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Self-consistent model of hydrogen chemisorption on ferromagnetic transition metals

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A self-consistent model of hydrogen chemisorption on ferromagnetic 3*d* metals is presented. It is based on an Anderson-Hubbard Hamiltonian, and the substrate electronic structure is solved by means of the cluster-Bethe-lattice approximation. The magnitude of the magnetic moment at the adatom and at the surface atoms is determined self-consistently. Results are given for the change in the substrate magnetization upon chemisorption and for the chemisorption energy.

I. INTRODUCTION

Chemisorption of hydrogen on transition metals has been the subject of extensive research in recent years. Experiments have been performed on ferromagnetic 3*d* metals in the paramagnetic[1,2] as well as in the ferromagnetic phases.[3–5] These studies have shown that the adsorption of hydrogen is changed as the substrate goes through the magnetic transition.

This problem has also been studied intensively from the theoretical point of view. However, most of the studies have been performed under the assumption that the substrate is in the paramagnetic state.[6,7] In order to understand the low-temperature experiments it is necessary to take explicit account of the substrate magnetization. Recent papers have addressed this problem.[8–11]

Here we are interested in studying, among other things, how hydrogen chemisorption influences the surface magnetization and how the energy of chemisorption changes with substrate magnetization. For that purpose, the substrate is described by a model for itinerant magnets, in which local moments are assumed to exist on each lattice site in both the magnetically ordered and in the paramagnetic state.[12]

In Sec. II the characteristics of the substrate are described. Section III is devoted to the theory of chemisorption. Section IV contains the results and discussion.

II. SUBSTRATE CHARACTERIZATION

The metallic ferromagnetic substrate is characterized by means of a Hubbard Hamiltonian, treated in the unrestricted Hartree-Fock (UHF) approximation

$$H_m=\sum_{\substack{ij\\ \alpha\sigma}} t_{ij}c^{\dagger}_{i\alpha\sigma}c_{j\alpha\sigma}+\sum_{\substack{i\\ \alpha\beta\sigma}} U\langle n_{i\beta\bar{\sigma}}\rangle n_{i\alpha\sigma} -\sum_{i\alpha\beta} U\langle n_{i\beta\uparrow}\rangle\langle n_{i\alpha\downarrow}\rangle \;, \qquad (2.1)$$

where t_{ij} denotes the hopping integral for electronic transitions between sites i and j, σ is the spin index, $\bar{\sigma}$ indicates the spin opposite to σ, α and β are band indices $(\alpha,\beta=1,2,\ldots,5)$, U is an intrasite Coulomb interaction. $c^{\dagger}_{i\alpha\sigma}$, $c_{i\alpha\sigma}$, and $n_{i\alpha\sigma}$ are the usual creation, annihilation, and number operators for electrons at site i, spin σ, and band α, and $\langle n_{i\alpha\sigma}\rangle$ is the average number of electrons of spin σ and band α at site i. It should be noted that in this model all five d bands are degenerate and have identical occupation.

We can rewrite the Hamiltonian (2.1) in the form

$$H_m=\sum_{\alpha\sigma}\left[\sum_{ij} t_{ij}c^{\dagger}_{i\alpha\sigma}c_{j\alpha\sigma}+\sum_{i}\tfrac{1}{2}U(n\pm\mu_i)n_{i\alpha\sigma}\right] -\tfrac{1}{4}U\sum_{i}(n^2-\mu_i^2) \;, \qquad (2.2)$$

where the magnetic moment at site i is defined by

$$\mu_i=\sum_{\alpha}(\langle n_{i\alpha\uparrow}\rangle-\langle n_{i\alpha\downarrow}\rangle) \;, \qquad (2.3)$$

and where n is the spatially constant number of electrons at each site

$$n=\sum_{\alpha\sigma}\langle n_{i\alpha\sigma}\rangle \;. \qquad (2.4)$$

In (2.2) the minus sign holds for spin-up electrons and the plus sign for spin-down electrons, respectively.

The ground-state solutions of the Hubbard Hamiltonian (2.1) have been extensively studied in recent years.[13–15] It has been shown that, depending on the renormalized Coulomb repulsion (U/W) (where W is half of the d bandwidth) and on the electron concentration n, the ground state corresponds to a Pauli paramagnet, a ferromagnet, an antiferromagnet, or a ferrimagnet. Here we choose parameters such that the ground state is ferromagnetic.

At zero temperature all the magnetic moments μ_i are equal and are aligned. The value for μ is obtained in a self-consistent manner; this is done by requiring that

$$\mu \equiv \int_{-\infty}^{\epsilon_F} (\rho_\uparrow - \rho_\downarrow) d\omega \tag{2.5}$$

and the value of μ_i used in Eq. (2.2) are equal. In (2.5)

$$\rho_\sigma(\omega) \equiv -\frac{5}{\pi} \operatorname{Im} G_{00,\sigma}(\omega) \; . \tag{2.6}$$

The local Green's function for spin-σ electrons, in the Bethe-lattice approximation[12] is given by

$$G_{00,\sigma}(\omega) = (\omega - \epsilon_0^\sigma + zt\gamma^\sigma)^{-1} \; , \tag{2.7}$$

where

$$\epsilon_0^\sigma = \begin{cases} \frac{1}{2} U(n-\mu) & \text{for } \sigma = \uparrow \; , \\ \frac{1}{2} U(n+\mu) & \text{for } \sigma = \downarrow \; , \end{cases} \tag{2.8}$$

$$\gamma^\sigma = \{ -(\omega - \epsilon_0^\sigma) + i[4(z-1)t^2 - (\omega - \epsilon_0^\sigma)^2]^{1/2} \} / 2(z-1)t \; , \tag{2.9}$$

and z is the coordination number. The parameters in our model are $U = 0.76$ eV, the bandwidth $2W = 4.0$ eV, $z = 8$, and $n = 7.7$, which correspond approximately to iron. The self-consistent value obtained for μ is 1.99.

III. HYDROGEN CHEMISORPTION

To study hydrogen chemisorption on the ferromagnetic substrate we use an Anderson-Hubbard Hamiltonian in the UHF approximation:

$$H = H_m + \sum_\sigma [(\epsilon_a + U_a \langle n_{a\bar{\sigma}} \rangle) n_{a\sigma} + t_a c_{a\sigma}^\dagger c_{01\sigma} + t_a^* c_{01\sigma}^\dagger c_{a\sigma}] - U_a \langle n_{a\uparrow} \rangle \langle n_{a\downarrow} \rangle \; , \tag{3.1}$$

where the metal substrate Hamiltonian H_m is given by (2.1); ϵ_a is the energy level of the hydrogen atom, relative to the substrate and before chemisorption, U_a is the intra-atomic Coulomb interaction energy of the hydrogen atom, t_a is the hopping integral for electronic transition between adatom and substrate, and $c_{a\sigma}^\dagger$, $c_{a\sigma}$, and $n_{a\sigma}$, which refer to the adatom, have the usual meanings. It should be noted that the electronic states of the adatom ($a\sigma$) are connected in our model to the electronic states of the atom at site 0 in the substrate, and only to the band of correct symmetry (labeled 1) and of same spin σ.

At zero temperature the substrate is in the perfect ferromagnetic state with all atomic magnetic moments pointing in a given direction. In this case, the local Green's functions at the adatom and at the substrate atom 0 are given by

$$G_{aa;\sigma} = \left[\omega - E_a^\sigma - \frac{t_a^2}{\omega - zt\gamma^\sigma} \right]^{-1} \tag{3.2}$$

and

$$G_{01,01;\sigma} = \left[\omega - \epsilon_0^\sigma + zt\gamma^\sigma - \frac{t_a^2}{\omega - E_a^\sigma} \right]^{-1} \; , \tag{3.3}$$

where

$$E_a^\sigma = \epsilon_a + U_a \langle n_{a\bar{\sigma}} \rangle \; , \tag{3.4}$$

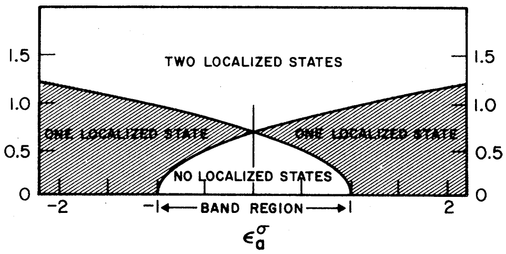

FIG. 1. Phase diagram in (ϵ_a^σ, t_a) parameter space, showing the different regions where localized states exist. The boundaries are given by (3.5) and (3.6) in the text.

and ϵ_0^σ and γ^σ are given by Eqs. (2.8) and (2.9), respectively.

In general, one might find two, one, or no localized states (delta functions), depending on the hopping integral t_a and on the value of E_a^σ.

If we define $\epsilon_a^\sigma \equiv E_a^\sigma - \epsilon_0^\sigma$, in Fig. 1 we show the region in (ϵ_a^σ, t_a) parameter space where the various cases are found. All energies are measured in units of W, the half-bandwidth $[W \equiv 2t(z-1)^{1/2}]$. For

$$\frac{2t_a^2(z-1)}{z-2} - 1 < \epsilon_a^\sigma < 0 \, ,$$

or

$$0 < \epsilon_a^\sigma < 1 - \frac{2t_a^2(z-1)}{z-2} \, , \tag{3.5}$$

there are no localized states and the adsorbate states are part of the ferromagnetic continuum band states. For

$$1 - \frac{2t_a^2(z-1)}{z-2} < \epsilon_a^\sigma < 0 \, ,$$

or

$$0 < \epsilon_a^\sigma < \frac{2t_a^2(z-1)}{z-2} - 1 \, , \tag{3.6}$$

there are two bound states; these can be thought of as the bonding and antibonding states of the "molecule" formed by the adsorbate atom and the atom at site 0. Elsewhere (shaded area of Fig. 1) there is only one localized state either below or above the electronic band of the same spin σ.

The energy of the localized states, ϵ_L^σ, is obtained by solving a quartic equation for $\omega_L \equiv \epsilon_L^\sigma - \epsilon_0^\sigma$. This equation is

$$\omega_L^4 + Q_3\omega_L^3 + Q_2\omega_L^2 + Q_1\omega_L + Q_0 = 0 \, , \tag{3.7}$$

where

$$\begin{aligned} Q_3 &= -2\epsilon_a^\sigma \, , \\ Q_2 &= (\epsilon_a^\sigma)^2 + (z-2)t_a^2 - z^2t^2 \, , \\ Q_1 &= \epsilon_a^\sigma[2z^2t^2 - (z-2)t_a^2] \, , \\ Q_0 &= -t^2z^2(\epsilon_a^\sigma)^2 + (z-1)t_a^4 \, . \end{aligned} \tag{3.8}$$

The spectral weight of the localized states which lie below the band are as follows: For the adatom

$$a = \frac{\Gamma_L}{\Gamma_L + 2(z-1)t_a[(z-2)^2\Gamma_L - z\omega_L][(z-2)\omega_L - z\Gamma_L]^{-2}} \, , \tag{3.9}$$

and for the metal atom at site 0

$$b = \frac{2(z-1)(\omega_L - \epsilon_a^\sigma)^2\Gamma_L}{(z-2)(\omega_L - \epsilon_a^\sigma)^2\Gamma_L + 2(z-1)\Gamma_L t_a^2 - z\omega_L(\omega_L - \epsilon_a^\sigma)^2} \, . \tag{3.10}$$

We have used $\Gamma_L \equiv [\omega_L^2 - 4(z-1)t^2]^{1/2}$.

In Fig. 2 we show the results for ω_L, a, and b as functions of t_a for $\epsilon_a^\sigma = -0.5W$. The results for the

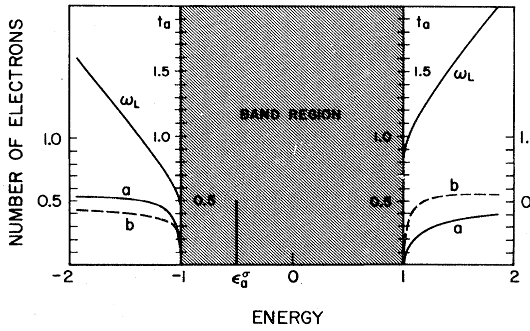

FIG. 2. Energy of the localized state ω_L as a function of t_a for $\epsilon_a^\sigma = -0.5W$. The weights of the localized state at the adatom, a, and at the atom on site 0 below, b, are also shown. All energies in units of W, the half-bandwidth.

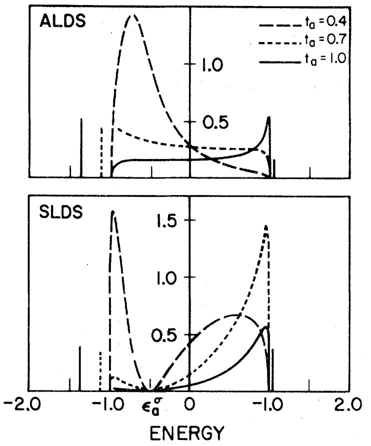

FIG. 3. Local density of states at the adatom (ALDS) and at the atom below (SLDS) for different values of t_a: long dashed line, $t_a = 0.4$ (no localized states), short dashed line, $t_a = 0.6$ (one localized state below the band), and solid line, $t_a = 1.0$ (two localized states). All energies are in units of W, the half-bandwidth.

local density of states at the adatom (ALDS) and at the atom at site 0 (SLDS) are presented in Fig. 3 for three values of t_a: $0.4W$ (no localized states), $0.6W$ (one localized state), and W (two localized states).

The next step in the calculation, as in the Anderson model,[16] is to achieve self-consistency. This requires the solution of a large number of loops which calculate local occupancy of the two states of the adsorbate ($\sigma=\uparrow$ and $\downarrow$), and the ten states of each atom of the ferromagnetic substrate ($\alpha=1$ to 5, $\alpha=\uparrow$ and $\downarrow$, and all sites i). In the case of the adsorbate hydrogen atom it requires the solution of the simultaneous equations

$$N[N(n_{a\sigma})]-n_{a\sigma}=0 \quad (\sigma=\uparrow,\downarrow)\;, \tag{3.11}$$

where

$$\begin{aligned} n_{a\sigma}&=N(n_{a\bar{\sigma}}) \\ &=-\frac{1}{\pi}\int_{-\infty}^{\epsilon_F}\mathrm{Im}G_{aa,\sigma}(\omega)d\omega+a_\sigma\;. \end{aligned} \tag{3.12}$$

The last term is the contribution of localized states below the band and is given by (3.9). In the paramagnetic substrate state, (3.11) has three solutions[7] for small t_a. Two of them are "magnetic" and the third one is "nonmagnetic." The magnetic solutions are symmetric and of equal energy. One we label ferromagnetic

$$\mu_a=\langle n_{a\uparrow}\rangle-\langle n_{a\downarrow}\rangle>0\;, \tag{3.13}$$

and the other one antiferromagnetic ($\mu_a<0$). They have a lower energy than the $\mu_a=0$ nonmagnetic solution (local maximum). As t_a increases beyond a critical value t_{ac}, the three solutions degenerate into

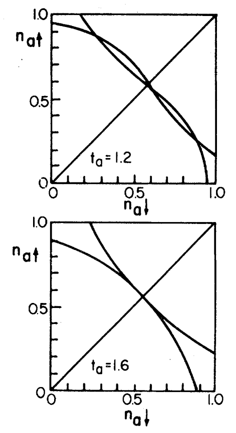

FIG. 4. Graphic solution of the equation $N[N(n_{a\sigma})]-n_{a\sigma}=0$ for a paramagnetic substrate and for values of the parameters $U_a/W=5.16$, $\epsilon_a/W=-3.0$, $n=7.7$ electrons; $t_a/W=1.2$ (upper figure) and $t_a/W=1.3$ (lower figure).

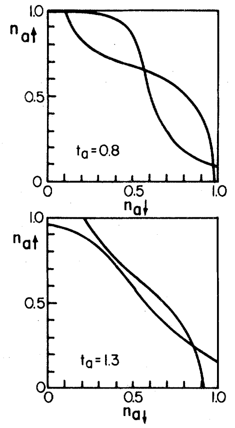

FIG. 5. Graphic solution of the equation $N[N(n_{a\sigma})]-n_{a\sigma}=0$ for $\mu_0=1.99$, $U_a/W=5.16$, $U/W=0.38$, $\epsilon_a/W=-3.0$, and $n=7.7$; $t_a/W=0.8$ (upper figure) and $t_a/W=1.3$ (lower figure).

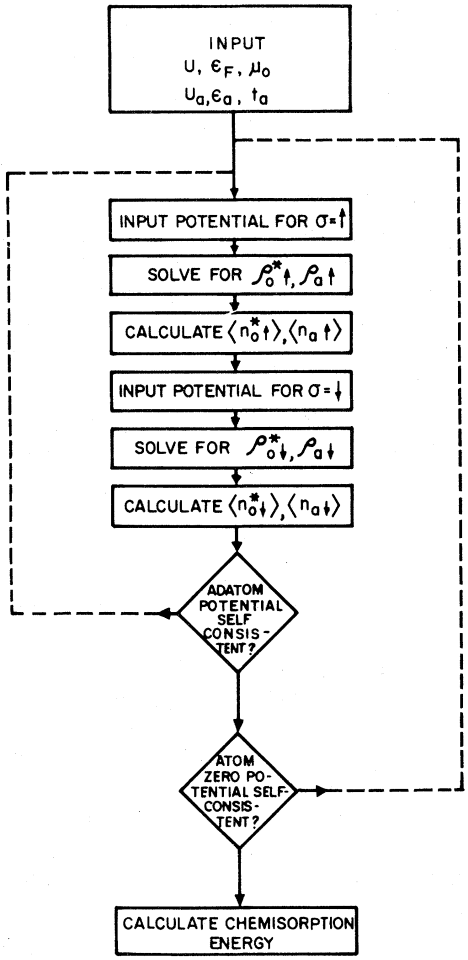

FIG. 6. Block diagram indicating the basic steps for achieving the self-consistent electronic density of states at the adatom (a) and at the metal atom below (0), and for determining the chemisorption energy.

the nonmagnetic solution. This is shown in Fig. 4 where graphic solutions of (3.11) are presented for a paramagnetic substrate. If, on the other hand, the substrate is in the ferromagnetic state, all three solutions for small t_a are magnetic, two ferromagnetic ($\mu_a > 0$, adsorbate moment parallel to the substrate) and one antiferromagnetic ($\mu_a > 0$, absorbate moment antiparallel to the substrate). The lowest energy corresponds to this last one. For large t_a the only solution is the antiferromagnetic one. This is shown in Fig. 5. The parameters, indicated in the caption, correspond to hydrogen absorbed on ferromagnetic iron ($W \cong 2$ eV). Many other larger and larger loops are necessary if self-consistency is to be achieved for the various orbitals of the various substrate atoms.

For the sake of simplicity and viability, we only included the $\alpha = 1$ d orbital for both spins, and only at the atom at site 0 that is directly linked to the chemisorbed hydrogen atom. We therefore assumed

$$n_{i\alpha\uparrow} = 0.969, \quad n_{i\alpha\downarrow} = 0.571 \quad \text{for } i\alpha \neq 01 \tag{3.14}$$

a constant Fermi level ϵ_F, and that only the occupancy of the (01σ) states, in addition to the $(a\sigma)$ states, are to be determined self-consistently. If we label $\rho^*_{0\sigma}(\omega)$ and $n^*_{0\sigma}$ the spectral density of states and occupancy of the (01σ) states and $\rho_{a\sigma}$ and $n_{a\sigma}$ the corresponding functions for the absorbate, Fig. 6 shows the block diagram which describes the steps necessary to achieve self-consistency.

When self-consistency is obtained, the hydrogen chemisorption energy can be calculate from the expression

$$\begin{aligned} \Delta E = {} & \sum_{\sigma} \int_{-\infty}^{\epsilon_F} (\omega - \epsilon_F) \rho_{a\sigma}(\omega) d\omega - U_a \langle n_{a\uparrow} \rangle \langle n_{a\downarrow} \rangle - (\epsilon_a - \epsilon_F) \\ & + \sum_{\sigma} \int_{-\infty}^{\infty} (\omega - \epsilon_F) [\rho^*_{0\sigma}(\omega) - \tfrac{1}{5} \rho_\sigma(\omega)] d\omega - U [\langle n^*_{0\uparrow} \rangle \langle n^*_{0\downarrow} \rangle - 0.01 (n^2 - \mu^2)] \, . \end{aligned} \tag{3.15}$$

Here the first three terms are the contributions from the chemisorbed hydrogen atom; the rest is the contribution from the rearrangement in the occupation of the $\alpha = 1$ orbitals in the metal atom at site 0. In (3.15) $\rho_\sigma(\omega)$ is given by (2.6), n by (2.4), and μ by (2.5); they are properties of the clean substrate metal. It should be emphasized once again that our approximation neglects the contribution to the chemisorption energy from all orbitals in the metal atom at site 0 other than $\alpha = 1$, and from all other metal atoms other than $i = 0$.

IV. RESULTS AND DISCUSSION

We have presented a self-consistent theory of hydrogen chemisorption on ferromagnets. It is a zero-temperature theory where we have assumed that the substrate is in the completely ordered configuration, with all the local moments pointing along the magnetization direction. Finite-temperature calculations, which are lengthy but straightforward, can be accomplished by the use of the theory presented in Ref. 12.

We have assumed that the s hydrogen electrons couple to only one of the five d degenerate transition-metal bands, and only through a single atom (on-top configuration). This approximation has been justified before.[16]

In Fig. 7 we show the self-consistent antiferromagnetic solution as a function of t_a for the paramagnetic as well as for the ferromagnetic substrate. In the paramagnetic case, chemisorption induces a magnetic moment on the metal atom immediately below in the range of spin-polarized solutions for the hydrogen atom ($0 \le t_a \le t_{ac}$). More interesting is the case of chemisorption on ferromagnetic substrates. In that case, we see that there is a range of t_a values where the magnetic moment at the atom below, μ_0, increases upon chemisorption,

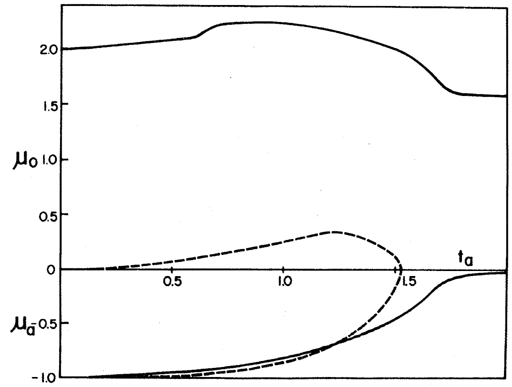

FIG. 7. Magnetic moment at the adatom μ_a and at the metal atom below μ_0 as a function of t_a for the cases of a paramagnetic (broken line) and ferromagnetic (solid line) substrate. The parameters are the same as in Fig. 5.

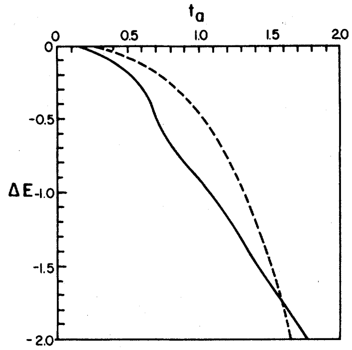

FIG. 8. Binding energy of hydrogen chemisorbed on a paramagnetic (broken line) and a ferromagnetic (solid line) substrate as a function of t_a. The energy is measured in units of W, the d half-bandwidth (~ 2 eV).

and another range where the effect is the opposite. It is also clear from the results that the range of values of t_a for which the hydrogen atom is appreciably spin polarized is larger for the ferromagnetic substrate than for the paramagnetic substrate.

In Fig. 8 we show the results for the chemisorption energy ΔE as a function of the hopping matrix element t_a. We display the results for the ferromagnetic substrate (solid line) as well as those obtained assuming the substrate to be in the paramagnetic state.

We see that ΔE is lower for the ferromagnetic state than for the paramagnetic case over a wide range of t_a values, and that only for very large t_a does the opposite hold. Over the range on which the hydrogen atom is spin polarized, the chemisorption is stronger on the ferromagnetic substrate.

From measurements of hydrogen chemisorption on paramagnetic transition-metal substrates,[16] the value for t_a should be between $1.2W$ and $1.4W$ for Fe, Co, and Ni. Therefore, we expect that the hydrogen atoms would be more tightly bound to the substrate as one goes from the paramagnetic to the ferromagnetic phase. This might explain the observed[5] decrease in the net desorption rate of the H_2-Ni system observed in going across the magnetic phase transition.

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