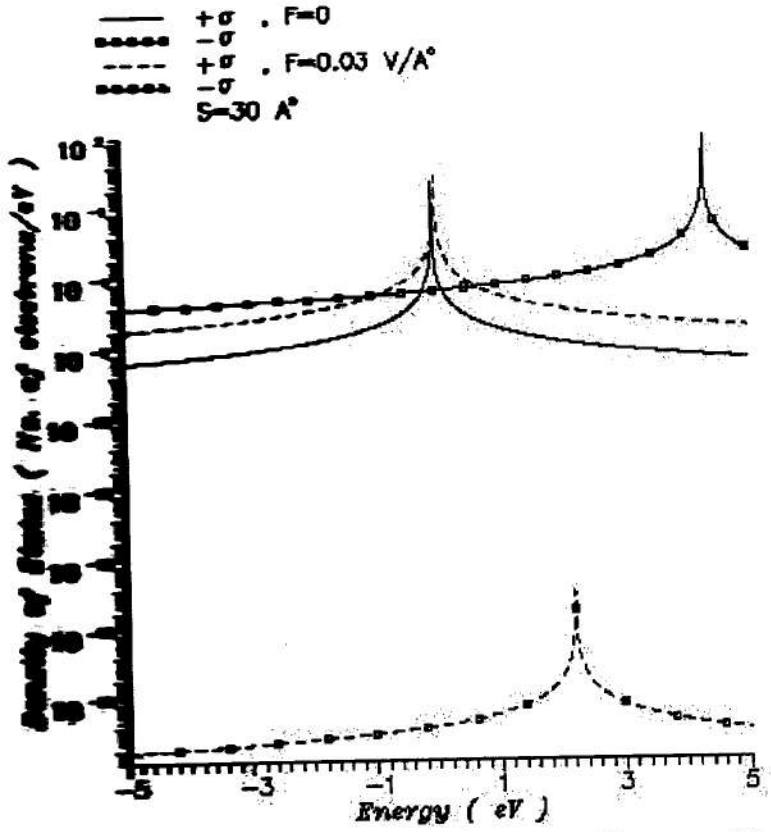

Figure (2): The density of states on the adatom at distance (S=30 A°) from the surface.

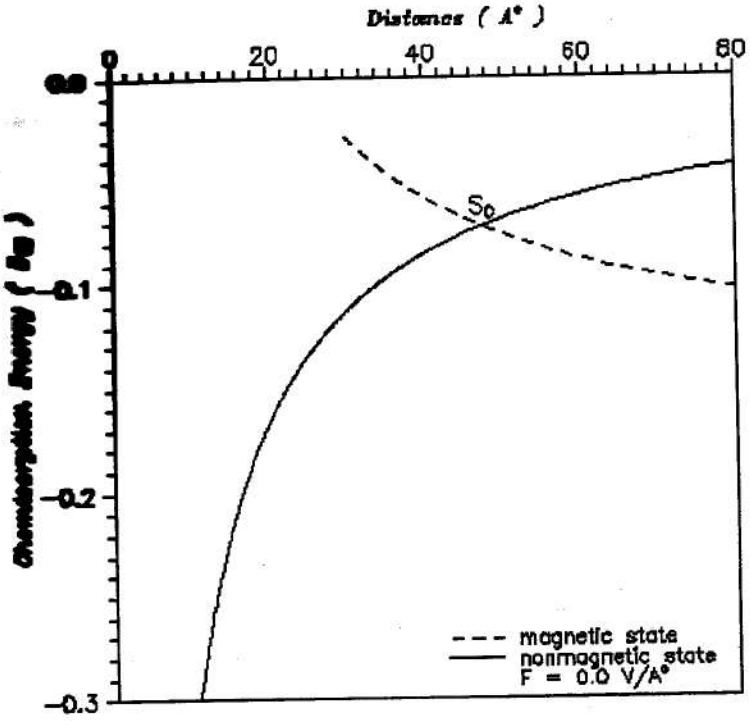

Figure (3):The PES for the system Na/Ni(110).

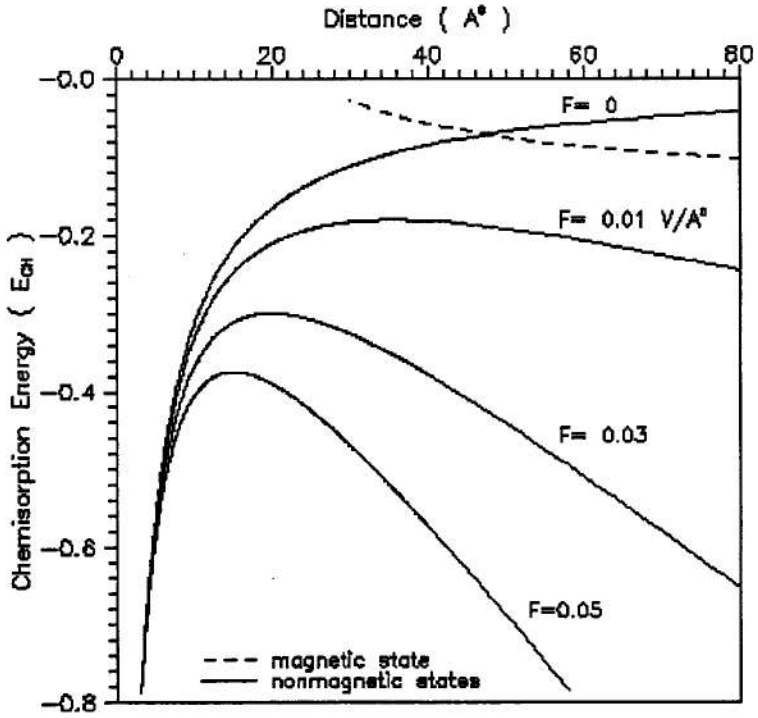

Figure (4): The PES for the system Na/Ni(110) with applying an electrical field.

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