

LASER FIELD EFFECTS ON THE CHEMISORPTION PROCESS

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Abstract

Detailed theoretical treatment and model calculations for describing the interaction between species and solid surface in the presence of a monochromatic electromagnetic field (laser field) throughout the chemisorption process, have been developed.

Our theoretical treatment [1,2] for the scattering process in the presence of laser field and the well known Anderson model for atomic chemisorption [3,4] are the basis in deriving our theoretical treatment in the case of the chemisorption of the species on solid surface in the presence of laser field. The derived occupation number and the chemisorption energy are calculated as a function of laser parameters and as a function of normal distance from the surface as the adatom approaches to the surface. The model calculation is applied to the systems Na/W(111) and H/Cu(110) for their experimental and academic importance. Many important features are explained concerning the adatom charge state and the bonding type. From our results, one can conclude that the laser field is a tool of ionization, which is experimentally the truth.

Keywords: chemisorption process; monochromatic electromagnetic field; occupation number; chemisorption energy

1. Introduction

Surface chemical reactions, in which at least one of the reaching species is adsorbed on solid surface, are important for chemical industry. It is hence of interest to investigate laser-stimulated surface processes [5] which include surface excitation [6-8], desorption [9,10], dissociation [11,12] and catalysis [13] (see fig. (1)).

Laser-stimulated surface processes usually combine laser-excitation effects with surface-induced excitation and relaxation effects on the dynamics of adspecies (atom, molecules, or clusters that are physisorbed or chemisorbed on solid surfaces). Laser-stimulated surface processes have been investigated during the past several years, due to both their academic interest and industrial potential. Recent progress in the experimental and theoretical studies and applications of laser-stimulated surface processes have been reported [14]. Laser excitation or desorption of adspecies have been investigated theoretically by a variety of techniques including Morse potential models [15] and master equation approaches [16].

The surface-atom charge exchange process can be controlled by laser field [1,2]. So we expect that the transfer of charge between solid surface and adatoms above the surface to be greatly enhanced.

Since the charge transfer is the essence of chemistry, surface catalysis would be greatly affected by this phenomenon. With laser, chemists have begun to control chemical reaction dynamics in gas-phase reactions and the reactions occurring at the gas-solid interface, using ultra short laser flashes on the time scale on which the reactions actually occur [17].

In this paper, the chemisorption of atoms on solid surfaces in the presence of laser field is studied. The theoretical treatment in our pervious paper [2], and the well-known Anderson model [3,4] for atomic chemisorption, are our basis in deriving the occupation numbers and the binding energy formulas in the static case of u (atomic velocity) $\rightarrow 0$. In order to develop a "basis treatment", many complications must be avoided such as,

1. The variation of the screening length with laser field parameters is not taken into account.
 2. The dependence of the intra-atomic Coulomb interaction on laser field parameters is not considered as well as the correlation effect on the surface site.
 3. The electronic excitations in the adatom-surface orbitals are neglected.
 4. The effect of surface temperature is not considered since by including it, one must establish the heating of the system due to laser field.
- Each of these remarks may have a wide-range of researching both theoretically and experimentally, which may be considered as future work

2. Derivation of the Adatom Occupation Numbers

To derive a formula for the occupation number n_A of the adatom level, we get use of the following equation that is derived in our previous paper [2](eq. (20),

$$\dot{C}_{A\mu'}(t) = -\frac{i}{\hbar} \varepsilon_{im}(t) C_{A\mu'}(t) - \frac{i}{\hbar} \left[\tilde{V}_{A\mu'}(t) + \tilde{W}_{A\mu'}(t) \right] - \frac{1}{\hbar^2} \sum_{\mu} \left[\tilde{V}_{A\mu'}(t) + \tilde{W}_{A\mu'}(t) \right] \int_{t_0}^t \left[\tilde{V}_{\mu A}(t') + \tilde{W}_{\mu A}(t') \right] C_{A\mu'}(t') dt' \tag{1}$$

which is treated firstly as the velocity of the atom goes to zero. This means, that the occupation number and all the related chemisorptions functions are calculated as a function of the normal distance from the surface. By using the following definitions,

$$C_{A\mu'}(t) = \bar{C}_{A\mu'}(t) e^{-i \int_{t_0}^t \varepsilon_{im}(t') dt'}, \quad \tilde{V}_{A\mu'}(t) = V_{A\mu'}(t) e^{-i(E_{\mu'} - E_A^{\infty})t}$$

$$\tilde{W}_{A\mu'}(t) = W_{A\mu'}(t) e^{-i(E_{\mu'} - E_A^{\infty})t} \left(e^{i\delta} e^{i\omega_L t} + e^{-i\delta} e^{-i\omega_L t} \right) \tag{2}$$

However, $\left| C_{A\mu'}(t) \right|^2 = \left| \bar{C}_{A\mu'}(t) \right|^2$. Then we get from eq.(1),

$$\bar{C}_{A\mu'}(t) = -i e^{-iE_A^{\infty}t} \int_0^t G(t') dt' \int_0^t \left[V_{A\mu'}(t') + W_{A\mu'}(t') (e^{i\delta} e^{i\omega_L t'} + e^{-i\delta} e^{-i\omega_L t'}) \right] \times e^{-i(E_{\mu'} - E_A(Z))t' + \int_0^{t'} G(t'') dt''} dt' \tag{3}$$

where the function $G(t)$ at certain Z is given by,

$$G(t) = \pi \sum_{\mu} \left\{ \left| V_{A\mu}(t) \right|^2 + 2V_{A\mu}(t)W_{A\mu}(t) (e^{i\delta+i\omega_L t} + e^{-i\delta-i\omega_L t}) + \left| W_{A\mu}(t) \right|^2 (2 + e^{2i\delta+2i\omega_L t} + e^{-2i\delta-2i\omega_L t}) \right\} \tag{4}$$

The first term of eq. (4) includes the adatom energy level broadening due to coupling interaction while the third one includes the adatom level broadening due to laser field coupling interaction. The second one includes the interference between the two above-mentioned coupling interactions. Then by using the definition of the atomic level broadening [18], we can write

$$\Delta_C(Z) = \pi \sum_{\mu} |V_{A\mu}(Z)|^2 \delta(E - E_{\mu}), \quad \Delta_L(Z) = \pi \sum_{\mu} |W_{A\mu}(Z)|^2 \delta(E - E_{\mu})$$

$$\Delta_{int}(Z) = \pi \sum_{\mu} |V_{A\mu}(Z) W_{A\mu}(Z)| \delta(E - E_{\mu}) \tag{5}$$

As our

derivation works in the limit $u \rightarrow 0$, the atomic normal distance. So eq. (4) can be written in the level broadenings are written as a function of the wide band approximation limit as,

$$G(t) = \Delta_C + 2\Delta_{int} (e^{i\delta+i\omega_L t} + e^{-i\delta-i\omega_L t}) + \Delta_L (2 + e^{2i\delta+2i\omega_L t} + e^{-2i\delta-2i\omega_L t})$$

$$\Delta_C = \pi \bar{\rho} |V(Z)|^2, \quad \Delta_L = \pi \bar{\rho} |W(Z)|^2, \tag{7}$$

$$\Delta_{int} = \pi \bar{\rho} V(Z) W(Z), \quad \bar{\rho} = 1/\text{band width} \tag{6}$$

Then by integrating eq. (6), we get

$$\int G(t') dt'$$

$$= (\Delta_C + 2\Delta_L)t + \frac{2\Delta_{int}}{i\omega_L} (e^{i\delta+i\omega_L t} - e^{-i\delta-i\omega_L t}) + \frac{\Delta_L}{i2\omega_L} (e^{2i\delta+2i\omega_L t} - e^{-2i\delta-2i\omega_L t})$$

and by

$$= (\Delta_C + 2\Delta_L)t - \frac{2i\Delta_{int}}{\omega_L} (e^{i\delta+i\omega_L t} - e^{-i\delta-i\omega_L t}) - \frac{i\Delta_L}{2\omega_L} (e^{2i\delta+2i\omega_L t} - e^{-2i\delta-2i\omega_L t}) \tag{8}$$

getting use of the definition of exponential function [19], we write,

$$e^{\int G(t') dt' - i(E_{\mu} - E_A(Z))t}$$

$$= e^{-i(E_{\mu} - E_A(Z))t} e^{(\Delta_C + 2\Delta_L)t} \sum_{nmlk} \left(\frac{-2i\Delta_{int}}{\omega_L} \right)^n \left(\frac{2i\Delta_{int}}{\omega_L} \right)^m \left(\frac{-i\Delta_L}{2\omega_L} \right)^l \left(\frac{i\Delta_L}{2\omega_L} \right)^k$$

$$e^{n(i\delta+i\omega_L t)} e^{m(-i\delta-i\omega_L t)} e^{l(2i\delta+2i\omega_L t)} e^{k(-2i\delta-2i\omega_L t)} \tag{9}$$

By substituting eq. (9) in eq. (3) we get,

$$\bar{C}_{A\mu}'(t) = -i e^{-iE_A t - \int_0^t G(t') dt'} \sum_{nmlk} (-1)^{n+l} \left(\frac{2i\Delta_{int}}{\omega_L} \right)^{n+m} \left(\frac{i\Delta_L}{2\omega_L} \right)^{l+k}$$

$$e^{i\delta(n-m+2l-2k)} \left\{ \frac{V_{A\mu} e^{-i[E_{\mu} - E_A(Z) + i(\Delta_C + 2\Delta_L) + \omega_L(n-m+2l-2k)]t}}{E_{\mu} - E_A(Z) + \omega_L(n-m+2l-2k) + i(\Delta_C + 2\Delta_L)} \right.$$

(10)

$$+ \frac{W_{A\mu} e^{i\delta} e^{-i[E_{\mu} - E_A(Z) + \omega_L(-1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)]t}}{E_{\mu} - E_A(Z) + \omega_L(-1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)}$$

$$\left. + \frac{W_{A\mu} e^{-i\delta} e^{-i[E_{\mu} - E_A(Z) + \omega_L(1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)]t}}{E_{\mu} - E_A(Z) + \omega_L(1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)} \right\}$$

However, if the perturbation is time dependent harmonic one, then the system levels generated from $E_A(Z)$ will be $E_A(Z) + n\omega_L$, with $n = 0, \pm 1, \pm 2, \dots$. Some of these levels are

thrown above Fermi level and the others below the conduction band bottom position. So they may do not effectively take parts in the resonance charge exchange process. Accordingly, all the terms in eq. (10) are

neglected except for $n = m = l = k = 1$, so eq. (10) can be written as,

$$\bar{C}_{A\mu}(t) = e^{-i(E_{\mu}-E_A(Z))t} \left\{ \frac{V_{A\mu}}{E_{\mu} - E_A(Z) + i(\Delta_C + 2\Delta_L)} + \frac{W_{A\mu} e^{i\delta+i\omega_L t}}{(E_{\mu} - E_A(Z) - \omega_L) + i(\Delta_C + 2\Delta_L)} + \frac{W_{A\mu} e^{-i\delta-i\omega_L t}}{(E_{\mu} - E_A(Z) + \omega_L) + i(\Delta_C + 2\Delta_L)} \right\} \quad (11)$$

The adatom's occupation level can be given by [20],

$$n_A = \frac{1}{\pi} \int \sum_{\mu} |\bar{C}_{A\mu}|^2 \delta(E - E_{\mu}) dE \quad (12)$$

Substituting eq. (11) in eq. (12), we get the following expression,

$$\begin{aligned} n_A &= \frac{1}{\pi} \int \frac{\Delta_C dE}{(E - E_A(Z))^2 + (\Delta_C + 2\Delta_L)^2} + \frac{1}{\pi} \int \frac{\Delta_L dE}{(E - E_A(Z) - \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} \\ &+ \frac{1}{\pi} \int \frac{\Delta_L dE}{(E - E_A(Z) + \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} \\ &+ \frac{1}{\pi} \int \frac{\Delta_{int} e^{-i\delta-i\omega_L t} dE}{[(E - E_A(Z)) + i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) - i(\Delta_C + 2\Delta_L)]} \\ &+ \frac{1}{\pi} \int \frac{\Delta_{int} e^{i\delta+i\omega_L t} dE}{[(E - E_A(Z)) - i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) + i(\Delta_C + 2\Delta_L)]} \\ &+ \frac{1}{\pi} \int \frac{\Delta_{int} e^{-i\delta-i\omega_L t} dE}{[(E - E_A(Z)) - i(\Delta_C + 2\Delta_L)][(E - E_A(Z) + \omega_L) + i(\Delta_C + 2\Delta_L)]} \\ &+ \frac{1}{\pi} \int \frac{\Delta_{int} e^{i\delta+i\omega_L t} dE}{[(E - E_A(Z)) + i(\Delta_C + 2\Delta_L)][(E - E_A(Z) + \omega_L) - i(\Delta_C + 2\Delta_L)]} \\ &+ \frac{1}{\pi} \int \frac{\Delta_L e^{2i\delta+2i\omega_L t} dE}{[(E - E_A(Z) + \omega_L) - i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) + i(\Delta_C + 2\Delta_L)]} \\ &+ \frac{1}{\pi} \int \frac{\Delta_L e^{-2i\delta-2i\omega_L t} dE}{[(E - E_A(Z) + \omega_L) + i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) - i(\Delta_C + 2\Delta_L)]} \end{aligned} \quad (13)$$

There are nine terms, the first three terms do not include the timedependent exponential term while the others include it. These six terms turn

to zero due to averaging over the phase, with n is an integer

$$\frac{1}{2\pi} \int_0^{2\pi} e^{\pm i n \delta} d\delta = 0$$

That leaves the occupation number time-independent term.

3. The Model Calculation

Eq. (13) is employed to calculate the occupation number of the atomic energy level

which can be written as,

$$n_A = \frac{1}{\pi} \frac{\Delta_C}{\Delta_C + 2\Delta_L} \int_{u_0}^{E_F} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z))^2 + (\Delta_C + 2\Delta_L)^2} dE$$

$$+ \frac{1}{\pi} \frac{\Delta_L}{\Delta_C + 2\Delta_L} \int_{u_0}^{E_F} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z) - \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} dE$$

$$+ \frac{1}{\pi} \frac{\Delta_L}{\Delta_C + 2\Delta_L} \int_{u_0}^{E_F} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z) + \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} dE \tag{14}$$

with u_0 and E_F are the bottom of the band and Fermi energy respectively. Accordingly, eq. (14) can also be written as [20],

$$n_A = \sum_n g_n \int_{u_0}^{E_F} \rho_n(E) dE \tag{15}$$

with,

$$\rho_n(E) = \frac{1}{\pi} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z) + n\omega_L)^2 + (\Delta_C + 2\Delta_L)^2} \tag{16}$$

$$g_0 = \frac{\Delta_C}{\Delta_C + 2\Delta_L}, \quad g_1 = g_{-1} = \frac{\Delta_L}{\Delta_C + 2\Delta_L} \tag{17}$$

Since $\sum_n \rho_n$ is the local density of states on the adatom in the presence of laser field. The spin dependence of $n_A \Rightarrow n_A^\sigma$ and $\rho_n \Rightarrow \rho_n^\sigma$ is considered throughout the adatom energy level $E_A(Z)$ as well as the chemisorption function, i.e. the broadening one. $E_A(Z)$ is written as $E_A^{\pm\sigma}(Z)$, $+\sigma$ for spin up and $-\sigma$ for spin down atomic levels respectively. By incorporating the repulsive electron-electron Coulomb interaction U [21,22] on the adatom, $E_A^\sigma(Z)$ takes the following expression,

$$E_A^{\pm\sigma}(Z) = E_A^\infty + U n_A^{\mp\sigma}(Z) \quad ; \quad E_A^\infty = \phi - V_i \tag{18}$$

ϕ and V_i are the metal work function and the ionization energy of the adsorbed atom respectively.

$E_A^{+\sigma}$ and $E_A^{-\sigma}$ differ by U whose value may be taken for as $V_i - V_A$, with V_i and V_A are the ionization and the affinity energies respectively. As the atom is far away from the surface $n_A^{+\sigma} = 1$ and $E_A^{+\sigma} = \phi - V_i$ while $n_A^{-\sigma} = 0$ and $E_A^{-\sigma} = (\phi - V_i) + U$. Now as the atom approaches the surface, U decreases due to the screening out of the electron-electron interaction and its effective value can be given by [23,24],

$$U = V_i - V_A - 2\varepsilon_{im}(Z) \quad \dots \tag{19}$$

where $\varepsilon_{im}(Z)$ is the image shift [25],

$$\varepsilon_{im}(Z) = \frac{e^2}{4(Z + Z_0)} \text{ with } Z_0 \text{ is the screening length.}$$

In chemisorption theory calculation, the broadening function as well as the intra-atomic electron-electron interaction, both make the

theoretical treatments achieve higher a priori accuracy in calculations of charge fractions (i.e. $n_A^{\pm\sigma}$). In the limit of wide band

$$\Delta_C^\sigma(Z) = \Delta_{C_0} e^{-2\alpha_C^\sigma Z} \quad ; \quad \Delta_L(Z) = \Delta_{L_0} e^{-2\alpha_L Z}$$

With, $\alpha_L = \sqrt{2|V_i|}$ and α_C^σ will be defined later. Δ_{C_0} and Δ_{L_0} represent the broadening at $Z = 0$ with Δ_{L_0} equal to $\pi\bar{\rho}W_0^2$.

$$n_A^\sigma = \frac{1}{\pi} \frac{\Delta_C^\sigma}{\Delta_C^\sigma + 2\Delta_L} \left(\tan^{-1} \frac{E_F - E_A^\sigma}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{u_o - E_A^\sigma}{\Delta_C^\sigma + 2\Delta_L} \right)$$

$$+ \frac{1}{\pi} \frac{\Delta_L}{\Delta_C^\sigma + 2\Delta_L} \left(\tan^{-1} \frac{E_F - E_A^\sigma - \omega_L}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{u_o - E_A^\sigma - \omega_L}{\Delta_C^\sigma + 2\Delta_L} \right) \\ + \frac{1}{\pi} \frac{\Delta_L}{\Delta_C^\sigma + 2\Delta_L} \left(\tan^{-1} \frac{E_F - E_A^\sigma + \omega_L}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{u_o - E_A^\sigma + \omega_L}{\Delta_C^\sigma + 2\Delta_L} \right) \quad (21)$$

Then eq. (21) and (18) must be solved self-consistently using the following initial conditions as the species is far away from the

approximation, Δ_C^σ and Δ_L are calculated from the following formalisms [26],

$$(20)$$

In order to calculate the occupation numbers and all the related functions, we firstly solved eq. (14) analytically,

surface (i.e. at $Z = 100 \text{ \AA}^0$), $n_A^{+\sigma} = 1$ and $n_A^{-\sigma} = 0$.

4. The Chemisorption Energy

The occupation numbers and related chemisorption functions are considered as an "input-data" to calculate the chemisorption energy. The calculation of the chemisorption energy as a function of normal distance to the surface, i.e. the potential energy surfaces calculation is an important step in the chemisorption theory calculation. The potential energy surfaces give the type of binding at every normal distance from surface, which is what one needs for comparison with the experimental founding.

The chemisorption energy, E_{che} , in general, is defined as being the difference between the final and the initial energies of the

$$E_M(Z) = \sum_{\sigma} \int_{-\infty}^0 E \rho_A^\sigma(E) dE - U n_A^{+\sigma} n_A^{-\sigma} \quad (22)$$

Then, by substituting the formula of local density of states on the adatom in the presence of laser field eq.(12) in eq. (22), we get

$$E_M(Z) = \sum_{\sigma} \sum_{n=0,\pm 1} g_n \int_{u_o}^{E_F} E \rho_n^\sigma(E) dE - U n_A^{+\sigma} n_A^{-\sigma} \quad (23)$$

system. According to Anderson model, the chemisorption energy is the change in the initial ground state energy on switching on the coupling assuming one electron on the adatom initially. In general, the chemisorption energy is divided into two parts. These are the metallic part and the ionic part [27].

The metallic part of the bond energy, which may be called delocalization energy, results from allowing the valance electron of the adatom to spread throughout the metal and the metal electrons to spread a bit into the region of the adatom. This part is given by [28],

$$\begin{aligned}
 E_M(Z) = \frac{1}{\pi} \sum_{\sigma} \left[E_A^{\sigma} \frac{\Delta_C^{\sigma}}{\Delta_C^{\sigma} + 2\Delta_L} \left\{ \tan^{-1} \frac{E_F - E_A^{\sigma}}{\Delta_C^{\sigma} + 2\Delta_L} - \tan^{-1} \frac{-2\beta - E_A^{\sigma}}{\Delta_C^{\sigma} + 2\Delta_L} \right\} \right. \\
 + (E_A^{\sigma} - \omega_L) \frac{\Delta_L}{\Delta_C^{\sigma} + 2\Delta_L} \left\{ \tan^{-1} \frac{E_F - (E_A^{\sigma} - \omega_L)}{\Delta_C^{\sigma} + 2\Delta_L} - \tan^{-1} \frac{-2\beta - (E_A^{\sigma} - \omega_L)}{\Delta_C^{\sigma} + 2\Delta_L} \right\} \\
 + (E_A^{\sigma} + \omega_L) \frac{\Delta_L}{\Delta_C^{\sigma} + 2\Delta_L} \left\{ \tan^{-1} \frac{E_F - (E_A^{\sigma} + \omega_L)}{\Delta_C^{\sigma} + 2\Delta_L} - \tan^{-1} \frac{-2\beta - (E_A^{\sigma} + \omega_L)}{\Delta_C^{\sigma} + 2\Delta_L} \right\} \\
 + \frac{\Delta_C^{\sigma}}{2} \ln \left\{ \frac{(E_F - E_A^{\sigma})^2 + (\Delta_C^{\sigma} + 2\Delta_L)^2}{(-2\beta - E_A^{\sigma})^2 + (\Delta_C^{\sigma} + 2\Delta_L)^2} \right\} \\
 + \frac{\Delta_L}{2} \ln \left\{ \frac{(E_F - E_A^{\sigma} + \omega_L)^2 + (\Delta_C^{\sigma} + 2\Delta_L)^2}{(-2\beta - E_A^{\sigma} + \omega_L)^2 + (\Delta_C^{\sigma} + 2\Delta_L)^2} \right\} \\
 \left. + \frac{\Delta_L}{2} \ln \left\{ \frac{(E_F - E_A^{\sigma} - \omega_L)^2 + (\Delta_C^{\sigma} + 2\Delta_L)^2}{(-2\beta - E_A^{\sigma} - \omega_L)^2 + (\Delta_C^{\sigma} + 2\Delta_L)^2} \right\} \right] \\
 - U n_A^{\sigma} n_A^{-\sigma} \tag{24}
 \end{aligned}$$

Note that in eq. (24), the laser field effect is added explicitly to the atomic energy levels positions and the broadening function.

The ionic energy is the energy associated with bringing a unit of charge infinitely far removed from the metal up to a [28],

$$Z_{\text{eff}}(Z) = 1 - n_A^{\sigma} - n_A^{-\sigma} \tag{25}$$

Now, the work or the change in energy to bring the charge from $Z' = \infty$ to $Z' = Z$ is given by,

$$W(Z) = - \int_Z^{\infty} \frac{Z_{\text{eff}}^2(Z') dZ'}{4(Z' + Z_0)^2} \tag{26}$$

distance Z from the surface. However as the atom is brought to the surface, its sharp state broadens and overlaps a bit with the metal conduction band such that the effective net charge on the ion is now a function of distance

Finally, eqs.(24) and (26) are calculated numerically to get the total chemisorption energy,

$$E_{\text{che}}(Z) = E_M(Z) + W(Z) \tag{27}$$

The dominant energy contribution depends on whether the adatom is one of electronegative nature or electropositive one, as well as on the surface electronic structure, i.e. whether the surface is clean or not.

5. The effects of the laser field on the chemisorption of Na/W(111) and H/Cu(110) : Results and Discussion

We apply our theoretical treatment as presented to real systems in order to illustrate its applicability and to extract some physical useful conclusions about the effects of laser field throughout the chemisorption process. Two real systems are considered, these are the

chemisorption of Na on W(111) and H on Cu(110).

5.1 The Chemisorptions of Na on W(111)

In this section, the chemisorption dynamics of Na-atom

($V_i = 5.14$ eV and $V_A = 0.54$ eV [29]) as it approaches the surface of W(111) ($\phi = 4.4$ eV [30]) is investigated. This system is of the type $\phi < V_i$.

The screening length is fixed on $Z_o = 1.1635A^o$, this value gives the experimental atomic chemisorption energy

$$\Delta_C^{\pm\sigma}(Z) = \frac{(q_A^{\pm\sigma})^2}{16V(Z+r_i)} \sqrt{2V - q_A^{\pm\sigma^2}} \left(1 + \frac{1}{2(Z+r_i)q_A^{\pm\sigma}} \right) e^{-2(Z+r_i)q_A^{\pm\sigma}} \quad (28)$$

where, $q_A^{\pm\sigma} = \sqrt{2|E_A^{\pm\sigma}|}$, $V = 2\beta + \phi$ and r_i is the atomic radius of the adatom. The Δ_C^σ -laser field parameters dependence is being throughout E_A^σ . This formula is usually used for the alkali adatoms adsorption on transition metal surface because it gives the general physical features for their chemisorption dynamics, while Δ_L is given by equation (20).

Figs. (2) show our results for the occupation numbers as a function of the normal distance Z for different values of laser coupling strength W_o while ω_L is fixed on 0.112 a.u.. Two types of solutions can be recognized. The first is magnetic solution ($n_A^\sigma \neq n_A^{-\sigma}$) where there is net spin on the adatom at large distance, while the other one is non- magnetic solution ($n_A^\sigma = n_A^{-\sigma}$) where there is no net spin on the adatom at relatively small distance. Z_{ch} is referred to as the point where the solution is changed from magnetic to non magnetic as the adatom approaches to the surface. For $Z > Z_{ch}$ the adatom has atomic character while at $Z < Z_{ch}$ the adatom is positively ionized. Table (1) shows the variation of Z_{ch} with W_o , which reveals that Z_{ch} increases slowly and by step with W_o . By laser field one can mark the distance at which the ionization began.

In figs. (3) the corresponding $E_A^{\pm\sigma}$ are presented as a function of Z for the same values of W_o and ω_L . The general features are very obvious, where the values of high occupation are due to the lying of the corresponding E_A^σ below Fermi level and vice versa. The values of

which is equal to 2.35 eV [31] in the absence of laser field. The parameter β (the band width = 4β) is fixed on 12 eV which works in the limit of the wide band approximation.

The adatom energy level broadening function that is used for this system is given by [32],

$E_A^{\pm\sigma}$ at Z_{ch} as a function of W_o are listed in table (1), where $E_A^{\pm\sigma}$ increases with W_o which ensures that the increasing of laser strength coupling enhanced the adatom positive ionization at Z_{ch} .

In figs.(4), the chemisorption energy and its contributions (the ionic and metallic curves are crossing at Z_{cr} . It is clear that for $Z > Z_{cr}$, the ground parts) are presented as a function of Z for different values of W_o . These contributions state is metallic while for $Z < Z_{cr}$, the ground state is ionic for $W_o = 0$ and $W_o \leq 0.04$ a.u..

As W_o increases, i.e. $W_o = 0.05$ a.u., fig.(4b) shows the effect of laser field on the system Na/W(111) which produces a double intersection, as illustrated. So one can conclude that the desorption of the adatom using laser field can occur along two paths,

1. The adatom is desorbed, along the ground state of the system, from the neutral state to the ionic state and then from the ionic one to the neutral one throughout double transitions, both are non-adiabatic. The later transition is an analogy to the neutralization process due to time-independent electric field [21,31].
2. The adatom is desorbed throughout one adiabatic transition along the metallic curve.

As W_o increases $W_o \geq 0.1$ a.u., we notice that the contributions are splitting and the ground state energy dominantly metallic. From which one can conclude that direct metallic desorption over "Schottky Saddle" may occur.

At the surface the occupation number and all the related chemisorption functions at $Z = 0$, are

listed in table (2), from which many important points are reported:

1. The solutions are all non-magnetic.
2. The values of $n_A^{+\sigma}(=n_A^{-\sigma})$ increase with W_o till $W_o = 0.08$ a.u.. As W_o increases it shows opposite behavior.
3. The value of $W_o = 0.08$ a.u. can be considered as a turning point to another type of chemisorption, for example molecular chemisorption.

The chemisorption energies and its contributions as a function of W_o , at $Z = 0$, are listed in table (3).

It is seen that as W_o increases the type of bond is changed from ionic bond to metallic one while $n_A^{\sigma} + n_A^{-\sigma} < 1$ for all values of W_o , i.e. the solutions are all non-magnetic.

It is well known that the Na atom adsorbed at W surface as positive ion with ionic bond [21] but by using laser field the Na atom also adsorbed as positive ion but with metallic bond. From this, one can conclude that the type of bond on the surface can be controlled by laser field. This is not contracted with the experimental role of using laser field for the desorption of atoms or ions from solid surfaces.

In figs.(5), an "adsorption potential well" is noticed for $W_o \geq 0.4$ a.u. at which the value of Z may considered as equilibrium distance or "the adsorption position", Z_{ad} . Table (4) reports the values of Z_{ad} and all the corresponding chemisorption functions as a function of $W_o \geq 0.4$ a.u.. At Z_{ad} , the solutions are also non-magnetic and all the notes that are above mentioned at $Z = 0$ are the same.

5.2 The Chemisorption of H on Cu(110)

The second system that is investigated in this chapter is H atom ($V_i = 13.6$ eV and $V_A = 0.74$ eV [29]) as it approaches the surface Cu(110) ($\phi = 4.48$ eV [30]). This system is of type $\phi \ll V_i$.

The screening length is fixed on $Z_o = 1.35 A^\circ$, this value represents the atomic radius of Cu

atom. The parameter β is fixed on 5 eV which also works in the limit of the wide band approximation to get the H/Cu(110) system's general features [33]. Equation (20) is used to calculate the energy level broadening function due to coupling interaction with surface, where α_C is given by

$$\alpha_C^{\pm\sigma} = \sqrt{2E_A^{\pm\sigma}} \quad (31)$$

The Δ_C^σ laser field parameters dependence is being throughout E_A^σ . So, $\Delta_C(Z)$ will be spin-dependent.

$$\Delta_C^\sigma(Z) = \Delta_{C_0}^\sigma e^{-2\alpha_C^\sigma Z} \quad (32)$$

where, $\Delta_{C_0}^\sigma = \Delta_{C_0}^{-\sigma}$, which is fixed on 0.05eV to get the well known general features[21]of the system in the absence of laser field.

The system general features in the presence of laser field will be presented in two figures only. Figs. (6) show our results for the occupation numbers $n_A^{\pm\sigma}$ as a function of the normal distance Z for different values of laser coupling strength W_o , while ω_L is fixed also on 0.112 a.u..

Three types of solutions can be recognized, which are well illustrated in fig. (6b). In region I, the solution is magnetic with $n_A^\sigma \neq n_A^{-\sigma}$ and $n_A^\sigma + n_A^{-\sigma} \approx 1$, where there is a net spin on the adatom large distance. In region II, $n_A^\sigma \neq n_A^{-\sigma}$ but $n_A^\sigma + n_A^{-\sigma} > 1$ where there is a net spin on the adatom. The adatom is a negative ion.

In the third region, the solution is non-magnetic one with $n_A^\sigma = n_A^{-\sigma}$ and $n_A^\sigma + n_A^{-\sigma} > 1$, where there is no net spin on the adatom. The adatom is a negative ion also. From this classification, one can conclude that the solution is mixed. It is neither magnetic nor non-magnetic. The above-mentioned Z_{ch} point increases with W_o . Figs. (6) ensure that by laser, the adatom negative ionization is enhanced.

In figs. (7), the chemisorption energy is only presented as a function of Z for different values of W_o , where the metallic part is nearly equal to the chemisorption energy for this system and the ionic part has very small

contribution even at small distance and high W_0 . The laser effect on the ground state potential energy surfaces is well illustrated in fig. (7b) where $W_0 = 0.07$ a.u.. Corresponding to the values of $n_A^{\pm\sigma}$ in fig. (6b), three types of potential energy surfaces can also be recognized. All the more interesting conclusions are listed in table (5) especially for the adatom charge state and the bond type which is metallic for all regions (I, II, and III) and for all values of W_0 .

6. CONCLUSION

1. Our theoretical treatment and the model calculation describe and explain precisely the dynamics of the chemisorption process in the presence of laser field throughout potential surfaces calculations.
2. One of the most interesting features in our treatment is introducing the level broadening due to the interference

The total chemisorption energies and their contributions at $Z=0$ as a function of W_0 are listed in table (6). It is well illustrated that for $W_0 > 0.04$ a.u., the metallic part decreases with W_0 increasing. From this, one can conclude that the interaction dynamics may be changed for $W_0 > 0.04$ a.u.. Finally, all the solutions for $W_0 > 0.1$ a.u. are not physical.

3. We note that our aim was to develop theoretical treatment for the chemisorption process illustrating all the reaction dynamics for the adsorption process, which we consider as a "basis treatment" for other related surface processes such as adatom desorption from solid surface.

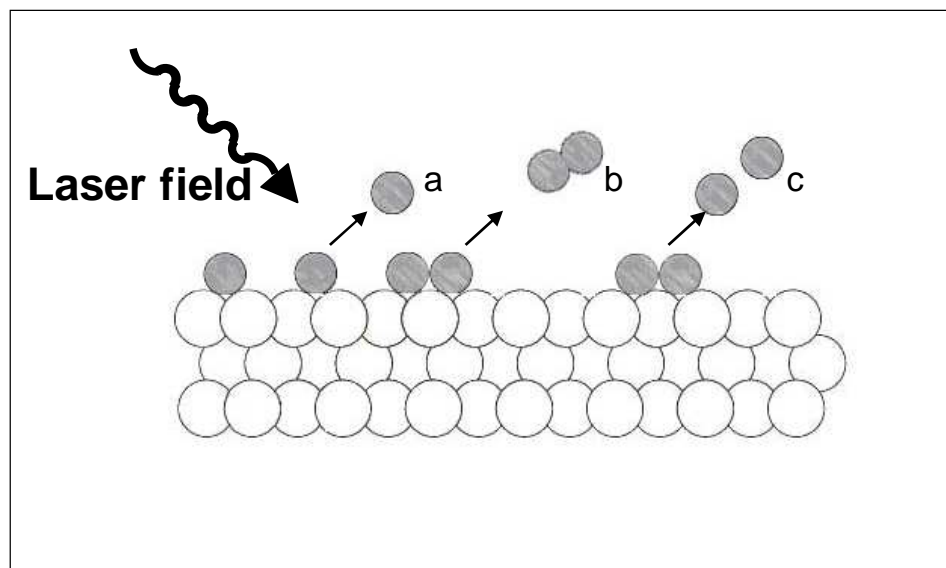
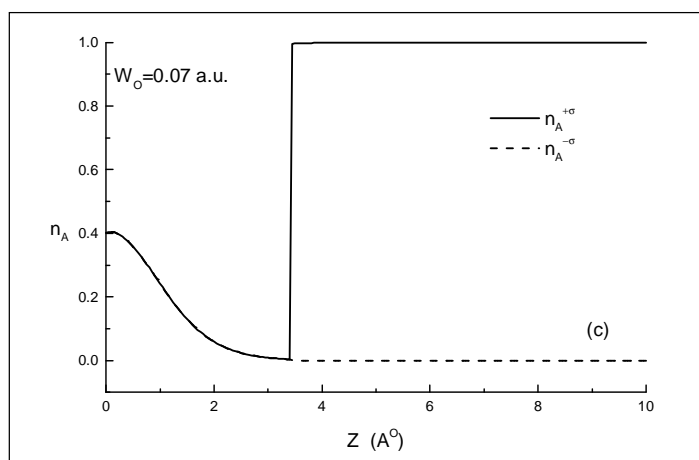
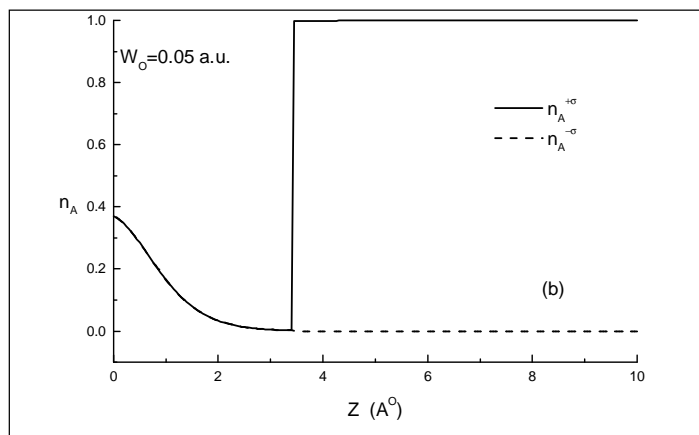
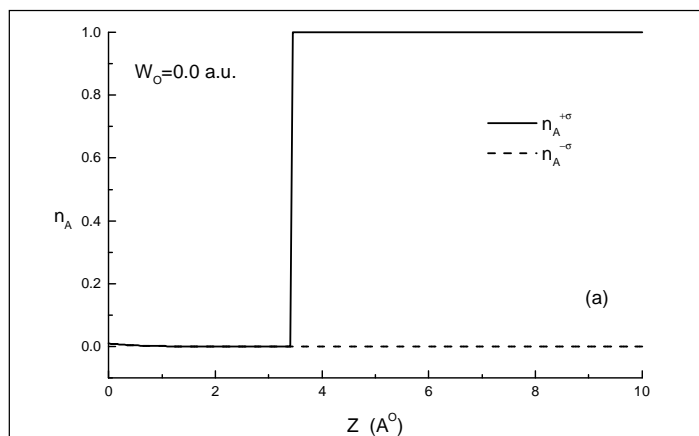
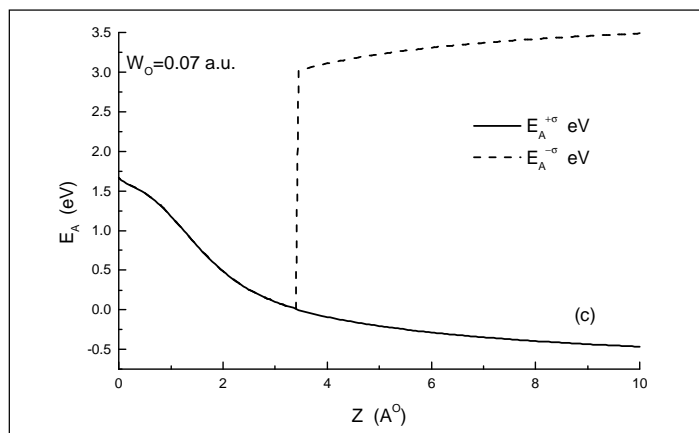
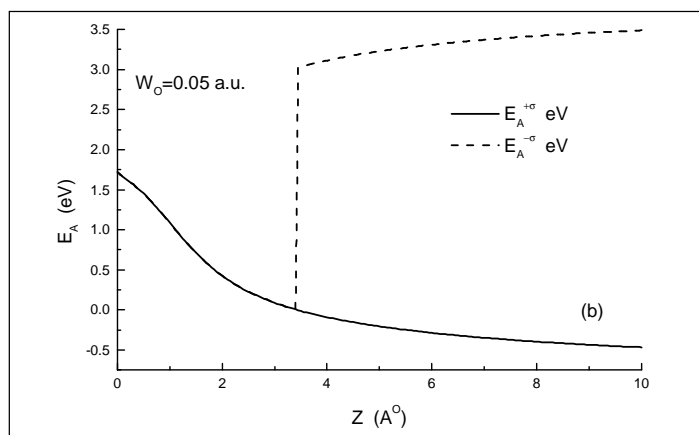
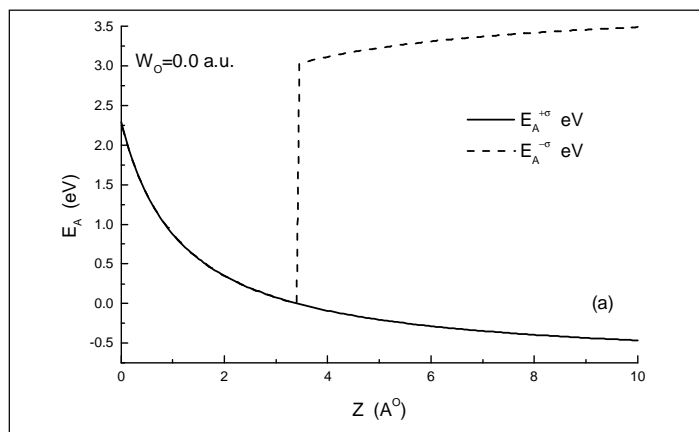


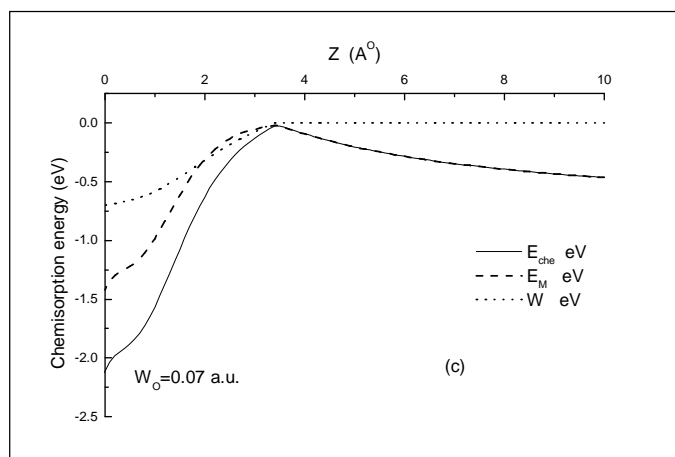
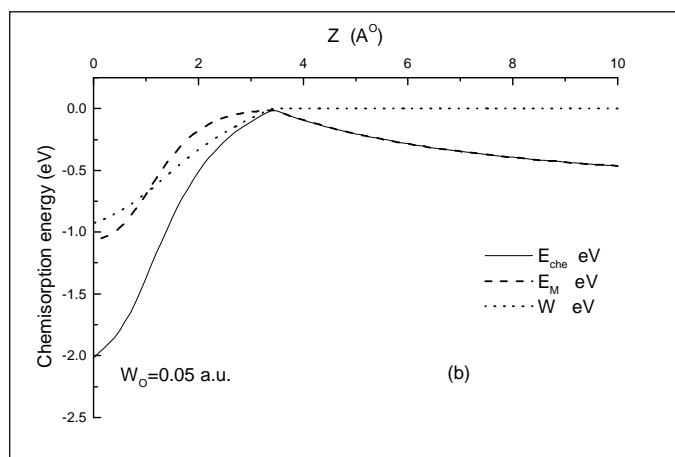
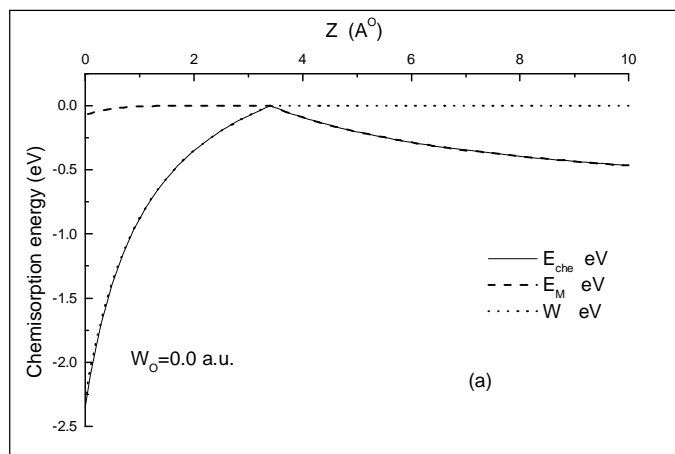
Fig.(1): The laser-stimulated surface processes. a) desorption of adsorbed atom. b) desorption of adsorbed molecule. c) desorption and dissociation of molecule.



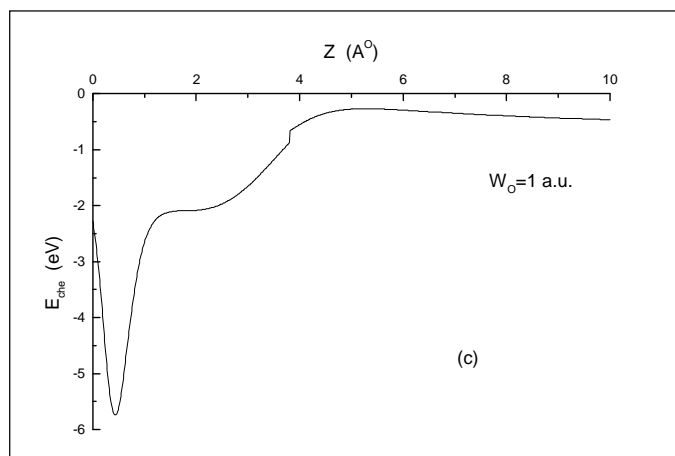
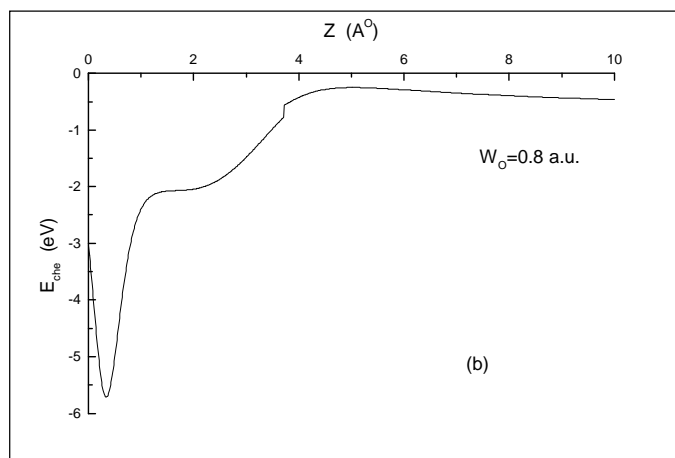
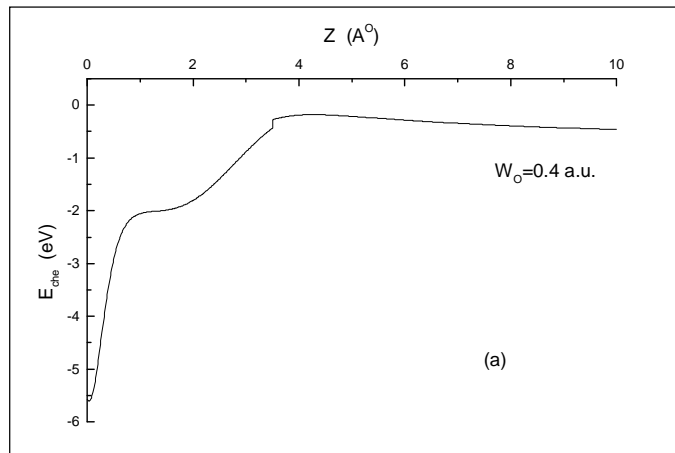
Figs.(2): The values of $n_A^{\pm\sigma}$ as a function of species-surface distance Z for different values of W_0 as indicated for the system Na / W(111).



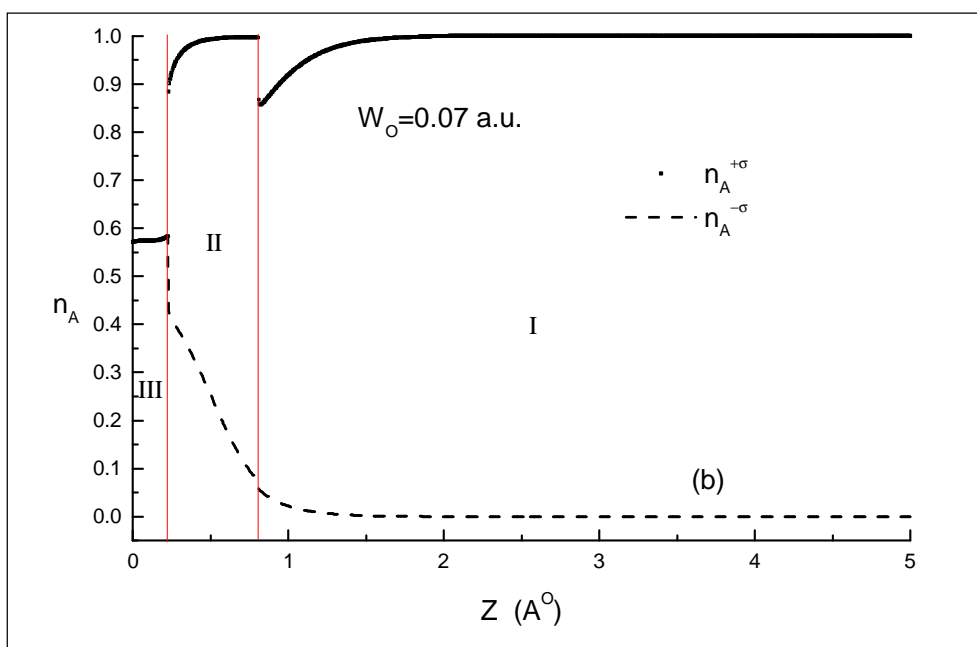
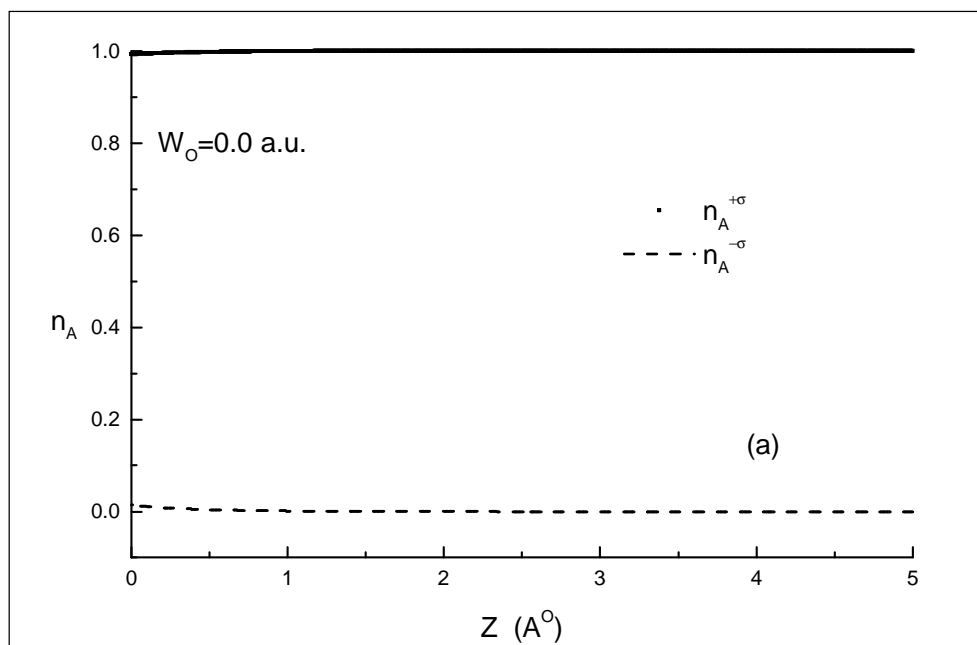
Figs.(3): The values of $E_A^{\pm\sigma}$ as a function of species-surface distance Z for different values of W_0 as indicated for the system Na / W(111).



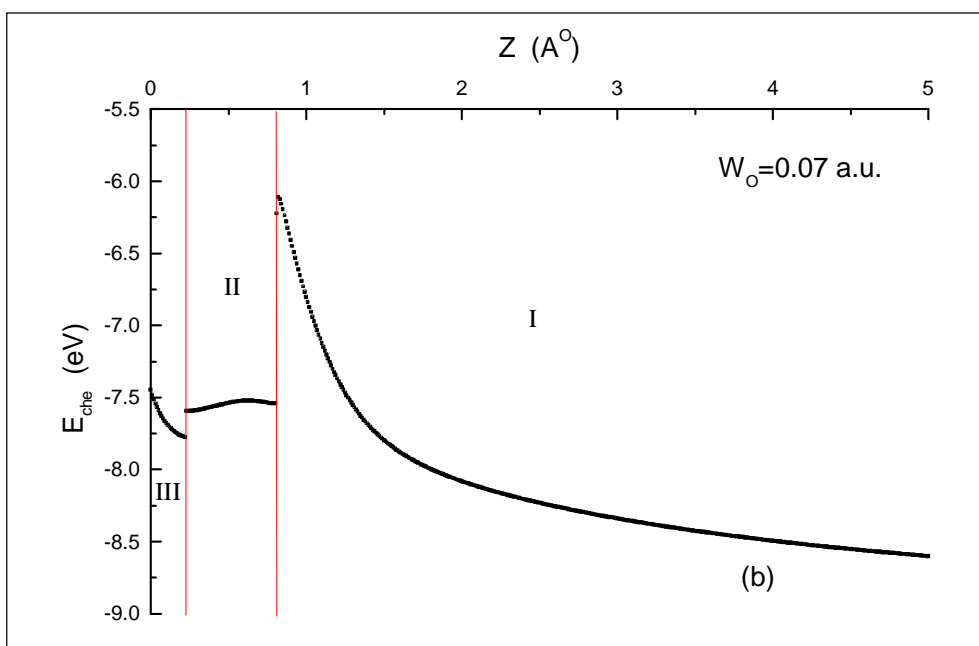
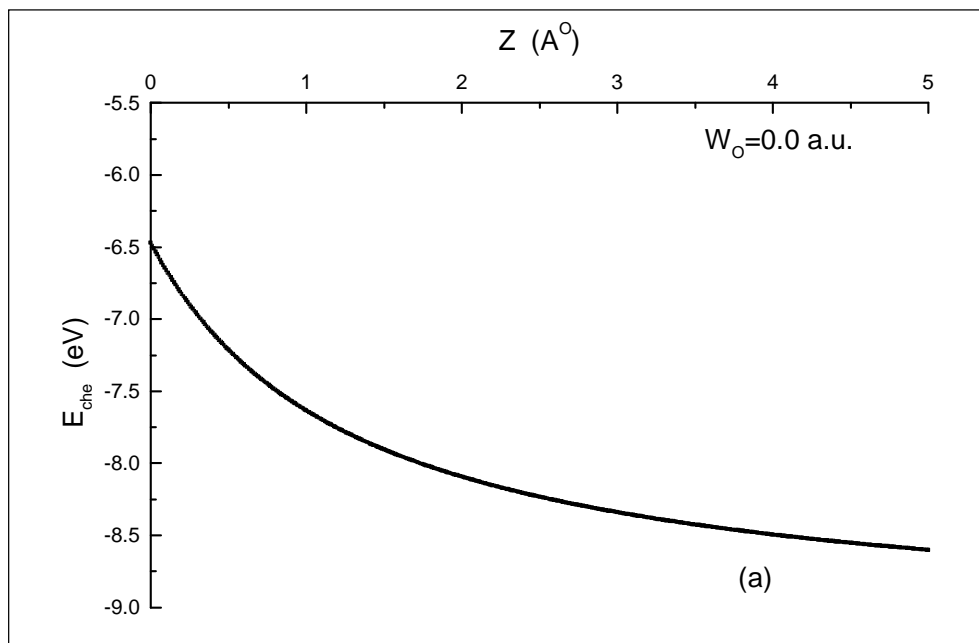
Figs.(4): The chemisorption energy and its contributions (the ionic and metallic parts) as a function of species-surface distance Z for different values of W_0 as indicated for the system Na/W(111).



Figs.(5): The chemisorption energy as a function of species-surface distance Z for different values of $W_0 \geq 0.4$ a.u. as indicated for the system Na / W(111).



Figs.(6): The occupation numbers $n_A^{\pm\sigma}$ as a function of the normal distance Z for different values of W_0 as indicated for the system H/Cu(110).



Figs.(7): The chemisorption energy as a function of Z for different values of W_0 as indicated for the system H/Cu(110).

Table (1): The variation of W_o with Z_{ch} and $E_A^{\pm\sigma}$ for the system Na / W(111).

W_o (a.u.)	Z_{ch} (A°)	$E_A^\sigma = E_A^{-\sigma}$ (eV)
0.0	3.400	3.267530×10^{-3}
0.01	3.400	3.413159×10^{-3}
0.02	3.400	3.879873×10^{-3}
0.03	3.405	4.098761×10^{-3}
0.04	3.405	5.358845×10^{-3}
0.05	3.405	7.172219×10^{-3}
0.06	3.405	9.547097×10^{-3}
0.07	3.405	1.245448×10^{-2}
0.08	3.410	1.487358×10^{-2}
0.09	3.410	1.869385×10^{-2}
0.1	3.410	2.294999×10^{-2}
0.2	3.430	7.807353×10^{-2}
0.3	3.465	1.435838×10^{-1}

Table (2): The occupation number and all the related chemisorption functions at $Z = 0$ for the system Na / W(111).

W_o (a.u.)	$n_A^\sigma = n_A^{-\sigma}$ ($Z = 0$)	$E_A^\sigma = E_A^{-\sigma}$ ($Z = 0$)eV	$\Delta_C^\sigma = \Delta_C^{-\sigma}$ ($Z = 0$)eV	$\Delta_L(Z = 0)$ eV
0.0	9.698127×10^{-3}	2.290710	0.076485	0.0
0.01	6.464267×10^{-2}	2.203446	0.076593	0.004846
0.02	1.736764×10^{-1}	2.030275	0.076671	0.019383
0.03	2.681024×10^{-1}	1.880305	0.076610	0.043612
0.04	3.313761×10^{-1}	1.779812	0.076512	0.077533
0.05	3.696941×10^{-1}	1.718955	0.076433	0.121145
0.06	3.912070×10^{-1}	1.684787	0.076382	0.174449
0.07	4.017258×10^{-1}	1.668081	0.076355	0.237444
0.08	4.050479×10^{-1}	1.662805	0.076347	0.310132
0.09	4.037439×10^{-1}	1.664876	0.076350	0.392510
0.1	3.996661×10^{-1}	1.671352	0.076361	0.484581
0.2	3.610853×10^{-1}	1.732628	0.076452	1.938322
0.3	3.371961×10^{-1}	1.770569	0.076501	4.361225

Table (3): The chemisorption energies and its contributions as a function of W_o , at $Z = 0$ for the system Na / W(111).

W_o (a.u.)	$E_M(Z=0)$ eV	$W(Z=0)$ eV	$E_{che}(Z=0)$ eV
0.0	-0.074218	-2.275791	-2.350009
0.01	-0.174004	-2.089644	-2.263648
0.02	-0.410105	-1.710739	-2.120844
0.03	-0.669236	-1.364838	-2.034074
0.04	-0.896374	-1.110094	-2.006468
0.05	-1.089538	-0.929675	-2.019213
0.06	-1.261456	-0.799461	-2.060917
0.07	-1.423710	-0.702329	-2.126038
0.08	-1.584032	-0.627498	-2.211530
0.09	-1.746939	-0.568250	-2.315189
0.1	-1.914693	-0.50292	-2.434985
0.2	-3.752287	-0.301717	-4.054003
0.3	-5.082188	-0.238802	-5.320989

Figs.(4): The chemisorption energy and its contributions (the ionic and metallic parts) as a function of species-surface distance Z for different values of W_o as indicated for the system Na / W(111).

W_o (a.u.)	$Z_{ad}(A^o) = \Delta Z_{oL}$	$n_A^\sigma = n_A^{-\sigma}$	$E_A^\sigma = E_A^{-\sigma}$ (eV)	$\Delta_C^\sigma = \Delta_C^{-\sigma}$ (eV)	Δ_L (eV)	$E_{che} = E_{ad}$ (eV)	The total screening length(A^o)
0.4	0.03	3.046270×10^{-1}	1.791906	0.069849	6.744530	-5.606458	1.1935
0.5	0.13	3.081133×10^{-1}	1.697418	0.051778	6.622061	-5.641807	1.2935
0.6	0.21	3.099684×10^{-1}	1.634015	0.041017	6.575561	-5.669867	1.3735
0.7	0.28	3.125171×10^{-1}	1.584720	0.033591	6.465192	-5.692857	1.4435
0.8	0.34	3.143523×10^{-1}	1.547055	0.028385	6.389961	-5.712194	1.5035
0.9	0.39	3.145860×10^{-1}	1.518433	0.024715	6.410825	-5.729450	1.5535
1	0.43	3.148850×10^{-1}	1.496696	0.022146	6.572302	-5.743783	1.5935

Table (5): Interesting conclusions are listed for the adatom charge state and the bond type for all regions (I, II, and III) and for all values of W_0 .

The regions	Normal Distance (A°)	The self-consistent solution	The adatom charge state	The dominant bond type
I	$Z \geq 0.81$	Magnetic $n_A^\sigma \gg n_A^{-\sigma}$, $n_A^\sigma + n_A^{-\sigma} \approx 1$	Atom	Metallic
II	$0.23 \leq Z \leq 0.80$	$n_A^\sigma > n_A^{-\sigma}$, $n_A^\sigma + n_A^{-\sigma} > 1$	Mixed unstable transition state (negative ion)	Metallic
III	$0 \leq Z \leq 0.22$	Non-magnetic $n_A^\sigma = n_A^{-\sigma}$, $n_A^\sigma + n_A^{-\sigma} > 1$	Negative ion	Metallic

Table (6): The total chemisorption energies and its contributions at $Z=0$ as a function of W_o for the system H / Cu(110) .

W_o (a.u.)	$E_M(Z=0)$ eV	$W(Z=0)$ eV	$E_{che}(Z=0)$ eV	E_B eV
0.0	-6.471672	-0.000017	-6.471672	2.6963
0.01	-6.788952	-0.004608	-6.793560	2.3790
0.02	-7.130810	-0.025063	-7.155872	2.0371
0.03	-7.507659	-0.042020	-7.549680	1.6603
0.04	-7.540740	-0.046152	-7.586892	1.6272
0.05	-7.526336	-0.047681	-7.574018	1.6416
0.06	-7.479390	-0.049097	-7.528487	1.6886
0.07	-7.398890	-0.050204	-7.449094	1.7691
0.08	-7.279461	-0.050857	-7.330318	1.8885
0.09	-7.115030	-0.051137	-7.166167	2.0529
0.1	-6.901184	-0.051123	-6.952307	2.2668

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المستخلص

لقد تم تطوير معالجة نظرية موسعة و نموذج حسابي لوصف التفاعل بوجود مجال كهرومغناطيسي احادي الطول الموجي (مجال الليزر) بين الجسيمات و سطح الصلب في عملية الالتصاق الكيميائي.

ان معالجتنا النظرية لعملية الاستطارة بوجود مجال الليزر و انموذج أندرسون المعروف للالتصاق الكيميائي الذري كانا الاساس لاشتقاق معالجتنا النظرية في حالة الالتصاق الكيميائي للجسيمات على سطح الصلب بوجود مجال الليزر.

تم حساب عدد الاشغال و طاقة الالتصاق الكيميائي كدالة للمسافة العمودية من السطح عند اقتراب الذرة الملتصقة من السطح و كذلك كدالة لمعاملات الليزر.

تم تطبيق أنموذجنا الحسابي للأنظمة (Na/W(111) و H/Cu(110) لاهميتها العملية و الاكاديمية. تم توضيح مظاهر مهمة تتعلق بحالة شحنة الذرة الملتصقة و حالة التأصر. من نتائجنا ، يمكن ان نستنتج انه يمكن استخدام مجال الليزر كأداة للتأين و هذه هي الحقيقة عمليا.