Studying the Effect of Laser Field on the Chemisorption Process for the System H / W (111)

دراسة تأثير مجال الليزر على عملية الالتصاق الكيميائي للنظام H / W (111)

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Abstract

In this paper , a study is presented for the effect of laser field on the chemisorption process for atom adsorbed on solid surface . The mathematical model is based on the Anderson model by using the mean field approximation (MFA) . The laser field characteristics (the frequency and the field strength) are incorporated in the treatment , since the frequency is added to the energy levels of the adsorbed atom and the effect of field strength is incorporated throughout the chemisorption functions. The model is applied to the system H / W (111), since the laser field characteristics effects are studied. The role of the AFM-parameter in the determination of weak and strong coupling types is investigated.

الملخص

في هذا البحث قدمت دراسة لتأثير مجال الليزر على عملية الالتصاق الكيميائي لذرة ملتصقة على سطح صلب . استند الأنموذج الرياضي في وصف عملية الالتصاق الكيميائي على أنموذج أندرسون باستخدام تقريب معدل – مجال MFA (Mean – Field Approximation) . تم إدخال مميزات الليزر (التردد وشدة المجال) إلى المعالجة ،إذ تم إضافة التردد إلى موقع المستوي الذري للذرة الملتصقة كما أدخل تأثير شدة المجال من خلال دوال الالتصاق الكيميائي. طبق هذا الأنموذج على النظام H/W(111) إذ درس تأثير مميزات المجال في تحديد حالتي الاقتران القوي والضعيف

1-Introduction

When the particles in gas phase approach to a surfaces , the collisions between them and the surfaces lead to adsorption which many be physisorption or chemisorption depending on the forces that are responsible for the adsorption process [1 – 5] . The adsorption rate depends on :-

1- The mass transition rate from the gas phase to the surfaces [6 – 9] .
2- The heat transition rate between the particle that approaches to the surfaces and the surfaces [10 – 14] .
3- The migration rate of the adsorbed particles to the adsorption sites [15 – 17] .

So , the full description of the adsorption kinetics considered the adatoms numbers variation with time as well as the relation between the adsorption rate, pressure and temperature .

Now , if laser field [18 – 19] is applied , its effect will be thermal or not thermal depending on the field frequency . The chemisorption or physisorption are enhanced by laser field in different ways such as ;

The dissociation of the interacting molecules on the surfaces or the atoms in the gas phase be in vibration excitation or the surfaces is heated . Many theoretical studies [20] were accomplished all of them make sure that the charge exchange processes between the atom or ion and solid surface

and the chemical bonding which combines the atom or the molecule with surfaces can be controlled by laser field (i.e. by its frequency and intensity) .
In the over mentioned references the laser field is considered as a tool to control all the kinetic and the dynamical processes that happen on the surfaces .

In our research , the effect of laser field on the chemisorption process for an adatom on metal surfaces will be studied theoretically .
The effect of laser field on the charge and spin types on the adatom as well as the chemisorption energy are calculated and investigated in detail .

2- The Mean – Field Approximation

Anderson model for studying the chemisorption of atoms on the surfaces gives the most accurate description for the adsorption type because it provides us with the detailed information about the distribution of charge and spin on the system . In many studies , in addition to the Anderson model , the mean field approximation MFA is also incorporated .
In this model calculation , the spin dependent effective hopping matrix elements V_{ak}^{σ} that appears in the MFA treatment of the charge transfer as an additional term in the Anderson Hamiltonian . This term is called the correlated hopping term and it coincides to the transfer of surface electron (with spin $\uparrow$) to the atom orbital when the atom orbital with (spin $\downarrow$) is occupied . This Hamiltonian is given by [1] .

$$H = \sum_{k\sigma} E_k \, n_k^{\sigma} + \sum_{\sigma} E_a^{\sigma} \, n_a^{\sigma} + \sum_{k\sigma} [V_{ak} \, C_{a\,\sigma}^{+} \, C_{k\sigma} + h.c] + U n_a^{\sigma} n_a^{-\sigma} - \sum_{k\sigma} [V_{aaak} \, n_a^{-\sigma} \, C_a^{\sigma+} \, C_k^{\sigma} + h.c] \qquad \ldots . (1)$$

$n_a^{\sigma} = (C_a^{+\sigma} \, C_{\,a}^{\,\sigma})$ represents the occupation number of the atomic states (E_a^{σ}) of the adatom and ($n_k^{\sigma} = C_k^{+\sigma} \, C_k^{\sigma}$) represents the occupation number of the band energy state .E_k is a set of quantum numbers , h.c. is the harmonic conjugate . The treatment of MFA to the fifth term in eq.(1) gives Anderson Hamiltonian with effective matrix elements that depends on the adatom orbital's occupation numbers [15] ,

$$V_{aaak} \cong \alpha \, V_{ak} \quad , \qquad 0 \le \alpha \le 1 \qquad \ldots . (2)$$

V_{ak} is the spin – independent matrix element in Anderson model which is given by

$$V_{ak} = \left\langle \, k \, \middle| \, V \, \middle| \, a \, \right\rangle \qquad \ldots . . (3)$$

V refers to the perturbation due to the interaction between the adatom and metal surfaces .
The factor α characterizes the intensity of electron scattering off the adatom charge which represents the ratio between the intensity of inelastic electron scattering processes off the adatom to the intensity of the inelastic scattering for the electrons that transfer between the adatom and the surfaces band energy and vice versa . So $\alpha \le 1$, which $\alpha = 1$ this means that the distance between the atom and surface is very large , which development of $\alpha = 0$ given Anderson model [1] .
It was confirmed that this approximation does not contradicted with the concepts of the chemisorption theory and found that it works relatively well .

3- The Mathematical model

According to Anderson model and by using MFA which includes the dependence of the hybridization process on the adatom states occupation numbers , the Hamiltonian is given by [15] :

$$H=\sum_{k,\sigma}E_k\, n_k^{\sigma}+\sum_{\sigma}E_a^{\sigma}n_a^{\sigma}+\sum_{k\sigma}(V_{ak}^{\sigma}C_{a\sigma}^{+}C_{k\sigma}+h.c)+Un_a^{\sigma}n_a^{-\sigma}-\sum_{\sigma}n_a^{\sigma}\lambda_a^{\sigma} \qquad \ldots.(4)$$

U represents the intra – atomic Coulomb repulsion on the adatom site , which far away from the surfaces is given by :

$$U=V_i-V_A \qquad \ldots.(5)$$

V_i and V_A are the ionization and the affinity levels of the adatom . V_{ak}^{σ} is the matrix elements of interaction for the adsorbed atom atomic levels $|a\rangle$ and the level $|k\rangle$ in the surfaces band energy , which according to MFA is given by [1] :

$$V_{ak}^{\sigma}=(1-\alpha n_a^{-\sigma})\,V_{ak} \qquad \ldots.(6)$$

V_{ak}^{σ} determines the amount of the charge transfer between the adatom and the surfaces which depends on the occupation number of the adatom with spin $(-\sigma)$.

3-1 The Model Calculation for the Occupation Number

According to Anderson model , the occupation number of the adatom atomic energy level with spin σ (without taking the surface temperature into consideration) can be calculated by using the following formula .

$$n_a^{\sigma}=\int_{u_o}^{E_F}\rho_a^{\sigma}(E)\,dE \qquad \ldots.(7)$$

u_o And E_F are the energy of the band bottom and Fermi energy level of the surfaces energy band respectively . $\rho_a^{\sigma}(E)$ is the local density of states of the adatom and is given by [1] .

$$\rho_a^{\sigma}(E)=\frac{1}{\pi}\,\frac{\Delta^{\sigma}(E)}{(E-E_a^{\sigma}-\Lambda^{\sigma}(E))^2+(\Delta^{\sigma}(E))^2} \qquad \ldots.(8)$$

The chemisorption functions (the broadening of the atomic level $\Delta^{\sigma}(E)$ and the quantum shift according to MFA are given by [15] :

$$\Delta^{\sigma}(E)=(1-\alpha n_a^{-\sigma})^2\sum_k\left|V_{ak}^{\sigma}\right|^2\delta(E-E_k) \qquad \ldots.(9)$$

$$\Lambda^{\sigma}(E)=\frac{1}{\pi}P\int dE'\frac{\Delta^{\sigma}(E')}{E-E'} \qquad \ldots.(10)$$

is the delta function refers to the principle part of the integral and $\delta(E-E_k)$

And the adatoms energy level with spin σ is written as [15] :

$$E_a^{\sigma} = E_a^{\infty} + \Delta E + U n_a^{-\sigma} - \lambda^{-\sigma} \qquad (11)$$

represents the atomic energy position far away from surfaces E_a^{∞} measured with respect to Fermi level .

$$E_a^{\infty} = \varphi - V_i \qquad \ldots. (12)$$

φ is the surface work function while ΔE is the image shift . $\lambda^{-\sigma}$ is defined as the shift in the atomic level position of spin σ (i.e. E_a^{σ}) when the coupling depends on the occupation number of the adatoms energy level , λ^{σ} is given by [15],

$$\lambda^{\sigma} = \frac{2\alpha}{1-\alpha n_a^{-\sigma}} \int_{uo}^{E_F} (E - E_a^{\sigma}) \rho_a^{\sigma}(E)\, dE \qquad \ldots. (13)$$

Which , we write it in the following form :

$$\lambda^{\sigma} = \frac{2\alpha}{1-\alpha n_a^{-\sigma}} \left[\int_{uo}^{E_F} E \rho_a^{\sigma}(E)\, dE - n_a^{\sigma} E_a^{\sigma} \right] \qquad \ldots. (14)$$

And by taking the laser field frequency ω into account , the atomic energy of the adatom can be written as ,

$$E_a^{\sigma} = E_a^{\infty} + \Delta E + U n_a^{-\sigma} - \lambda^{-\sigma} + \hbar\omega \qquad \ldots. (15)$$

The occupation number n_a^{σ} depends on the external laser field frequency throughout its dependence on the position of the atomic level E_a^{σ} is determined by the correlation effect and the coupling – occupation number dependence .

3-2 The Chemisorption Functions

The broadening function in the adatom's energy level , $\Delta^{\sigma}(E)$, is usually given by semielliptical form :-

$$\Delta^{\sigma}(E) = \frac{V_C^2}{\beta} (1 - \alpha n_a^{-\sigma})^2 \sqrt{1 - (\frac{E}{2\beta})^2} \quad if \quad |E| < 2\beta$$

$$= 0 \qquad \text{else where} \qquad \ldots. (16)$$

4β is the width of the surface band and Fermi level lies on $E = 0$, i.e. on the middle of the band . V_c is the coupling strength between the electronic level of the adatom and the surfaces in the absence of laser field . And by incorporating the strength of coupling due to laser field W_L [20] the last equation becomes :-

$$\Delta^{\sigma}(E) = \frac{(V_C + W_L)^2}{\beta} (1 - \alpha n_a^{-\sigma})^2 \sqrt{1 - (\frac{E}{2\beta})^2} \quad if \quad |E| < 2\beta$$

$$= 0 \qquad \text{else where} \qquad \ldots.. (17)$$

According , the quantum shift in the presence of laser field will be given by :-

$$\Lambda^{\sigma}(E) = \frac{(V_C + W_L)^2}{\beta}(1-\alpha n_a^{-\sigma})^2 \frac{E}{2\beta} \qquad if \quad |E| < 2\beta$$
$$= \frac{(V_C + W_L)^2}{\beta}(1-\alpha n_a^{-\sigma})^2 \left[\frac{E}{2\beta} + \sqrt{(\frac{E}{2\beta})^2 - 1}\right] \qquad if \quad E < -2\beta$$
$$= \frac{(V_C + W_L)^2}{\beta}(1-\alpha n_a^{-\sigma})^2 \left[\frac{E}{2\beta} - \sqrt{(\frac{E}{2\beta})^2 - 1}\right] \qquad if \; E > 2\beta \qquad \ldots. (18)$$

Finally , we must write the following ,

1- The laser field frequency is incorporating throughout the addition of the term $\hbar\omega$ to the adatom energy level .
2- The coupling strength in the presence of laser field is added to the coupling strength in the absence of laser field .

4- The Calculations and Conclusion

In this section, the mathematical model will be applied to the system H / W (111) , i.e. adsorption of hydrogen atom on tungsten surface . The hydrogen ionization level $V_i = 13.6\ eV$ and the affinity level $V_A = 0.75\ eV$, these energies are measured with respect to vacuum level . The surface work function , $\varphi = 4.36 eV$, $V_i > \varphi$ and $\beta = 5 eV$ is related to surface band width 4β , the value of β lies within the wide band values . The initial conditions are given by :-

$$n_a^{\sigma} = 1.0 \quad , \quad n_a^{-\sigma} = 0.0 \quad , \quad E_a^{\sigma} = \varphi - V_i \quad , \quad E_a^{-\sigma} = (\varphi - V_i) + U \quad \ldots. (19)$$

All the energies are calculated with respect to $E_F = 0$.

The parameter α is fixed at 0.2 and the surface temperature is not taken into account .

In order to get the adatom levels occupation numbers and corresponding energy levels , eqs.(7) , (14) , and (15) must be solved self - consistently . Notably , we choose the solution that minimizes the following energy :-

$$E_{\min} = \sum_{\sigma} E_a^{\sigma} n_a^{\sigma} + U n_a^{\sigma} n_a^{-\sigma} + \sum_{\sigma} \lambda^{\sigma} n_a^{-\sigma} \qquad \ldots. (20)$$

To calculate the image shift ΔE , the following formula is used [1] :-

$$\Delta E = \frac{3.6}{Z_{\circ}} \qquad \ldots.. (21)$$

$Z_{\circ}$ (in unit of A°) is the screening length and it can be used as adjustable parameter . $Z_{\circ}$ is taken to be 2.9 A° . The occupation numbers $n_a^{\pm\sigma}$ give important information about the chemisortion process properties for any type of atom adsorbed on solid surface . The occupation numbers are calculated as a function of the laser field characteristics $\hbar\omega = 1, 2, 3\ eV$ and W_L lies in the range 1-10eV with $\alpha = 0.2$, $V_C = 2 eV$ and $\beta = 5 eV$. The coupling types (in the case of laser field absence) are given by ,

1- weak coupling $V_C < \beta$
2- strong coupling $V_C > \beta$

While in case of laser field presence , we write the coupling types as ,

1- weak coupling $(V_C + W_L) \langle \beta$

2- strong coupling $(V_C + W_L) \rangle \beta$

Fig (1) represents our calculation for occupation numbers for all the over mentioned parameters . It is confirmed that the type of coupling is weak (for all $\hbar\omega$ values) for $1eV \le W_L \langle 5eV$ where $n_a^{\sigma} \rangle n_a^{-\sigma}$ i.e. the type of solution is magnetic . So the system spin states is determined by the value of W_L , not by the value of $\hbar\omega$. This does not contradict with many studies that were accomplished to study the external laser field on the scattering and adsorption processes [1] . The value of W_L which the solution is changed from magnetic to nonmagnetic , can be considered as the interface between the strong and the weak coupling . The values of the occupation numbers $n_a^{\sigma} = n_a^{-\sigma}$ are decreasing with increasing W_L and the increasing of the frequency shifts the state E_a^{σ} up and $E_a^{-\sigma}$ is shifted down far away from Fermi level . Fig (2) represents the virtual atomic energy levels , which confirm the correctness of the general physical features , for the same parameters that used in fig . (1) . The most important energy $\lambda^{\pm\sigma}$, which shifts the energy level $E_a^{\pm\sigma}$ down , is shown in fig . (3) as a function of laser strength for different values of frequency for the same over mentioned parameters .

The effective charge on the adatom can be calculated using the following relation [1] :-

$$Z_{eff} = |e|\,(n_a^{\sigma} + n_a^{-\sigma}) \qquad \ldots\ldots (22)$$

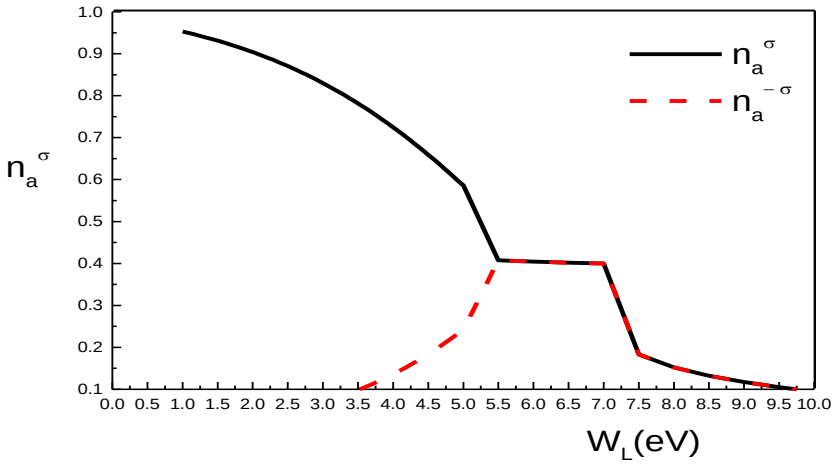
$|e|$ is the electron charge , and

The magnetic moment for the adatom is calculated using the following relation :-

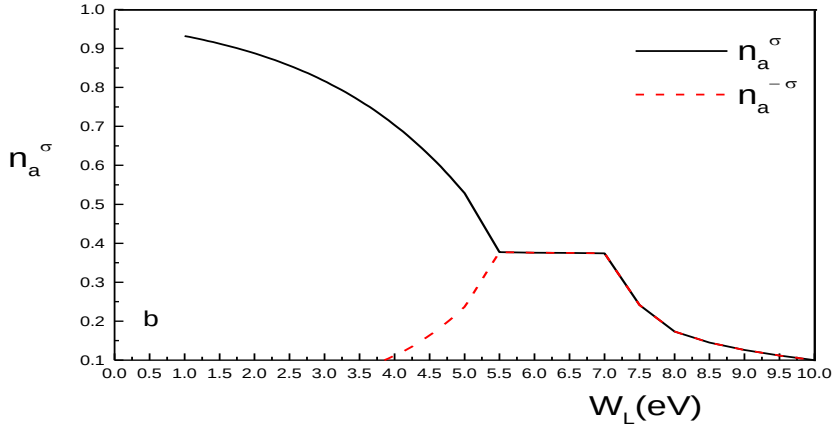
$$M = \mu_B\,(n_a^{\sigma} - n_a^{-\sigma}) \qquad \ldots (23)$$

The effective charge and the magnetic moment(in atomic unit) are shown in fig (4) which makes sure that the system magnetization type is determined only by laser strength . The value of $W_L = 5.5eV$ that characterizes the magnetic solution from the nonmagnetic one , is not determined by the value of W_L only but also by all the other parameters especially V_C and β in addition to the parameters that concern the type of the adatom and the surfaces as well as the parameter α

Finally , we conclude that the laser field characteristic (laser strength) is very important to control the charge and the magnetization on the species that approach to solid surface . Controlling the charge and the spin on nanostructures by laser field is one of the most interesting step in our future work .



a



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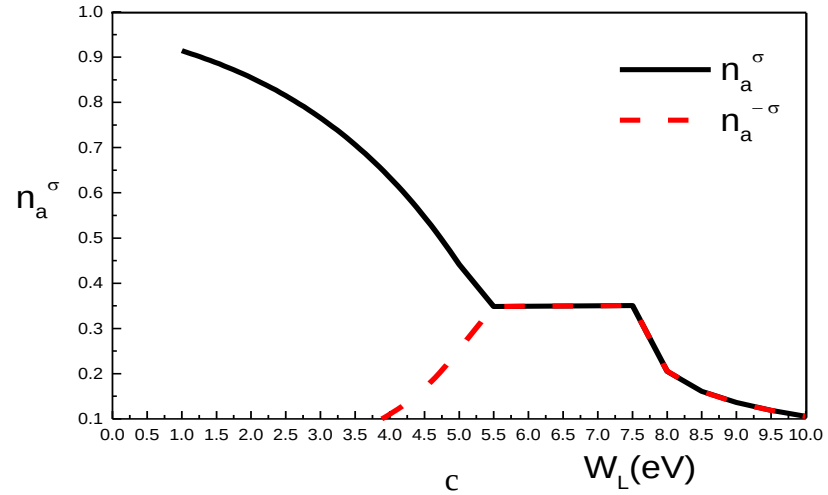

c

Fig. (1) : The occupation numbers as a function of laser field strength and frequency (a) $\hbar\omega = 1eV$ **, (b)** $\hbar\omega = 2eV$ **, (c)** $\hbar\omega = 3eV$.

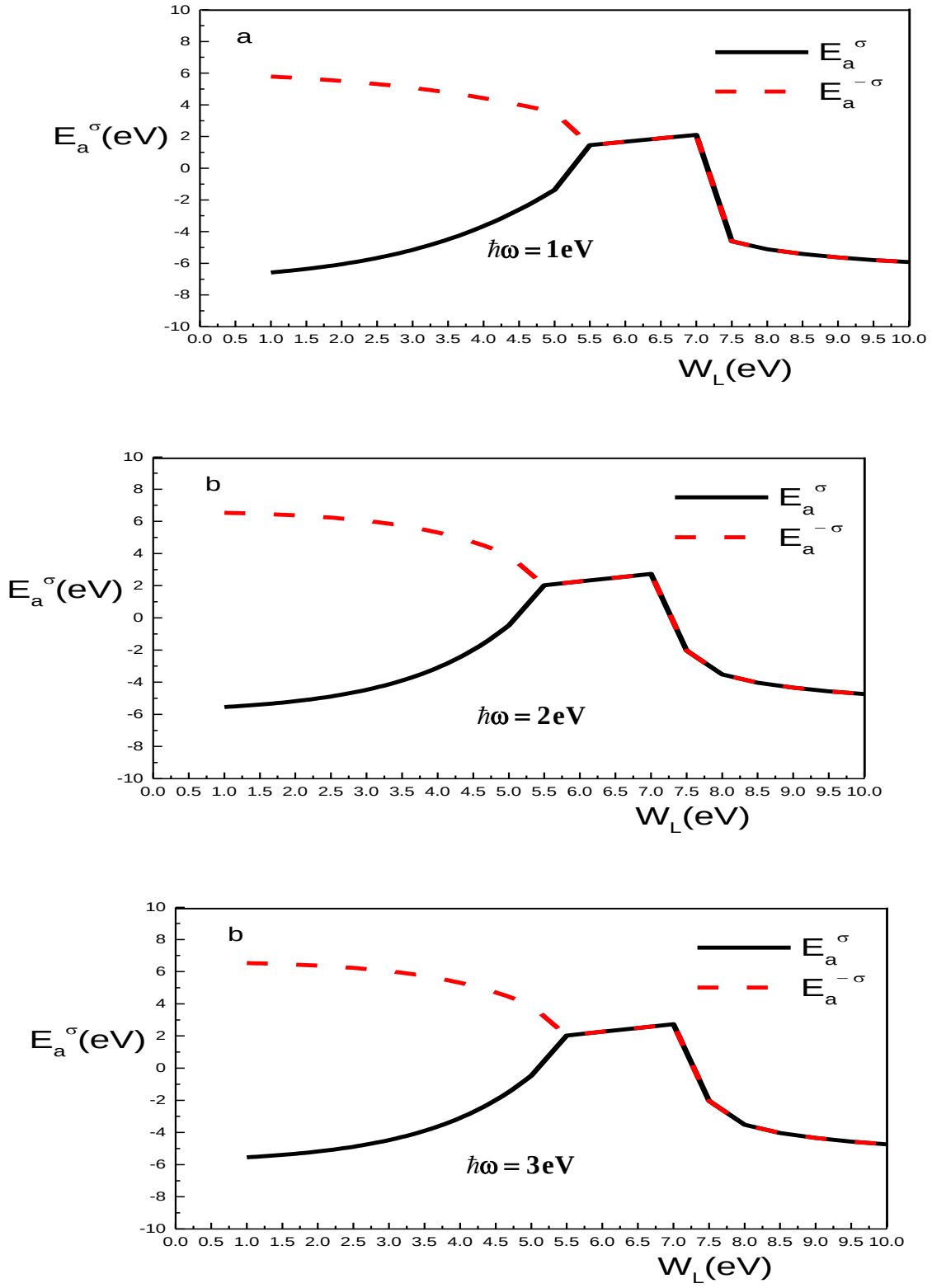

Fig. (2) : The adtom energy levels as a function of laser field strength and frequency (a) $\hbar\omega = 1eV$, (b) $\hbar\omega = 2eV$, (c) $\hbar\omega = 3eV$.

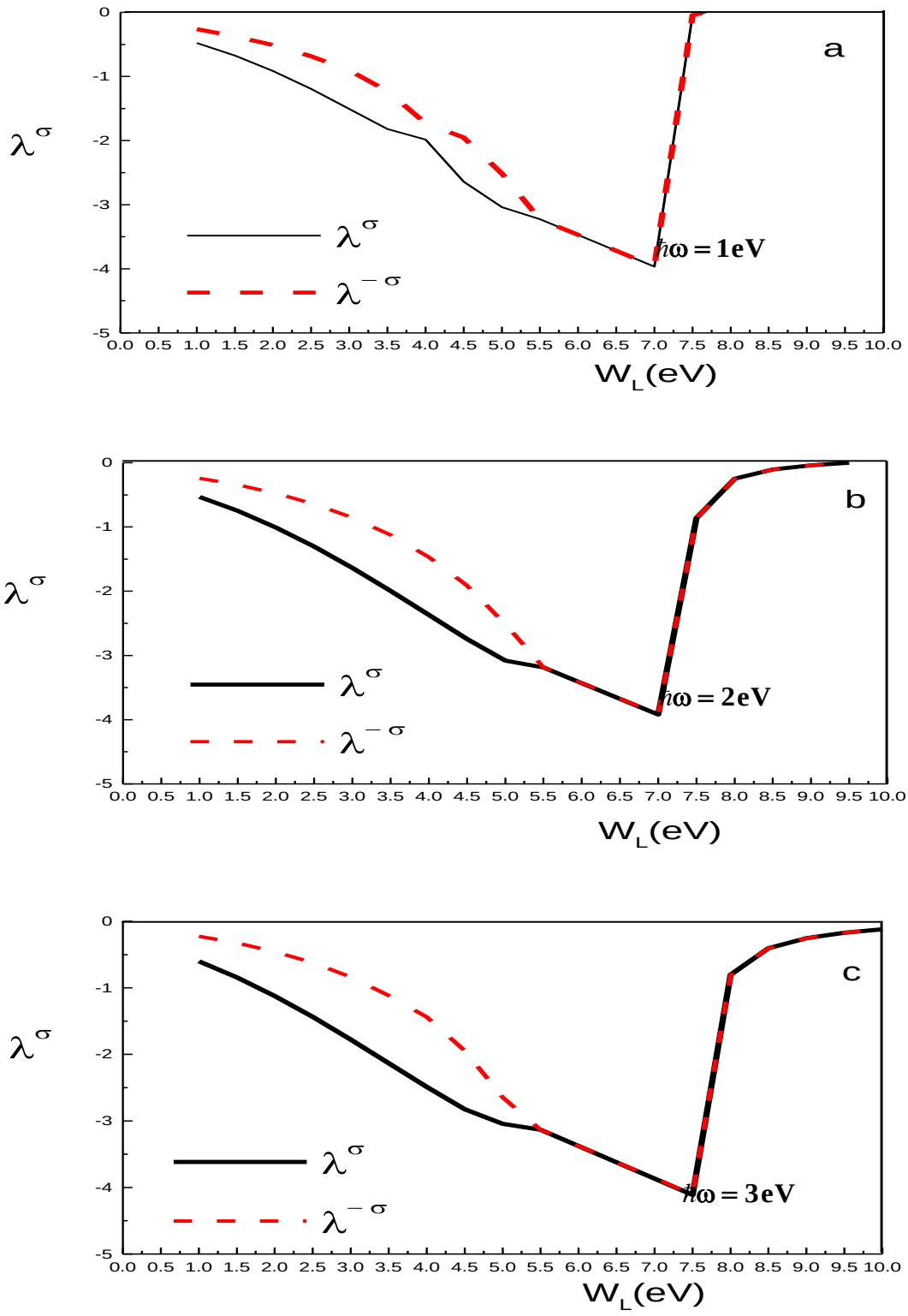

Fig. (3) : The energy $\lambda^{\pm\sigma}$ as a function of laser field strength and frequency (a) $\hbar\omega = 1eV$, (b) $\hbar\omega = 2eV$, (c) $\hbar\omega = 3eV$.

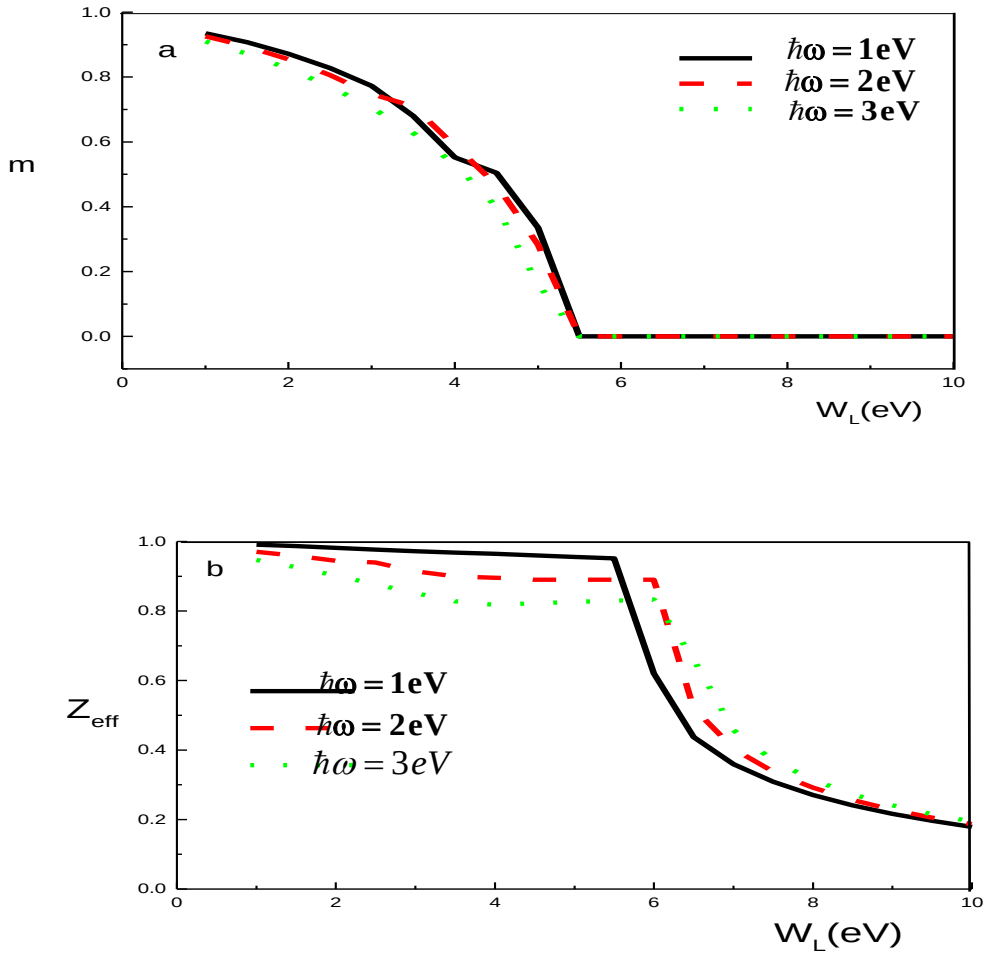

Fig. (4) : The magnetization (a) and the effective charge (b) on the adatom as a function of laser field strength and frequency $\hbar\omega = 1,2,3eV$

References

1- J. M. AL – Mukh , Ph . D . Thesis , University of Basrah , College of Science , Physics Department , Basrah , Iraq , (1997) .

2- R . Raymond Atta – Fynn , P . Biswas and D . A .Drobld , Physical Review B 69 , 245204 , (2004) .

3- Yu . Rudavskij , G . Ponedil Lok and M . Klapchuk , Ukr . J . Phys . Vol .50 , No .11 ,(2005)

4- J . L . Whitten and H . Yang , Surface Science Reports , 218 , 55-124,(1996) .

5- J . W . Gadzuk , Physical ReviewB , Vol . 10 , No. 12 (1974) .

6- T . L . Einsten , Physical Review B , Vol. 12 , No. 4 , (1975) .

7- J . G .Medvedev , Eur. Phys. J.B 17 , 189-200 (2000) .

8- D.W.Schranz , S.G.Davison , Journal of Molecular Structure , 501-502 , 465-477,(2000) .

9- D.W.Schranz , S.G.Davison , International Journal of Quantum Chemistry , Vol.67 , 377-397 (1998) .

10- Ganhua Liu , I. Matsuda , R. Hobara , and S. Hasegawa , Physical. Review Letters , PRL 96 , 036803 (2006) .

11- H.Ishida , Physical Review B ,Vol 38 , No.12, (1988) .

12- M.C.O.Aguiar , E . Miranda , V. Dobrosavljevic , E . Abrahams and G . Kotliar , Europhysico Letters , 67 (2) , pp. 226-232 (2004) .

13- G.Doyen and G.Erti , J . Chemical Physics 68 (12), (1978) .

14- B.Gumhalter and S.G.Davison , Physical Review B , Vol.30. No.6,(1984) .

15- R. D.Al-Kafaaji , M. Sc. Thesis , College of Education , Basrah University , Basrah , Iraq , (2006) .

16- Hai- Lung Dai and W. Ho , " Laser Spectroscopy and Photochemistry on Metal Surfaces " Part I and Part II , Advanced Series in Physical Chemistry ,World Scientific (1995) .

17- J. G . Medvedev , Surface Science 389 , 287-299, (1997) .

18- I.Q.Taha , J. M . AL Mukh and S.I. Easa , Journal of Basrah Researches (Sciences) ,Vol . 35 , No .6 , (2009) .

19- I .Q . Taha , J. M . AL Mukh and S.I. Easa , Journal of Basrah Researches (Sciences) , Vol . 36 , No . 4, (2010) .

20- I.Q. Taha , Ph . D . Thesis , University of Basrah, Basrah , Iraq (2008) .