

Composite Anderson–Newns model and density of states due to chemisorption: Quasi-chemical approximation

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Abstract. In this paper a variation in density of states (DOS) of the substrate due to chemisorption of hydrogen on transition metals using composite Anderson–Newns model has been investigated for different coverages in quasi-chemical approximation of Fowler and Guggenheim, which in the limit $z \rightarrow \infty$ gives the Bragg–Williams approximation as a special case. Variation in density of states has been studied for one-dimensional periodic substrate with change in adatom interaction energy and coverage. With increase in coverage, the bonding and antibonding (B–AB) peaks are found to shift towards higher energies and at the same time relative height of the peaks also increases. The interesting feature to observe is that both approximations for a particular coverage, give split-off states with different height for both (B–AB) peaks. It particularly indicates change in B–AB states, representing amount of chemisorption, with the change in interaction energy between adatoms. At the same time bond strength is also found to decrease with interaction between adatoms.

Keywords. Chemisorption; density of states; quasi-chemical approximation and coverage.

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1. Introduction

One of the most interesting problems in solid state physics is chemisorption of gases on surfaces of metals. This has deepened our understanding of various processes taking place on the surface like corrosion, hydrolysis and catalysis. At present, chemisorption theories can be divided into two groups: semi-empirical model Hamiltonian theories and first principal methods. A good progress has been made in ab initio calculations using density functional theory and its local approximation, cluster calculations or coherent potential approximation. These methods allow us to carry high precision calculations of space distribution of electric charge, binding energy, work function changes and other experimental characteristics of adsorbate-adsorbant system, but, there are numerous difficulties with these methods when many body effects and correlations in electronic and ionic component of adsorbate are considered. On the other hand, the model Hamiltonian method appears to be well suited for understanding the experimentally observed features due to relatively simple microscopic picture of the system and possibility of including correlation effects and additional interactions in the adsorbed system by using different approximations [1, 2]. Furthermore equation of motion method can be useful, especially when one is trying to include the correlation effects [1]. In the model Hamiltonian method, the major step was taken

by Newns [3] which was improved further by many workers [1]. They adapted the Anderson model–Hamiltonian for magnetic alloys, to treat the chemisorbed atom as an impurity on the surface and then solved the problem within the self-consistent Hartree–Fock scheme. A more generalized version of Anderson–Newns model called composite Anderson–Ising model, was proposed by Gavrilenko [5] in which an attempt has been made to incorporate the Coulomb correlations and interactions in the adsorbed system. This model was applied to the case of stochastic arrangement of adatoms on metal surface by Gavrilenko [6] and it was shown that the Anderson criterion for impurity magnetism in metals holds for this type of phase-transition as well. Later, using this model, characteristics of chemisorption were further investigated by Cardena [2]. Calculations were carried out within the framework of Hartree–Fock approximation for electronic component of adsorbate and using Bragg–Williams approximation for ionic component. Anderson–Newns model requires proper parameterization to take into account all the correlation effects [7]. The composite Anderson–Newns model is a step in that direction but restricting to the most simple Bragg–Williams approximation (BWA) to include correlation among adatoms on the surface.

In this paper we improve upon the situation by introducing correlators in the quasi-chemical approximation (QCA). This approximation was first proposed by Guggenheim and Fowler [8] in the context of chemisorption problem, by introducing an interaction energy term $c = [1 - 4\theta(1 - \theta)(1 - \exp(-2W/ZKT))]$, where θ is coverage and KT is the thermal energy, subject to the restriction that the interaction term $-W/KT \geq 2$, a critical value below which desorption starts. They pointed out that the BWA is too crude an approximation as the value of critical temperature (T_c) for the phase-transition during chemisorption is found to be very much off its correct value. On the other hand, QCA takes care of long- as well as short-range interactions, which improves the situation and brings T_c closer to the correct value. It is interesting to note that in the limit $Z \rightarrow \infty$, QCA gives the same results as the BWA. But, since Z cannot be equal to infinity, the BWA is not a realistic approximation and thus QCA is supposed to give better results [8]. Therefore, it will be more appropriate to apply QCA to study the chemisorption characteristics within the composite Anderson model. However, no systematic attempt has been made so far to analyze the chemisorption behaviour as a function of the interaction between adatoms within the framework of the above mentioned QCA.

In this paper we have studied the change in density of states (DOS) on chemisorption of hydrogen on transition metals using this composite Anderson–Newns model [5] using QCA. We solve this model self-consistently within the Hartree–Fock scheme. Later, we take the specific form of weighted density of states (WDOS) for atop case, to be a semi-elliptical one which has been used by most of the workers [2, 3, 6] to make the problem analytically tractable. The possibility of other (triangular) weighted DOS has been discussed by authors in a recent paper [9]. Our aim is to study chemisorption behaviour as a function of the coverage using the semi-elliptical WDOS in QCA.

In §2 we discuss the general formalism and its assumptions. In §3 we define the quasi-chemical correlators to derive a basic expression for the DOS. Later, we choose specific form of WDOS to perform numerical calculations. Finally, in §4, we discuss the numerical results obtained followed by the conclusions.

2. Basic equations and formalism

We consider a system of N_A adsorbed hydrogen-like atoms (adatoms) distributed over N -active centres (adsorption centres) on the metal surface (substrate), $N_A \leq N$. Each atom has a rigid bond with substrate. The configuration of the adatom arrangement over the adsorption centres is not fixed. In the simplest case, Hamiltonian of this system can be written [5, 9] in the form

$$H = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\alpha} N_{\alpha} \left[\sum_{\sigma} E n_{\alpha\sigma} + U n_{\alpha\uparrow} n_{\alpha\downarrow} + \sum_{k,\sigma} (V_{\alpha k} b_{\alpha\sigma}^{\dagger} a_{k\sigma} + \text{h.c.}) \right]. \quad (1)$$

Here, the sum over α in (1) is over all the adsorption centres, the operator $N_{\alpha} = C_{\alpha}^{\dagger} C_{\alpha}$ has eigen values 0 or 1. $C_{\alpha}^{\dagger}, C_{\alpha}$ are the Fermi amplitude of the creation and annihilation operators of adsorption centre α , ε_k is the energy spectrum of clean substrate, E is the ionization potential of adatom. $n_{k\sigma} = a_{k\sigma}^{\dagger} a_{k\sigma}$, $n_{\alpha\sigma} = b_{\alpha\sigma}^{\dagger} b_{\alpha\sigma}$, where $a_{k\sigma}, b_{\alpha\sigma}$ are the electron variables for substrate electrons and adatoms electrons, respectively. U describes the Coulomb interaction of atomic electrons and h.c. means Hermitian conjugate.

Here, the difference from usual form is because of the hopping interactions term proportional to $V_{\alpha k} (V_{k\alpha})$ which takes into account the indirect interactions between the adatoms. Although this model is linear with respect to ion operator N_{α} , it is not equivalent to ideal lattice model due to these interactions. To solve this model, we take only one localized impurity atom, consequently $N_{\alpha} = 1$ if $\alpha = A$ and $N_{\alpha} = 0$ if $\alpha \neq A$. Using unrestricted Hartree-Fock approximation which considers the averaged interactions of all the adatoms and the substrate, the Hamiltonian reduces to a form which can be easily solved [9]. The electronic properties of the system are described by correlators of type $\langle n_{\alpha\sigma} \rangle, \langle N_{\alpha} n_{\alpha\sigma} \rangle, \langle N_{\alpha} b_{\alpha\sigma}^{\dagger} a_{k\sigma} \rangle, \dots$, whereas ionic properties are described by correlators of Ising type i.e., $\langle N_{\alpha} \rangle, \langle N_{\alpha} N_{\beta} \rangle, \dots, \langle N_{\alpha} N_{\beta} \dots N_{\delta} \rangle, \dots$.

To derive the properties of the system, we shall use double-time Green's functions which are derived by equation of motion method. All the related electronic properties of system, can be calculated from these Green's function equations [9]. We shall discuss the state of the system at a temperature restricted to where $-W/KT \geq 2$, below which, desorption occurs [8].

3. Quasi-chemical approximation and correlators

To obtain the electronic properties of the system, in final form, Gavrilenko used the BWA which assumes the distribution of spins as random and consider interactions only between nearest neighbours. In BWA

$$\begin{aligned} \langle N_{\alpha} N_{\beta} \rangle &\simeq \Delta_{\alpha\beta} \langle N_{\alpha} \rangle + (1 - \Delta_{\alpha\beta}) \langle N_{\alpha} \rangle \langle N_{\beta} \rangle \\ &= \Delta_{\alpha\beta} \theta(1 - \theta) + \theta^2 = \theta [\Delta_{\alpha\beta} (1 - \theta) + \theta]. \end{aligned} \quad (2)$$

Here $N_{\alpha}^2 = N_{\alpha}$ is used. This approximation gives simpler formulae. The second approximation which can be used to approximate the correlator is, the QCA of Fowler and Guggenheim [8]. Using this approximation correlator $\langle N_{\alpha} N_{\beta} \rangle$ is

approximated as

$$\begin{aligned} \langle N_\alpha N_\beta \rangle &\simeq \left(\Delta_{\alpha\beta} \frac{2\theta}{C+1} (1-\theta) + \Delta_{\alpha\beta} \theta \left(1 - \frac{2}{C+1} \right) + \frac{2\theta^2}{C+1} \right) \\ &= \theta \left(\Delta_{\alpha\beta} \left(1 - \frac{2\theta}{C+1} \right) + \frac{2\theta}{C+1} \right) \end{aligned} \quad (3)$$

where

$$c = \left(1 - 4(1-\theta) \left(1 - \exp \left(-\frac{2W}{ZKT} \right) \right) \right)^{1/2}. \quad (4)$$

Here Z is the number of nearest neighbors of an atom (coordination number) and exponential factor ($e^{-2W/ZKT}$) takes care of both (short as well as long range) interactions between adatoms. It may be noted that in the limit $Z \rightarrow \infty$, QCA (eq. (3)) reduces to (2) of BWA. Of the two approximations, the QCA is certainly better [10] as it gives the exact solution in the (artificial) one-dimensional case which BWA does not, moreover it also gives the temperature dependence of chemisorption characteristics. The QCA is exact in one-dimension not only for nearest neighbor systems but also for arbitrarily higher neighbor systems [10]. We shall study the situation at and below a critical temperature above which the desorption starts. In the QCA, the function $Q_q(\omega)$ has the form

$$Q_q^{\text{QC}}(\omega) = \left(1 - \frac{2\theta}{C+1} \right) L(\omega) + \frac{2\theta}{C+1} P_q(\omega) \quad (5)$$

where $L(\omega)$ is the Newns function and $P_q(\omega)$ is the q -representation of Grimley's function [9]. For single site, Green's function ($\alpha = \beta$) describing the charge distribution on impurity level becomes

$$G_{\alpha,\sigma}(\omega) = \frac{i}{2\pi} \left(\frac{a}{2\pi} \right)^d \int \frac{dq}{\left(\omega - E_\sigma + \varepsilon_F - \left(1 - \frac{2\theta}{C+1} \right) L(\omega) - \frac{2\theta}{C+1} P_q(\omega) \right)}. \quad (6)$$

To derive (6), we have used approximations described by (3) and (5). Now, as $\theta \rightarrow 0$ and $z \rightarrow \infty$ (6) gives us Newns theory [3], and as $\theta \rightarrow 1$, $z \rightarrow \infty$ it gives solvable limit of Grimley's model. Equation (6) is also solvable for all intermediate values of θ . The interesting feature of the composite Anderson model is that it takes care of both the cases as well as the intermediate values of the coverage. The density of states (DOS) of this system using (6) and the assumptions [6] involved, can be written in the form

$$D_\sigma(\omega) = \frac{1}{\theta} \left(\frac{a}{2\pi} \right)^d \text{Im} \int \frac{d\omega}{\left(\omega - E_\sigma + \varepsilon_F - \left(1 - \frac{2\theta}{C+1} \right) L(\omega) - \frac{2\theta}{C+1} P_q(\omega) \right)} \Bigg|_{\omega - i0} \quad (7)$$

In our calculations we take one-dimensional model of periodically arranged atoms with lattice constant $a = 1$ interacting only with its nearest neighbours and using periodic boundary conditions. Here, we have taken the energy spectrum $\delta_K = \Gamma \cos(K)$

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with respect to the centre of the band. We are also taking one chemisorption centre per site. For this case after some simplifications (7) can be written as

$$D_{\sigma}(\omega) = \frac{1}{\pi} \left(\frac{a}{2\pi} \right)^d \times \int_{-\pi/a}^{\pi/a} \frac{\left(1 - \frac{2\theta}{C+1}\right) \Delta(\omega) dq}{\left(\left(\omega - E_{\sigma} + \varepsilon_F - \left(1 - \frac{2\theta}{C+1}\right) \gamma(\omega) - \frac{(2\theta/C+1)\beta^2}{\omega - \varepsilon_q + \varepsilon_F}\right)^2 + \left(1 - \frac{2\theta}{C+1}\right)^2 \Delta(\omega)^2\right)}, \quad (8)$$

where $\gamma(\omega) + i\Delta(\omega) = L(\omega - i\theta)$; $\Delta(\omega) = \pi\beta^2 \bar{\rho}(\omega + \varepsilon_F)$ is the weighted DOS states and $\gamma(\omega)$ is the Hilbert transform of $\Delta(\omega)$ -function and is given by

$$\gamma(\omega) = \int \frac{\Delta(\omega)}{(\omega - y)} dy, \quad \text{where } -\pi \leq \arctg \leq \pi. \quad (9)$$

The functions $\Delta(\omega)$ and $\gamma(\omega)$ are called chemisorption functions, latter being the Hilbert transform of the former. These are related to each other through $G_{\alpha,\sigma}(\omega) = \gamma(\omega) + i\Delta(\omega)$. Here we have chosen the semi-elliptical form of WDOS given by

$$\Delta(\omega) = \text{Im}[G(\omega)] = \begin{cases} \beta^2(1 - \omega^2)^{1/2} & \text{for } |\omega| < 1 \text{ and} \\ 0 & \text{for } |\omega| > 1. \end{cases} \quad (10)$$

The Hilbert transform of $\Delta(\omega)$ is

$$\gamma(\omega) = \text{Re}[G_{\alpha,\sigma}(\omega)] = \beta^2 \omega. \quad (11)$$

4. Numerical results and conclusions

In order to have numerical values of DOS of substrate on chemisorption of hydrogen on the transition metals using composite Anderson–Newns model, the basic input parameters are: ionization level E , the electron affinity level $E + U$, where U is the Coulomb interaction between electrons on impurity level; $\varepsilon_F^0 =$ Fermi level, $\beta =$ hybridization parameter and $2\Gamma = (\varepsilon_1 - \varepsilon_0)$ is the band width of the unperturbed system. $\varepsilon_1, \varepsilon_0$ are the upper and lower edges of the band respectively. There are three situations corresponding to different positions of ionization and affinity level with respect to Fermi level parameterized by $\cap = E - \varepsilon_F + U/2$. We shall concentrate on the case $\cap = 0$ corresponding to symmetric Anderson’s model. Here all the parameters are chosen within the Anderson’s model [11], and all energies are measured in terms of half band-width (Γ), and the position of energy levels is with respect to substrate band centre, also $\varepsilon_F^0 = 0$. In the present case we take $Z = 6$, which is also the most suitable choice for Z in two-dimensional case [8].

Now, if U/β is small, we have non-magnetic case. In this paper, we shall restrict the interaction term ($-W/KT$) to values beyond the critical one i.e. 2, and thus avoid the possibility of desorption [8].

The interesting features of the results (associated with QCA) obtained are as follows:

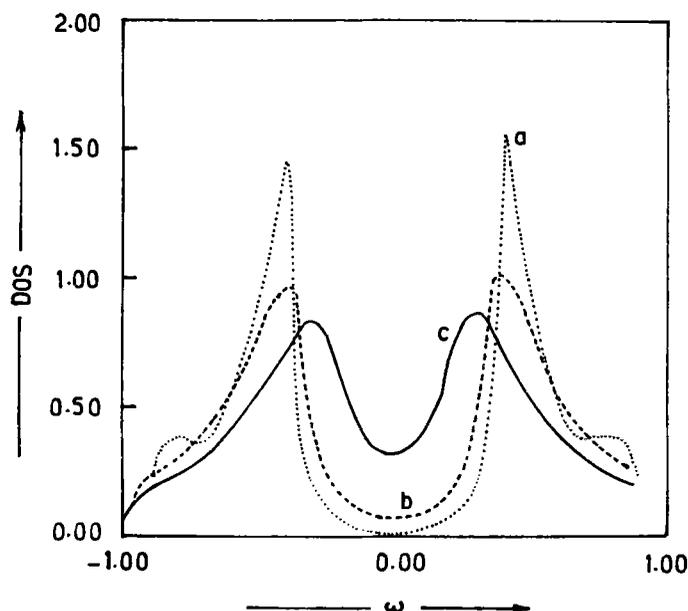


Figure 1. Comparison of DOS on chemisorption using curve (a) Bragg–Williams approximation and curves (b), (c) quasi-chemical approximation, with two different values of interaction energy term $-W/KT = 2$ and 8 , respectively for high coverage, $\theta = 0.8$.

4.1 Comparison of the values of DOS using Bragg–Williams and quasi-chemical approximation for fixed coverages

The DOS corresponding, respectively, to high ($\theta = 0.8$) and low ($\theta = 0.2$) coverages are presented in figures 1 and 2 in both the approximations, curve (a) represents the BWA and curves (b) and (c) correspond to QCA. The latter shows a decrease in depth between B–AB peaks as compared to that for curve (a), implying, the effect of interaction energy term in both the cases is to cause decrease in bond strength. Furthermore, the BWA is an approximation at 0 K , whereas the QCA corresponds to some finite temperature within the restriction as mentioned above. This implies that with rise in temperature there is decrease in adatom–substrate bond–strength. As expected, it provides activation energy for desorption in form of vibrational energy [12].

4.2 Effect of coverage on bond strength and number of B–AB states

The curves (a), (b) and (c) in figure 3 show variation of DOS for $\theta = 0.001, 0.2$, and 0.8 respectively, using the QCA by keeping the interaction term constant i.e. $-W/KT = 2$. Once again we get the split-off states (B–AB peaks) similar to that obtained using the BWA. There appears to be a critical value of the coverage beyond which the split-off states between B–AB appear. The splitting is found to increase with the increase in θ . It indicates an increase in bond strength with the coverage. At the same time, the depth between the B–AB peaks also gets enhanced, thereby implying an increase in the bond

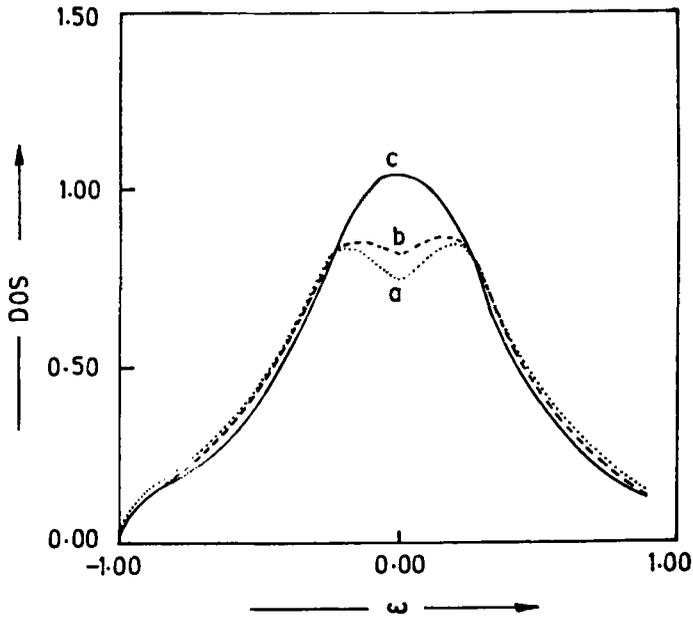


Figure 2. Comparison of DOS on chemisorption using curve (a) Bragg-Williams approximation and curves (b) and (c) quasi-chemical approximation, with two different values of interaction energy term $-W/KT = 2$ and 8 , respectively for low coverage, $\theta = 0.2$.

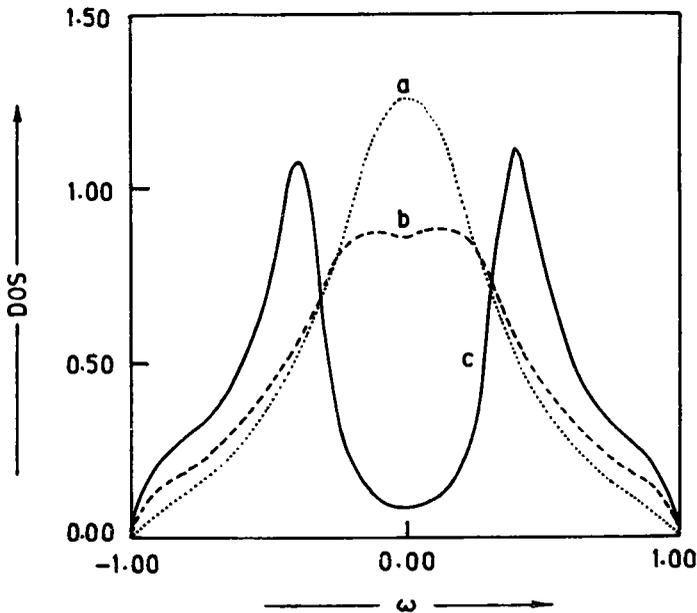


Figure 3. Coverage stimulated non-magnetic case (U/β small) DOS vs ω for different coverages, represented respectively, by curves (a) $\theta = 0.001$, (b) $\theta = 0.2$ and (c) $\theta = 0.8$, keeping the interaction energy term fixed ($-W/KT = 2$) in QCA.

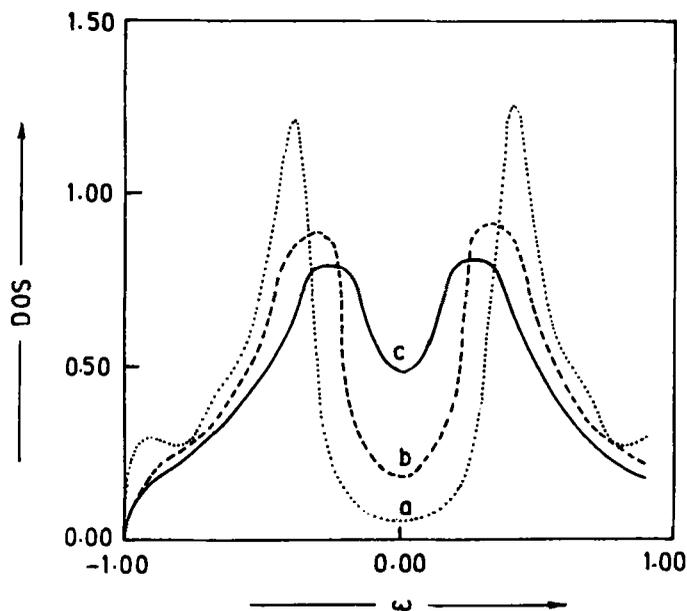


Figure 4. Coverage stimulated non-magnetic case (U/β small) DOS vs ω for different values of interaction energy term (W/KT) = 2, 6, and 10 plotted respectively by curves (a), (b) and (c), keeping coverage fixed, $\theta = 0.8$ in QCA.

strength between the adatom and the substrate, consistent with the results obtained within other approaches [13, 14] and that of Gavrilenko [6]. Furthermore, an increase in the heights of B-AB peaks with θ depicts an increase in the number of B-AB states and is found to be consistent with the findings of Brenig and Schonhammer [15].

4.3 Effect of interaction energy on bond strength and number of B-AB states

Both the bond strength and the number of B-AB states are found to decrease with increase in the interaction between adatoms as shown in figure 4. The typical curves DOS vs ω corresponding to different values of interaction energy term ($-W/KT$) = 2, 6 and 10 are plotted as (a), (b) and (c) respectively, at a fixed coverage $\theta = 0.8$. These curves clearly show that with the increase in the interaction between adatoms, the distance between peaks is decreasing, indicating the decrease in the bond strength between adatom and substrate. The depth between B-AB peaks is also found to decrease. This implies the weakening of binding of adatoms with surface.

The magnetic case (U/β large) can also be treated similarly.

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