Cooperation and competition between magnetism and chemisorption on ferromagnetic surfaces

Satadeep Bhattacharjee\textsuperscript{1} and Seung-Cheol Lee\textsuperscript{1,2}\textsuperscript{*}

\textsuperscript{1}Indo-Korea Science and Technology Center (IKST), Bangalore, India
\textsuperscript{2}Electronic Materials Research Center, Korea Institute of Science & Tech., Korea

Abstract

The chemisorption energy is formulated in terms of the change in surface magnetic moments. Using such formulation, we address the question of how the strength of binding of an adsorbate depends on the surface magnetic moments and vice versa. Our results indicates a possible adsorption energy scaling relationship in terms surface magnetic moments. We also discuss the condition for the appearance of magnetism due to chemisorption on an otherwise non-magnetic surface in terms of a modified Stoner criterion.

\textsuperscript{*}s.bhattacharjee@ikst.res.in
\textsuperscript{†}seung-cheol.lee@ikst.res.in
I. INTRODUCTION

The effect of surface magnetism on chemisorption and the impact of chemisorption on surface magnetism are both interesting subjects and demand thorough theoretical discussions. In the literature, we find the mention of both cooperation and rivalry between the magnetism and chemisorption. For example, some recent works suggest that the chemisorption of molecules helps the non-magnetic metals to overcome the Stoner criterion and make them ferromagnetic at room temperature [1]. Similarly chemisorption induced ferromagnetism is reported in Au and Pt nanoparticles [2, 3]. Such chemisorption induced changes of the magnetic properties of the metal surface promise various new avenues particularly in the field of spintronics [4–8].

On the other hands, it has been seen that the saturation magnetic moment of the Ni surfaces decrease due to chemisorption of gases [9, 10]. Conventional catalysts are non-magnetic heavy metals [11–13], and are not interesting platform for discussing the magnetic properties. The focus has, however, turned in recent years towards simple 3d-transition metals to be used as catalysts [14]. In most of the cases 3d transition metals are used as alloying elements in either binary or ternary alloys-catalysts [15, 16]. These materials offer additional degrees of freedom such as internal strain and magnetic moment when alloyed with traditional heavy metals. Therefore effect of magnetism on surface reactivity also becoming focus of many recent studies [17–19].

From the theoretical side, the chemisorption can be described by the Newns-Anderson-Grimely model [20–22] while the metallic ferromagnetism via Stoner model [23]. Within the Stoner model, the off-set of magnetism depends on the density of states (DOS) at Fermi energy while the covalent metal-adsorbate binding is described by Newns-Anderson-Grimeley approach in terms of a coupling between the adsorbate states with the metal states.

It is well-known that chemisorption of the molecules effects the density of states of the metals near the Fermi-energy. For example, it was proposed that the decrease of the magnetic moment on the Ni surfaces due to chemisorption of gases are result of the shift of the DOS towards the foot of the d-bands [9, 10].

In the present work, we formulate the chemisorption energy in terms of the change in magnetic moments due to the chemisorption. Furthermore, we try to understand the rules for collaborative and rivalry behaviour of the above two mechanisms. We organize our paper in the following way: We first do a general formulation of adsorption energy in terms of the chemisorption induced change in density of states and magnetic moment. We describe the metal surface in terms of Stoner
Hamiltonian with Bloch states as basis while the adsorbate is described in terms of a localized states and the coupling between the localized and extended states were introduced as in Newns-Anderson-Grimley model. Using such an approach we first derive an expression for the adsorption energy which is dependent on the change in the magnetic moment of the metal surface due to the adsorption. The interdependence of the magnetic properties and chemisorption are then evaluated by comparing two phase diagrams obtained from the same model: one is a magnetic phase diagram which describes how magnetic moments change due to chemisorption, the other is a chemisorption phase diagram describing how chemisorption energy changes with respect to change in surface magnetic moments. Both phase diagrams are obtained by varying the same sets of parameters with values within the same range. Finally, using the same Hamiltonian in it’s non spin-polarized form, i,e with an ordinary Newns-Anderson-Grimely model, we deduce an modified Stoner criterion and analyze how chemisorption may help to overcome the barrier laid by the standard Stoner criterion. We look for the cases where ferromagnetism can appear in a otherwise non-magnetic metals surfaces.

II. RELATION BETWEEN THE ADSORPTION ENERGY AND CHANGE IN SURFACE MOMENTS

Let $m_i$ is the magnetic moment per site of the ferromagnetic surface and $m_f$ is the magnetic moment after the adsorption happened. If $D(E)$ and $\hat{D}(E)$ are the DOS of the metal surface before and after the adsorption ($\sigma$ is the spin index), then the change in magnetic moment ($\delta m = m_f - m_i$) after the chemisorption is given by,

$$\delta m = \int_{-\infty}^{E_F} \left[ \hat{D}_\uparrow(E) - D_\uparrow(E) \right] dE - \left[ \hat{D}_\downarrow(E) - D_\downarrow(E) \right] dE$$  \hspace{1cm} (1)$$

Where $E_F$ is the Fermi energy. If we use $\hat{D}_\sigma(E) = D_\sigma(E) + \Delta D_\sigma(E)$ as DOS of the metal surface after the adsorption, then the change in magnetic moment can be written in terms of the change in the density of states: $\Delta D_\sigma(E) = \hat{D}_\sigma(E) - D_\sigma(E)$.

$$\delta m = \int_{-\infty}^{E_F} \left[ \Delta D_\uparrow(E) - \Delta D_\downarrow(E) \right] dE$$  \hspace{1cm} (2)$$
The adsorption energy of an adsorbate with renormalized energy level $\varepsilon_{a\sigma}$ is given by,

$$\Delta E(\delta m) = \sum_{\sigma} \int_{-\infty}^{E_F+\delta E_F} E\tilde{D}_\sigma(E) dE - \sum_{\sigma} \int_{-\infty}^{E_F} E\tilde{D}_\sigma(E) dE - \sum_{a\sigma} n_{a\sigma} \varepsilon_{a\sigma}$$

$$= \sum_{\sigma} \int_{-\infty}^{E_F} E\Delta D_\sigma(E) dE + E_F \left[ \delta m - 2 \int_{-\infty}^{E_F} \Delta D_{\uparrow\downarrow}(E) dE \right] + \sum_{\sigma} n_{a\sigma}(E_F - \varepsilon_{a\sigma})$$

(3)

$\delta E_F$ is the small variation of the Fermi energy upon adsorption, $n_a$ is the number of electrons in the adsorbate. To derive the Eq.3 we have used the Eq.2 and the charge neutrality condition as is given by

$$\sum_{\sigma} \int_{-\infty}^{E_F+\delta E_F} \tilde{D}_\sigma(E) dE - \sum_{\sigma} \int_{-\infty}^{E_F} E\tilde{D}_\sigma(E) dE = \sum_{a\sigma} n_{a\sigma}$$

The Eq.3 gives the adsorption energy of a molecule on a ferromagnetic metal surface with spin dependent density of states $\Delta D_\sigma(E)$. The first term in the equations refers to the change in the band energy due to the change in DOS, while second and third term are related to the change in the magnetic moment of the metal surface due the chemisorption. The last term in the Eq.3 refers the energy separation between the Fermi energy of the metal and the adsorbate energy level.

It is clear that for a metal surface with positive Fermi energy, if the chemisorption enhances it magnetic moment ($\delta m > 0$), this would lead a smaller (less negative) adsorption energy. While if the chemisorption reduces the magnetic moment ($\delta m < 0$), the chemisorption energy will depend on the magnitude of the reduced moment.

For the non-magnetic surfaces $\delta m = 0$ and $2 \int_{-\infty}^{E_F} \Delta D_{\uparrow\downarrow}(E) dE = \int_{-\infty}^{E_F} \Delta D(E) dE$, therefore the Eq.3 reduces to the well-known [24] form,

$$\Delta E = \int_{-\infty}^{E_F} (E - E_F) \Delta D(E) dE + \sum_{\sigma} E_F(n_{a\sigma} - \varepsilon_{a\sigma})$$

(4)

III. $\Delta E(\delta m)$ WITHIN NEWNS-ANDERSON-GRIMLEY-STONER FRAMEWORK

To calculate numerically the adsorption energy for a ferromagnetic metal surface we need to know $\Delta D_\sigma(E)$ which we obtain within a framework which combines the Newns-Anderson model with Stoner model as follows.

The Hamiltonian for the metal surface can be written in terms of the Bloch states [25, 26]

$$\hat{H}_M = \sum_{k j \sigma} \left( \varepsilon_{k j} + I \langle n_{j-\sigma} \rangle \right) c_{k j \sigma}^\dagger c_{k j \sigma} = \sum_{k j \sigma} \varepsilon_{k j \sigma} c_{k j \sigma}^\dagger c_{k j \sigma}$$

(5)
where $I$ is the Stoner parameter and $j$ refers band index. The adsorbate Hamiltonian can be written as

$$
\hat{H}_{ad} = \sum_{\sigma} \varepsilon_{a\sigma} \hat{n}_{a\sigma} 
$$

(6)

Here $\varepsilon_{a\sigma}$ is the adsorbate energy level with occupation $n_{a\sigma}$. The coupling between the two sub-systems (adsorbate and the surface) is given by,

$$
\hat{H}_C = \sum_{k,j,\sigma} V_{k,j,\sigma} c_{k,j,\sigma}^+ a_{\sigma} + h.c 
$$

(7)

The unperturbed Hamiltonian of the system can be written as, $\hat{H}_0 = \hat{H}_M + \hat{H}_{ad}$. While the total Hamiltonian of the system is given by $\hat{H} = \hat{H}_0 + \hat{H}_C$. The change in density of states referred in the Eq.3 can be obtained as,

$$
\Delta D_\sigma(E) = \Delta n_\sigma(E) + \delta(E - \varepsilon_{a\sigma}) 
$$

(8)

where $\Delta n_\sigma(E) = -\frac{1}{\pi} \Im \left[(G_\sigma(E) - G_\sigma^0(E))\right] = -\frac{1}{\pi} \Im \left[\frac{d}{dE} \text{Det} (1 - V G_\sigma^0)\right]$. $G_\sigma(E)$ and $G_\sigma^0(E)$ are the retarded single electron Green’s function of the coupled and decoupled metal adsorbate system.

It can be shown that, for a particular spin, $\sigma$ the change in DOS can be written as [24] (also refer supplemental material),

$$
\Delta D_\sigma(E) = -\frac{1}{\pi} \Im \left[ (1 - \frac{d\Sigma(E)_\sigma}{dE}) G_{\sigma,a}(E) \right] 
$$

(9)

where $\Sigma(E)_\sigma = \sum_k \frac{V^2}{E - \varepsilon_k - <n^{-\sigma}>I + i\delta}$ is the spin-dependent self-energy [24, 27]. $G_{\sigma,a}$ is the Green’s function of the adsorbate after it is adsorbed to the surface. We have ignored the band index and also assumed the $V$ to be independent of $k$. The adsorption energy can further be written by using Eq3 as,

$$
\Delta E(\delta m) = -\frac{1}{\pi} \sum_{\sigma} \int_{E_F}^{E_F} E \Im \left[ (1 - \frac{d\Sigma(E)_\sigma}{dE}) G_{\sigma,a}(E) \right] dE + E_F \delta m 
$$

$$
+ \frac{2E_F}{\pi} \int_{E_F}^{E_F} \Im \left[ (1 - \frac{d\Sigma(E)^\dagger_{\sigma}}{dE}) G_{\gamma,a}^\dagger \right] dE + \sum_{\sigma} n_{a\sigma}(E_F - \varepsilon_{a\sigma}) 
$$

(10)

The self-energy, $\Sigma(E)_\sigma$ has real and imaginary parts and is usually given by $\Sigma(E)_\sigma = \Lambda(E)_\sigma - i\Delta(E)_\sigma$. Where $\Delta(E)_\sigma = \pi V^2 \sum_k \delta(E - \varepsilon_k - <n^{-\sigma}>I) = \pi V^2 \sum_k \delta(E - \varepsilon_{k,\sigma}) = \pi V^2 D_\sigma(E)$ is the imaginary part. The real part is obtained through the Hilbert transform: $\Lambda_\sigma(E) = \frac{1}{\pi} \text{P} \int \frac{\Delta_\sigma(E)}{E - E'} dE'$. Eq10 gives the adsorption energy in terms of chemisorption induced surface magnetic moments. To estimate the mutual dependence of surface moments and adsorption energy, one needs to solve the Eq2, Eq9 and Eq10 simultaneously.
IV. NUMERICAL CALCULATIONS AND RESULTS

A. Chemisorption phase diagrams

To understand the effect of magnetism on chemisorption and vice versa we consider a simple example: The chemisorption of an adsorbate with a single energy level, $\varepsilon_a$ relative to the metal surface with occupation $n_a$. To obtain realistic results for our model calculation, we use realistic electronic structure as input for the calculation of the self energy $\Sigma(E)$. We used the electronic structure of a bcc (110) film of Iron (Fe) to calculate the real and imaginary part of the self energies ($\Lambda(E), \Delta(E)$). The Fe (110) surface was modelled as slabs of $2 \times 2$ in-plane unit cells and four atomic layers containing 16 atoms. We performed first-principles calculations within the framework of Density Functional Theory (DFT) with Perdew-Burke Ernzerhof exchange correlation energy functional [28] based on a generalized gradient approximation. We used a projector augmented wave method as implemented in Vienna ab-initio simulation package (VASP) [29]. Kohn-Sham wave functions of the valence electrons were expanded in plane wave basis with energy cut-off of 500 eV. The Brillouin zone sampling was carried out using Monkhorst Pack grid of $5 \times 5 \times 1$ k-points. Ionic relaxation was performed using conjugate-gradient method, until forces on unconstrained atoms were less than 0.04 eV/Angstrom for the non-constrained atoms. Vacuum of 10 Å was included. Dipole corrections were applied along the directions perpendicular to the metal surface in order to eliminate the unwanted electric fields arising from the asymmetry of the simulation cell. The structural relaxation were performed for only the top most two Fe layers. The bottom two layer are fixed to their bulk experimental values. To obtain the inputs for the model calculation using Eq.9 and Eq.10, the electronic structure inputs of the non-spin polarized calculations were used.

In the Fig.1(a), we show the adsorbate induced change in magnetic moment ($\delta m$) which are calculated by simultaneously solving the Eq.2 and Eq.9. From Eq.9 it can be understood that $\delta m$ depends on three parameters, the coupling constant $V$, the adsorbate energy level $\varepsilon_a$ and Stoner parameter $I$. The Stoner parameter was calculated using a fixed spin moment calculation (refer the supplemental material). In the Fig.1(a), we show such dependence in the form of a magnetic phase diagram. By sweeping different values of $V$ and $\varepsilon_a$, we identify different regions where surface magnetic moments are reduced/enhanced due to the chemisorption. The initial magnetic moment per Fe-atom was set to 2.2 $\mu_B$. We consider the adsorbate occupation as $\sum_{\sigma} n_{a\sigma} = 1$. 
From the Fig.1(a), we can clearly notice the dependence of $\delta m$ on $V$ and $e_a$. The general trend of the magnetic moment shows a decrement with increase in $V$. However, for the values of $V$ larger than 0.5 eV, the magnetic moment becomes almost intensive to $V$ and varies very little. So it appears that effect of chemisorption on the surface magnetic moments has a critical value of the coupling, beyond which the moments are not effected much. $\delta m < 0$ almost everywhere except $e_a = -3eV$ and $e_a = -2eV$. It should be noted that most DFT-based adsorption studies of atomic adsorbates, such as hydrogen on ferromagnetic surfaces or ferromagnetic islands, report a decrease in magnetic moment [30]. However, one can see here that magnetic moment can also increase depending on the adsorbate’s location in energy and the strength of the coupling.

In the Fig.1(b), we show the adsorption energy within the same regions of $V$ and $e_a$ as in Fig.1(a). The adsorption energies are computed using Eq.10. We can see the adsorption energies follow the change of surface magnetic moments, however such the variation of adsorption energy with the change in magnetic moment are different for cases $e_a > 0eV$ to cases $e_a < 0eV$. For the cases when $e_a > 0eV$ the adsorption energy simply decrease as the magnetic moment increases while in the case of $e_a < 0eV$ when the magnetic moment increase, the adsorption energy first shows slight increment and finally increase. Such behavior we further illustrate in the Fig.2 where we show the adsorption energy calculated using Eq.10 with the induced moment $\delta m$ for $e_a > 0eV$ (Fig.2(a)) and $e_a < 0eV$ (Fig.2(b)). It can be noticed that in both cases the adsorption energy shows universal behaviour. In both cases $\Delta E$ can be written as a third order polynomial in terms of $\delta m$. This analysis therefore indicates some sort of scaling relationship of adsorption energies in terms of the surface magnetic moments.

**B. Scaling relationships**

If we now imagine that the three levels with $e_a < 0eV$ as shown in Fig.2(a) correspond to three distinct adsorbates with distinct energy levels $e_a = 1eV$, $e_a = 2eV$ and $e_a = 3eV$ respectively and see how their adsorption energies are related, we notice that they are linearly dependent to each other as can be seen from the Fig.3. The scaling relationship can be expressed as

$$\Delta E_2 = \gamma_1 \Delta E_1 + \beta_1$$
$$\Delta E_3 = \gamma_2 \Delta E_1 + \beta_2,$$

Where $\Delta E_1$, $\Delta E_2$ and $\Delta E_3$ are respectively the adsorption energies for the adsorbate with renormalized energy levels 1, 2 and 3eV respectively. The slopes $\gamma_1$ and $\gamma_2$ usually depend on the valencies
of the adsorbates \[^{[31, 32]}\]. However, as the valencies are same for all the three adsorbates here, according to the original formulation of the scaling relationship \[^{[31]}\], the slopes should be same for both cases (i.e. \(\gamma_1 = \gamma_2 = 1\)). But one can see that it is not the case. This suggests the importance of the surface descriptors. To say more precisely, as the dependence of \(\Delta E_1\), \(\Delta E_2\) and \(\Delta E_3\) on the surface magnetic moments \(\delta m\) are not exactly the same, this brings some difference in \(\gamma_1\) and \(\gamma_2\). Recent studies suggest that the adsorption energies can be written in terms of a set of surface properties \[^{[33]}\],

\[
\Delta E_1 = F(\{\omega_i\}) + \alpha_0 \quad \Delta E_2 = G(\{\omega_i\}) + \beta_0 \quad \Delta E_3 = H(\{\omega_i\}) + \gamma_0
\]

where \(F\), \(G\) and \(H\) are the functions of the set \(\{\omega_i\}\) of certain surface properties and \(\alpha_0\), \(\beta_0\), \(\gamma_0\) depend on surface coordination number. In the present case, one can obtain from the Fig.2(a) that for the case of \(\varepsilon_a > 0\), the functions \(F\), \(G\) and \(H\) can be obtained from \(\Delta E_1 = 251\delta m + 730\delta m^2 + 623.21\delta m^3 + 20.13\); \(\Delta E_2 = 22.5\delta m + 95.3\delta m^2 + 121.65\delta m^3 - 0.82\); and \(\Delta E_3 = 14.36\delta m + 56.92\delta m^2 + 82.55\delta m^3 - 2.23\). As \(\frac{F(\{\alpha_i\})}{G(\{\alpha_i\})} \neq \frac{F(\{\alpha_i\})}{H(\{\alpha_i\})}\), \(\gamma_1 \neq \gamma_2\). Therefore, it can be seen that the adsorption energy scaling depends on surface properties as well and for ferromagnetic surfaces the most potential descriptor could be the surface magnetic moment itself as is claimed by other recent study \[^{[34]}\].

C. Modified Stoner Criterion due to the chemisorption

Our next objective is to understand how typically a non-magnetic surfaces become ferromagnetic as is observed by \[^{[1, 2]}\]. For this, we consider a nonmagnetic metal surface with density of states \(D(E)\). Let us keep the notations similar to the above case of spin-polarized surface and just drop the spin index "\(\sigma\)". As the surface is on-magnetic, it satisfies the usual Stoner condition \(D(E_F) < 1\), \(E_F\) is the Fermi energy. If the surface becomes ferromagnetic when it adsorbs a specific molecule, essentially the following condition has to be satisfied: \([D(E_F) + \Delta D(E_F)] I \geq 1\) that furthermore sets the condition in accordance with the Eq.\(^{[9]}\) as

\[
D(E_F) + D_a(E_F) + \frac{1}{\pi} \Im \left\{ \frac{d\Sigma(E)}{dE} G_a(E) \right\} E_F I = 1
\]

The above equation can be thought of as a modified criterion for appearance of ferromagnetism in an otherwise non-magnetic surface via chemisorption. To demonstrate in a numerical way, we again consider an hypothetical atomic adsorbate whose energy level we vary from -3.0 eV
to 3.0 eV and look at the behavior of the (modified) Stoner criterion. In order to be close to a realistic situation, we consider the electronic structure of (111) surface of Cu (copper) as input. The surface was modelled as slab of $2 \times 2$ in-plane unit cells and four atomic layers of Cu. The bottom two layers are fixed to their bulk values. We used the DOS of such system as an input for the self energy $\Sigma(E)$. The density of states $D(E)$ appear in Eq.13 corresponds to the density of states of the top two layers of the Cu (111) slab. In the Fig.4 we show the real and imaginary part of the self energy, $\Sigma(E)$. We then compute the left side of the Eq.13 for different values of the adsorbate energy and the coupling constants. The results are shown in the Fig.5. We used value of $I=0.5$ eV, for the Stoner parameter, which is close to the usual value for Cu [35]. The blue regions correspond to the non-magnetic states (less than 1.0), while yellow and red regions are the ferromagnetic ones (greater than 1). First, we see that, for $\varepsilon_a > 0.5$eV the criterion is not satisfied for any value of $V$ and the system remains non-magnetic. Next, we see that for each value of $\varepsilon_a < 0.5$eV the surface undergoes from non-magnetic to ferromagnetic transition for certain allowed values of the coupling constant, $V$. The lower critical value of $V$, for a given $\varepsilon_a$ depends on $\varepsilon_a$ itself. Deeper the $\varepsilon_a$, higher the critical value is. The reason for such behavior lies on how both $D_a(E_F)$ and $\frac{1}{\pi} \Im \{ \frac{d\Sigma(E)}{dE} G_a(E) \} _{E_F}$ depends on $V$ and $\varepsilon_a$. The Fermi energy is set at zero, here. It is seen that if the adsorbate level is close the Fermi energy of the metal and the coupling is very small, the modified Stoner criterion is satisfied. For very small coupling the metal-adsorbate bonding states are very close to the $E_F$ of the metal, and the Eq.13 is satisfied due to the contribution from $D_a(E_F)$ (refer Fig.6(a)). For $\varepsilon_a < 0$ the modified Stoner criterion is mainly satisfied via $\frac{1}{\pi} \Im \{ \frac{d\Sigma(E)}{dE} G_a(E) \} _{E_F}$ as can be seen from Fig.6(b). It can be seen that peak in $\frac{1}{\pi} \Im \{ \frac{d\Sigma(E)}{dE} G_a(E) \} _{E_F}$ move to higher value of coupling as $\varepsilon_a$ goes deeper in energy.

V. CONCLUSIONS

In conclusion, we have studied the problem of chemisorption of molecules on ferromagnetic metal surfaces by using an approach that combines the Newns-Anderson-Grimely model with the Stoner model of metallic ferromagnetism. We studied how the strength of chemisorption is related to the magnitude of the surface moments and vice versa. We also discussed how chemisorption affects Stoner’s criterion for the appearance of ferromagnetism and therefore allows the non-magnetic surface to become ferromagnetic. We have discussed how such a process depends on the position of the adsorbate level and the mixing strength of the adsorbate-metal levels. Even though,
this study is more relevant to the adsorbates with single occupied levels, the physical insights we gather should be useful for studying more complicated molecules on the ferromagnetic surfaces.

VI. ACKNOWLEDGMENT

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FIG. 1. (a) Change in magnetic moment of the surface $\delta m$ (b) corresponding adsorption energies calculated from the Eq. [10] for different values of the coupling constant ($V$) and adsorbate energies ($\varepsilon_a$)
FIG. 2. (Color online) The change of adsorption energy with chemisorption induced magnetic moment $\delta m$.

The results are shown for three values of $\varepsilon_a$. (a) for $\varepsilon_a > 0$ (b) $\varepsilon_a < 0$
FIG. 3. (Color online) Linear scaling relationship between the adsorption energies corresponding the adsorbate with renormalized level $\varepsilon_a = 1 \text{eV}$, $\varepsilon_a = 2 \text{eV}$ and $\varepsilon_a = 3 \text{eV}$ respectively.

$\Delta E_2 = 0.98 \Delta E_1 - 0.59$

$\Delta E_3 = 0.957 \Delta E_1 - 1.34$
FIG. 4. (Color online) The real and imaginary of part of the self-energy obtained from the density of states of Cu (111) surface.
FIG. 5. (Color online) Heat-map of the left side of the Eq[13] for different values of the coupling constant (V) and adsorbate energies (E_a). Red and yellow regions corresponds to ferromagnetism while the blue regions correspond to the non-magnetic state.
FIG. 6. (Color online) (a) The adsorbate DOS at Fermi energy (after chemisorption) as a function of V.
(b) \( \frac{1}{\pi} \sum \left\{ \frac{d\Sigma(E)}{dE} G_a(E) \right\}_{E_F} \) as a function of V.
Supplemental material of
“Cooperation and competition between magnetism and
chemisorption on ferromagnetic surfaces”

Satadeep Bhattacharjee and Seung-Cheol Lee

*Indo-Korea Science and Technology Center (IKST), Bangalore, India*

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Derivation of the Eq.3 of the manuscript

The adsorption energy is given by,

$$
\Delta E(\delta m) = \sum_{\sigma} \left\{ \int_{E_F}^{E_F+\delta E_F} E \tilde{D}_\sigma(E) dE - \int_{E_F}^{E_F} E D_\sigma(E) dE - n_{a\sigma} \varepsilon_{a\sigma} \right\}
$$

$$
= \sum_{\sigma} \left\{ \int_{E_F}^{E_F} E \tilde{D}_\sigma(E) dE + \int_{E_F}^{E_F+\delta E_F} E \tilde{D}_\sigma(E) dE - \int_{E_F}^{E_F} E D_\sigma(E) dE - n_{a\sigma} \varepsilon_{a\sigma} \right\}
$$

$$
= \sum_{\sigma} \left\{ \int_{E_F}^{E_F} E \Delta D_\sigma(E) dE + E_F \tilde{D}_\sigma(E_F) \delta E_F - n_{a\sigma} \varepsilon_{a\sigma} \right\}
$$

Now using the charge neutrality condition,

$$
\int_{E_F}^{E_F+\delta E_F} \tilde{D}_\sigma(E) dE - \int_{E_F}^{E_F} D_\sigma(E) dE = n_{a\sigma}
$$

or

$$
\int_{E_F}^{E_F} \Delta D_\sigma(E) dE + \tilde{D}_\sigma(E_F) \delta E_F = n_{a\sigma}
$$

we get,

$$
\Delta E(\delta m) = \sum_{\sigma} \int_{E_F}^{E_F} E \Delta D_\sigma(E) dE - E_F \int_{E_F}^{E_F} \Delta D_\sigma(E) dE + \sum_{\sigma} E_F (n_{a\sigma} - \varepsilon_{a\sigma})
$$

$$
= \sum_{\sigma} \int_{E_F}^{E_F} E \Delta D_\sigma(E) dE - E_F \int_{E_F}^{E_F} \Delta D_\uparrow(E) dE - E_F \int_{E_F}^{E_F} \Delta D_\downarrow(E) dE
$$

$$
+ \sum_{\sigma} E_F (n_{a\sigma} - \varepsilon_{a\sigma})
$$

Now by adding and subtracting $E_F \int_{E_F}^{E_F} \Delta D_\uparrow(E) dE$ to right hand side of the above equation we get the Eq.3 of the manuscript.

Calculation of the Stoner parameter for the Fe-(110) film

We have have performed the fixed spin moment calculations for the Fe (110) film. The
total energy of the film can be written as,

\[
E(m) = E(0) + \frac{1}{2} \chi^{-1} m^2 + \frac{1}{4} \beta m^4
\]  

(1)

Where \( E_0 \) corresponds to the contributions from the non-magnetic degrees of freedoms, \( \chi \) is the Stoner enhancement of the susceptibility. Therefore, \( \chi^{-1} = \frac{\partial^2 E(m)}{\partial E^2} \). The Stoner parameter is obtained from the following \[1\]

\[
I = \frac{1}{N(E_F)} - \frac{2}{\chi}
\]  

(2)

We calculate \( \chi \) by fitting the Eq.1 to the total energy as shown in the Fig[S1]. The calculated value is 0.26.
FIG. S1: (Color online) Fixed spin moment energy of bcc (110) surface as a function of the magnetic moment per Fe-atom

\[ E(m) = -111.46 - \frac{1}{2}8.74m^2 + \frac{1}{4}(1.32)m^2 \]
Derivation of the Eq.9 of the manuscript

The unperturbed Hamiltonian of the system is given by,

$$H_0 = \sum_{k\sigma} \varepsilon_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \varepsilon_{\alpha\sigma} n_{\alpha\sigma}$$  \hspace{1cm} (3)

Where the first term represents the metal Hamiltonian, while the second term is that of the adsorbate. The band index is omitted. The Green’s function of the the unperturbed system is given by,

$$G_{\sigma}^0 = \frac{1}{E - H_0 + i\delta}$$  \hspace{1cm} (4)

When we switch on the coupling between the two subsytems, the total Hamiltonian becomes,

$$H = H_0 + V \sum_{k,j,\sigma} c_{k\sigma}^\dagger c_{a\sigma} + h.c$$  \hspace{1cm} (5)

The Green’s function for the composite system is given by,

$$G_{\sigma} = \frac{1}{E - H + i\delta}$$  \hspace{1cm} (6)

For each spin, the change in density of states of the metal surface is given by,

$$\Delta D_{\sigma}(E) = \Delta n(E) + \sum_{\sigma} \delta(\varepsilon - \varepsilon_{a\sigma})$$  \hspace{1cm} (7)

Where,

$$\Delta n_{\sigma}(E) = -\frac{1}{\pi} Im \left( G_{\sigma}(E) - G_{\sigma}^0(E) \right)$$

$$= -\frac{1}{\pi} Im \left( \frac{d}{dE} ln det(1 - VG_{\sigma}^0) \right)$$

$$= -\frac{1}{\pi} Im \frac{d}{dE} ln(1 - V^2 \sum_k G_{k\sigma}^0 G_{a\sigma}^0)$$  \hspace{1cm} (8)

Where

$$G_{k\sigma}^0 = \frac{1}{E - \varepsilon_{k\sigma} + i\delta}$$

and

$$G_{a\sigma}^0 = \frac{1}{E - \varepsilon_{a\sigma} + i\delta}$$
are free metal and adsorbate Green’s function respectively Therefore from Eq 8

\[
\Delta n_\sigma(E) = -\frac{1}{\pi} Im \frac{d}{dE} \ln \left( 1 - V^2 \sum_k \frac{1}{E - \varepsilon_{k\sigma} + i\delta} \frac{1}{E - \varepsilon_{a\sigma} + i\delta} \right)
\]

\[= -\frac{1}{\pi} Im \frac{d}{dE} \ln (1 - \frac{\Sigma_\sigma(E)}{E - \varepsilon_{a\sigma} + i\delta}) \]

\[= -\frac{1}{\pi} Im \frac{d}{dE} \left[ \ln (E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)) - \ln (E - \varepsilon_{a\sigma} + i\delta) \right] \]

Using the identity below,

\[
\frac{d}{dx} \ln u(x) = \frac{u'(x)}{u(x)}
\]

we get

\[
\Delta n_\sigma(E) = -\frac{1}{\pi} Im \left[ \frac{(1 - \frac{d\Sigma_\sigma(E)}{dE})}{E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)} - \delta(E - \varepsilon_{a\sigma}) \right]
\]

after rearranging we get,

\[
\Delta n_\sigma(E) + \delta(E - \varepsilon_{a\sigma}) = -\frac{1}{\pi} Im \left[ \frac{(1 - \frac{d\Sigma_\sigma(E)}{dE})}{E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)} \right]
\]

\[
\Delta D_\sigma(E) = -\frac{1}{\pi} Im \left[ \frac{(1 - \frac{d\Sigma_\sigma(E)}{dE})}{E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)} \right]
\]

\[= -\frac{1}{\pi} Im \left[ (1 - \frac{d\Sigma_\sigma(E)}{dE}) G_{a\sigma}(E) \right] \]

The above equation gives the change in DOS of the adsorbent for a spin \(\sigma\) due to chemisorption. This is used in the manuscript to obtain the most important physical parameters such as adsorption energy, change in surface magnetic moments etc.

[1] L. Ortenzi, I. I. Mazin, P. Blaha, and L. Boeri, Phys. Rev. B 86, 064437