

Polarization effect on the chemisorption energy on transition metals.  
 II. Magnetic surface

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The previous calculation on the chemisorption energy in terms of the Anderson-Newns-type model with a quasimolecule approach has been extended to magnetic surfaces. Both half-filled band and band filling corresponding to Ni are considered. Depending on the electron density, the polarization effect on the chemisorption energy may or may not be sensitive to the degree of magnetization. Under certain conditions we have obtained a demagnetization of the surface by hydrogen chemisorption.

Recently, we have generalized Schönhammer's single-site projection technique<sup>1</sup> and applied it to the Anderson-Newns model<sup>2</sup> to investigate the polarization effect on the chemisorption energy on transition metals. In our work<sup>3</sup> (referred to as I) we have assumed a nonmagnetic surface. Such assumption is not valid for all transition metals according to experiments. For example, photoemission data indicate that the surface magnetization of Ni(100) is almost the same as that of the bulk,<sup>4</sup> and the electron-capture spectroscopy observes that only two atomic layers of Ni already show ferromagnetic behavior.<sup>5</sup> Furthermore, there is a demagnetization of the surface by hydrogen adsorption.<sup>6</sup> The situation is complicated by the recent discovery with polarized electron spectroscopy that the critical exponent  $\beta$  of the surface magnetization is different from that of the bulk.<sup>7</sup> In this paper we only consider the ground-state properties. Thus we will ignore the difference in  $\beta$ , but assume that the surface magnetization is the same as the bulk one.

The description of the model has been given in detail in I. The substrate is represented by a nearest-neighbor tight-binding band  $\sum'_{i,j,\sigma} t_{ij\sigma} a_{i\sigma}^\dagger a_{j\sigma}$ , where  $a_{i\sigma}^\dagger$  ( $a_{i\sigma}$ ) is the creation (annihilation) operator corresponding to the orbital localized at  $i$ . Only one valence level of the adsorbate is considered, with the associated creation (annihilation) operator  $a_{\alpha\sigma}^\dagger$  ( $a_{\alpha\sigma}$ ) for the adsorbate orbital localized at position  $\alpha$  on the surface. Far away from the surface the valence-level energy is  $E_{0\alpha}$  if singly occupied, but is  $2E_{0\alpha} + U$  if doubly occupied by two electrons of opposite spins. When the adsorbate is chemisorbed at  $\alpha$ , it is coupled to the nearest substrate atoms  $\langle i \rangle$  via the hybridization

$$\sum_{\langle i \rangle, \sigma} (V a_{i\sigma}^\dagger a_{\alpha\sigma} + V^* a_{\alpha\sigma}^\dagger a_{i\sigma})$$

and the Coulomb interaction  $\frac{1}{2} \sum_{\langle i \rangle, \sigma, \sigma'} W n_{i\sigma} n_{\alpha\sigma'}$ . Owing to the adsorbate potential, the hopping between atoms  $\langle ij \rangle$ , which are both nearest neighbors of  $\alpha$ , is modified to  $(1 + \gamma) t_{ij\sigma}$ , where  $\gamma$  is a parameter. The Hamiltonian can then be written as

$$H = H_m + \sum'_{i,j,\sigma} t_{ij\sigma} a_{i\sigma}^\dagger a_{j\sigma}, \tag{1}$$

where

$$H_m = E_\alpha \sum_\sigma n_{\alpha\sigma} + U n_{\alpha\uparrow} n_{\alpha\downarrow} + \sum_{\langle i \rangle, \sigma} (V a_{\alpha\sigma}^\dagger a_{i\sigma} + V^* a_{i\sigma}^\dagger a_{\alpha\sigma}) + \frac{1}{2} W \sum_{\langle i \rangle, \sigma, \sigma'} n_{i\sigma} n_{\alpha\sigma'} + (1 + \gamma) \sum_{\langle ij \rangle, \sigma} t_{ij\sigma} a_{i\sigma}^\dagger a_{j\sigma}. \tag{2}$$

The whole system can be visualized as a quasimolecule embedded in a matrix. The quasimolecule consists of the adsorbate and its nearest substrate atoms, and its Hamiltonian is just  $H_m$ . In (1) the sum excludes the case of both  $i$  and  $j$  in the quasimolecule. In (2)  $E_\alpha = E_{0\alpha} + V_{0\alpha}$ , where  $V_{0\alpha}$  is the valence-level shift due to the substrate lattice potential.

We should point out that in the above equations we have kept the explicit spin dependence of the transfer integral  $t_{ij\sigma}$ . Therefore, the density of states of the substrate becomes spin dependent, capable of accommodating a finite magnetization.

The Hamiltonian will be solved with the quasimolecule projection technique. Let the number of sites of the substrate lattice be  $L$ , and the total number of electrons be  $N$ . For a magnetic substrate we have

$$n_\uparrow = N_\uparrow / L = (N + M) / 2L = (n + m) / 2$$

and

$$n_\downarrow = N_\downarrow / L = (N - M) / 2L = (n - m) / 2,$$

where  $N_\sigma$  is the number of  $\sigma$ -spin electrons and  $m$  is the magnetization. If we remove the restriction  $N_\uparrow = N_\downarrow$ , then the analysis of Sec. III (quasimolecule projection method) in I applies directly to the present problem. Hence we will not repeat the mathematics, but explain the procedure in terms of the physical picture.

The quasimolecule projection method gives an almost exact solution of the quasimolecule if it is isolated from the rest of the substrate. The adsorbate has four configurations: doubly occupied, singly occupied by either up

spin ( $\uparrow$ ) or down spin ( $\downarrow$ ), or empty. The configurations of the surrounding nearest substrate atoms are classified according to their total number of up spins,  $\mu$ , and total number of down spins,  $\nu$ . Allowing all possible values of  $\mu$  and  $\nu$ , the spin and charge fluctuation within the quasimolecule is fully taken into account. In this paper we assume a square lattice surface with the chemisorption site  $\alpha$  at the center of one square. In this case, the quasimolecule has 100 configurations. When the quasimolecule is coupled to the rest of the substrate, let  $\Phi_{i\mu\nu}$  be a weighted sum over all the configurations which have the same subconfiguration of the quasimolecule. The subconfiguration of the quasimolecule is specified by  $i\mu\nu$ , with  $i = 1, 2, 3$ , or 4 to label the occupation of the adsorbate. Then the trial function for the ground state of the whole system can be constructed as

$$\psi = \sum_{i,\mu,\nu} f_{i\mu\nu} \Phi_{i\mu\nu}. \quad (3)$$

Minimization of the energy  $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$  with respect to the variational parameters  $f_{i\mu\nu}$  leads to 100 coupled linear equations

$$\sum_{j,\omega,\tau} \langle \Phi_{i\mu\nu} | H - E | \Phi_{j\omega\tau} \rangle f_{j\omega\tau} = 0 \quad (4)$$

for all the 100 sets ( $i\mu\nu$ ). All the matrix elements in the above equation can be calculated as mentioned in I. To present the final resulting formula, we define  $E_{0\sigma}$  as the center of gravity of the  $\sigma$ -spin density of states  $\rho_{\sigma}(E)$ ,  $\bar{\epsilon}_{\sigma}$  as the mean  $\sigma$ -band energy per site, and

$$\bar{V}_{\sigma} = \frac{V}{N} \sum_{\langle j \rangle} \sum_{\vec{k} \in K(\sigma)} \exp[i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)], \quad (5)$$

where  $\langle j \rangle$  is a nearest neighbor of  $i$  and  $K(\sigma)$  is the set of occupied  $\sigma$ -spin band states. Then we have

$$\begin{aligned} \frac{\langle \Phi_{i\mu\nu} | H | \Phi_{i\mu\nu} \rangle}{\langle \Phi_{i\mu\nu} | \Phi_{i\mu\nu} \rangle} &= (p+q)E_{\alpha} + pqU + (p+q)(\mu+\nu)W + (L-1)(\bar{\epsilon}_{\uparrow} + \bar{\epsilon}_{\downarrow}) + (N_{\uparrow} - 1 + p)E_{0\uparrow} + (N_{\downarrow} - 1 + q)E_{0\downarrow} \\ &+ \left[ (1-2n_{\uparrow}) \left( \frac{1-p}{1-n_{\uparrow}} - \frac{p}{n_{\uparrow}} \right) - \frac{1}{2} \left( \frac{4-\mu}{1-n_{\uparrow}} + \frac{\mu}{n_{\uparrow}} \right) + \frac{1}{9}(1+\gamma) \frac{\mu(4-\mu)}{n_{\uparrow}(1-n_{\uparrow})} \right] \bar{\epsilon}_{\uparrow} \\ &+ \left[ (1-2n_{\downarrow}) \left( \frac{1-q}{1-n_{\downarrow}} - \frac{q}{n_{\downarrow}} \right) - \frac{1}{2} \left( \frac{4-\nu}{1-n_{\downarrow}} + \frac{\nu}{n_{\downarrow}} \right) + \frac{1}{9}(1+\gamma) \frac{\nu(4-\nu)}{n_{\downarrow}(1-n_{\downarrow})} \right] \bar{\epsilon}_{\downarrow}, \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\langle \Phi_{3,\mu+1,\nu} | H | \Phi_{1\mu\nu} \rangle}{(\langle \Phi_{3,\mu+1,\nu} | \Phi_{3,\mu+1,\nu} \rangle \langle \Phi_{1\mu\nu} | \Phi_{1\mu\nu} \rangle)^{1/2}} &= \frac{\langle \Phi_{4,\mu+1,\nu} | H | \Phi_{2\mu\nu} \rangle}{(\langle \Phi_{4,\mu+1,\nu} | \Phi_{4,\mu+1,\nu} \rangle \langle \Phi_{2\mu\nu} | \Phi_{2\mu\nu} \rangle)^{1/2}} \\ &= \frac{1}{4n_{\uparrow}(1-n_{\uparrow})} [(4-\mu)(\mu+1)]^{1/2} \bar{V}_{\uparrow}, \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{\langle \Phi_{2,\mu,\nu+1} | H | \Phi_{1\mu\nu} \rangle}{(\langle \Phi_{2,\mu,\nu+1} | \Phi_{2,\mu,\nu+1} \rangle \langle \Phi_{1\mu\nu} | \Phi_{1\mu\nu} \rangle)^{1/2}} &= \frac{\langle \Phi_{4,\mu,\nu+1} | H | \Phi_{3\mu\nu} \rangle}{(\langle \Phi_{4,\mu,\nu+1} | \Phi_{4,\mu,\nu+1} \rangle \langle \Phi_{3\mu\nu} | \Phi_{3\mu\nu} \rangle)^{1/2}} \\ &= \frac{1}{4n_{\downarrow}(1-n_{\downarrow})} [(4-\nu)(\nu+1)]^{1/2} \bar{V}_{\downarrow}, \end{aligned} \quad (8)$$

$$\frac{\langle \Phi_{i,\mu+1,\nu} | H | \Phi_{i\mu\nu} \rangle}{(\langle \Phi_{i,\mu+1,\nu} | \Phi_{i,\mu+1,\nu} \rangle \langle \Phi_{i\mu\nu} | \Phi_{i\mu\nu} \rangle)^{1/2}} = \left[ \frac{(4-\mu)(\mu+1)}{n_{\uparrow}(1-n_{\uparrow})} \right]^{1/2} \bar{\epsilon}_{\uparrow}, \quad (9)$$

and

$$\frac{\langle \Phi_{i,\mu,\nu+1} | H | \Phi_{i\mu\nu} \rangle}{(\langle \Phi_{i,\mu,\nu+1} | \Phi_{i,\mu,\nu+1} \rangle \langle \Phi_{i\mu\nu} | \Phi_{i\mu\nu} \rangle)^{1/2}} = \left[ \frac{(4-\nu)(\nu+1)}{n_{\downarrow}(1-n_{\downarrow})} \right]^{1/2} \bar{\epsilon}_{\downarrow}. \quad (10)$$

The other nontrivial matrix elements are the reverse processes of (7)–(10). The rest of the elements are zero. In Eq. (6) the values of  $p$  and  $q$  are  $(p,q)=(1,1)$  for  $i=1$ ,  $(p,q)=(1,0)$  for  $i=2$ ,  $(p,q)=(0,1)$  for  $i=3$ , and  $(p,q)=(0,0)$  for  $i=4$ .

In order to investigate the spin and charge polarization effect, we also need to solve the same problem for the case without polarization. Now we only need to specify the four configurations of the adsorbate. Therefore, the trial function has only four components as

$$\Psi = \sum_{i=1}^4 f_i \Phi_i, \quad (11)$$

and the corresponding coupled equations are

$$\sum_{j=1}^4 \langle \Phi_i | (H - E) | \Phi_j \rangle f_j = 0, \quad i = 1, 2, 3, 4. \quad (12)$$

The matrix elements have the simple forms

$$\begin{aligned} \frac{\langle \Phi_i | H | \Phi_i \rangle}{\langle \Phi_i | \Phi_i \rangle} &= (p+q)E_\alpha + pqU + 4(p+q)(n_\uparrow + n_\downarrow)W \\ &+ [N_\uparrow - 1 + p]E_{0\uparrow} + [N_\downarrow - 1 + q]E_{0\downarrow} \\ &+ (L - 1 + 2\gamma)\bar{\epsilon}_\uparrow + (L - 1 + 2\gamma)\bar{\epsilon}_\downarrow, \quad (13) \end{aligned}$$

$$\begin{aligned} \frac{\langle \Phi_3 | H | \Phi_1 \rangle}{(\langle \Phi_3 | \Phi_3 \rangle \langle \Phi_1 | \Phi_1 \rangle)^{1/2}} &= \frac{\langle \Phi_4 | H | \Phi_2 \rangle}{(\langle \Phi_4 | \Phi_4 \rangle \langle \Phi_2 | \Phi_2 \rangle)^{1/2}} \\ &= [n_\uparrow(1-n_\uparrow)]^{1/2} \bar{V}_\uparrow, \quad (14) \end{aligned}$$

$$\begin{aligned} \frac{\langle \Phi_2 | H | \Phi_1 \rangle}{(\langle \Phi_2 | \Phi_2 \rangle \langle \Phi_1 | \Phi_1 \rangle)^{1/2}} &= \frac{\langle \Phi_4 | H | \Phi_3 \rangle}{(\langle \Phi_4 | \Phi_4 \rangle \langle \Phi_3 | \Phi_3 \rangle)^{1/2}} \\ &= [n_\downarrow(1-n_\downarrow)]^{1/2} \bar{V}_\downarrow. \quad (15) \end{aligned}$$

The other nontrivial matrix elements are the reverse processes of (14) and (15), and the rest of the elements are zero.

In our numerical calculation the spin-polarized density of states  $\rho_\sigma(E)$  of the narrow band is approximated by a rectangular density of states of bandwidth  $D=2$ . When the magnetization  $m=0$ , the center of gravity of  $\rho_\sigma(E)$  [same as that of  $\rho_{-\sigma}(E)$ ] is set as the zero reference energy. For given values of the electron density  $n$  and nonzero  $m$ , the centers of gravity of  $\rho_\sigma(E)$  and  $\rho_{-\sigma}(E)$  are shifted to achieve a constant Fermi energy for the whole system. It is not difficult to show that for a nearest-neighbor tight-binding band  $\bar{V}_\sigma$  can be well approximated as  $\bar{V}_\sigma = n_\sigma(1-n_\sigma)V$ . We also set  $E_\alpha = -0.5$ , and for such a value of  $E_\alpha$  the charge polarization on the adsorbate increases monotonically with  $-V$  (as will be shown in the following). Hence it is reasonable to assume that  $\gamma$  is proportional to  $\bar{V} = (\bar{V}_\uparrow + \bar{V}_\downarrow)$ . For simplicity we let  $\gamma = -\bar{V}/U$ . Since  $W$  is a two-particle coupling constant and  $\bar{V}$  is a single-particle coupling constant, we will set  $W/U = 0.4(\bar{V}/U)^2$ .

The input parameters for the numerical calculation are then reduced to only  $n$ ,  $m$ ,  $V$ , and  $U$ . We choose two values:  $n=1$  for the generally interested half-filled band and  $n=1.88$  corresponding to the "one-band" version of Ni. For  $U$  we also choose two values:  $U=1$  suitable for the narrow  $d$  band ( $U \sim D$ ) and  $U=10$  to simulate the "large- $U$ " limit. In order to cover the whole range from the nonmagnetic to the saturated ferromagnetic state, we set  $m=0, 0.3, 0.7$ , and  $1$  for  $n=1$ , and  $m=0, 0.036, 0.084$ , and  $0.12$  for  $n=1.88$ . Then all the physical quantities calculated are functions of  $V$ .

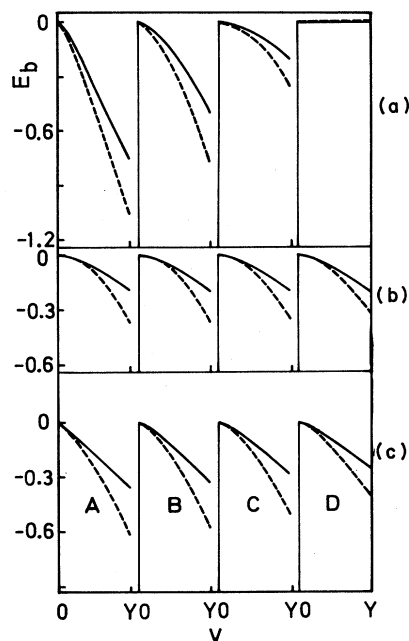


FIG. 1. Chemisorption energy for  $U=1$ . Solid curves for cases without polarization and dashed curves for cases with polarization. On horizontal axis  $Y = -0.25$ . A, B, C, and D correspond to magnetization  $m=0, 0.3(2-n), 0.7(2-n)$ , and  $1$ , respectively. The values of parameters are  $E_\alpha = -0.5$  and  $n=1$  for (a),  $E_\alpha = -0.5$  and  $n=1.88$  for (b), and  $E_\alpha = -0.1$  and  $n=1.88$  for (c).

Let us denote  $E_c$  as the total energy of the system when the adsorbate is far away from the surface, and  $E_p + E_c$  and  $E_u + E_c$  as the variational ground-state energies for the cases with and without the polarization effect, respectively. It has been shown in I that  $E_p - E_u = E_{bp} - E_{bu}$ ,

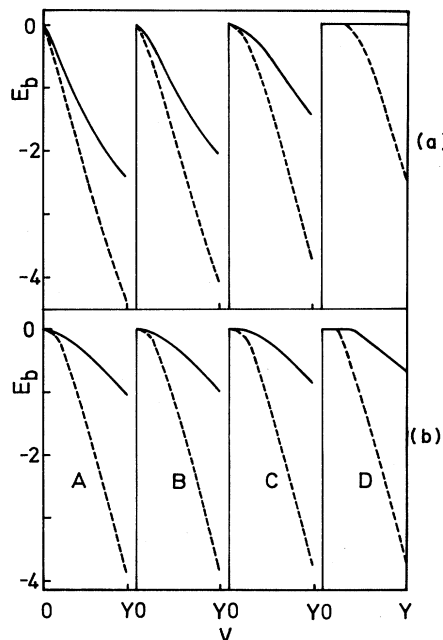


FIG. 2. Same as in Fig. 1 but for  $U=10$  and  $Y = -1.25$ .

where  $E_{bp}$  and  $E_{bu}$  are, respectively, the chemisorption energies for the case with and without the polarization effect. Therefore, as far as the polarization effect is concerned we can conveniently redefine  $E_{bp}$  and  $E_{bu}$  as the chemisorption energies. The chemisorption energies are shown in Fig. 1 for  $U=1$  and in Fig. 2 for  $U=10$ . The solid curves are for the case without polarization while the dashed curves are for the case with polarization. In both figures (a) is for  $n=1$  and (b) is for  $n=1.88$ . In all the figures presented in this paper, columns A, B, C, and D correspond to different magnetization  $m=0, 0.3(2-n), 0.7(2-n),$  and  $2-n$ , respectively. Because the number of holes is very small for  $n=1.88$ , the polarization effect on the chemisorption energy is very insensitive to the magnetization from the nonmagnetic to the saturated ferromagnetic state. It is not so, however, for the case  $n=1$  where the dynamics of the system depends strongly on the electronic response to the polarization within the quasimolecule. With increasing magnetization the number of electrons (holes) in the up-spin (down-spin) band increases from  $n/2$ , and so hinders the charge and spin polarizability of the system. At the limiting case  $n=1$  and  $m=1$ , we notice that there is no polarization effect at all. In order to demonstrate this general feature, in Fig. 1 we also show the case  $n=1.88$ ,  $E_a=-0.1$ , and  $U=1$  in part (c). Again, we see the chemisorption energies very insensitive to the degree of magnetization.

The polarization enhancement of the chemisorption energy manifests itself in the spin and charge relaxation within the quasimolecule. Let us define the operators  $Q_a=n_{a\uparrow}+n_{a\downarrow}$ ,  $P_a=n_{a\uparrow}-n_{a\downarrow}$ ,  $Q_s=\sum(n_{i\uparrow}+n_{i\downarrow})$ , and  $P_s=\sum(n_{i\uparrow}-n_{i\downarrow})$ , where the summation runs over the four substrate atoms within the quasimolecule. Then the expectation values

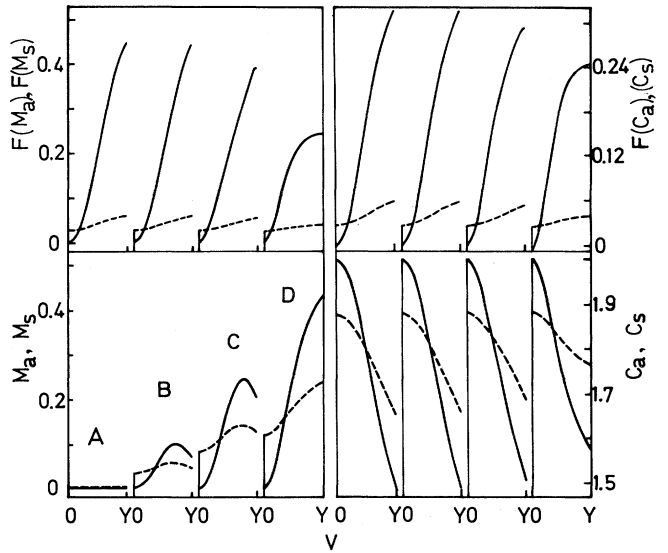


FIG. 4. Same as in Fig. 3 but for  $n=1.88$ .

$$M_a = \langle \Psi | P_a | \Psi \rangle / \langle \Psi | \Psi \rangle,$$

$$M_s = \langle \Psi | P_s | \Psi \rangle / \langle \Psi | \Psi \rangle,$$

$$C_a = \langle \Psi | Q_a | \Psi \rangle / \langle \Psi | \Psi \rangle,$$

and

$$C_s = \langle \Psi | Q_s | \Psi \rangle / \langle \Psi | \Psi \rangle$$

measure the spin and charge polarization within the quasimolecule. For a complete picture, we have also computed the fluctuations

$$F(A) = \langle \Psi | B^2 | \Psi \rangle / \langle \Psi | \Psi \rangle - A^2,$$

with  $(A, B) = (C_a, Q_a), (M_a, P_a), (C_s, Q_s),$  and  $(M_s, P_s)$ . The results are shown in Fig. 3 for  $n=1$  and  $U=1$ , and in

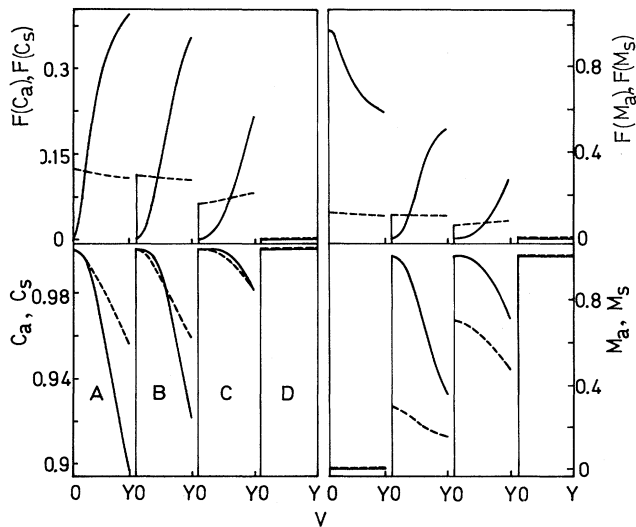


FIG. 3. Spin ( $M_a$  and  $M_s$ ) and charge ( $C_a$  and  $C_s$ ) and their fluctuations [ $F(M_a)$  and  $F(M_s)$  for spin and  $F(C_a)$  and  $F(C_s)$  for charge] within a quasimolecule for  $n=1$  and  $U=1$ . The subscripts  $a$  and  $s$  label, respectively, the adatom (solid curves) and its nearest-neighbor substrate atoms (dashed curves). On horizontal axis  $Y=-0.25$ .

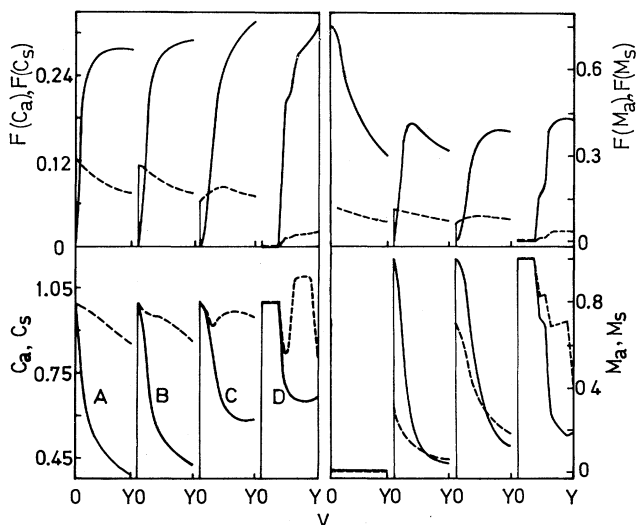


FIG. 5. Same as in Fig. 3 but for  $U=10$  and  $Y=-1.25$ .

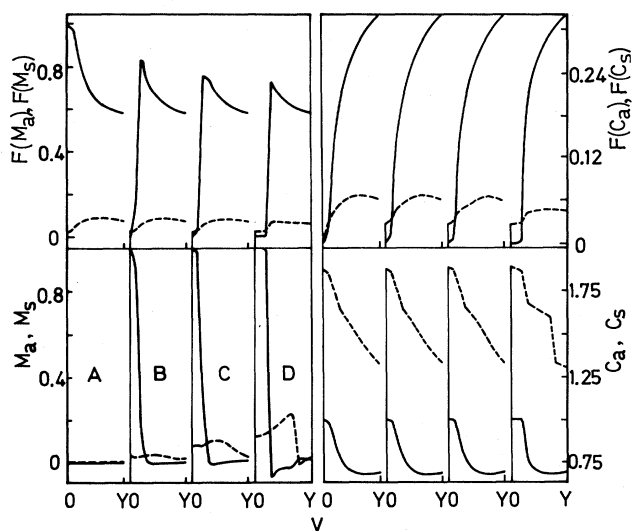


FIG. 6. Same as in Fig. 3 but for  $n=1.88$ ,  $U=10$ , and  $Y=-1.25$ .

Fig. 4 for  $n=1.88$  and  $U=1$ . For  $n=1$  the adsorbate is always singly occupied at  $V=0$ . Hence for  $m=0$  we have both  $M_a=0$  and  $M_s=0$ . However, if  $m \neq 0$  the mean energies of up-spin electrons and down-spin electrons are different even at  $V=0$ . Hence at  $V=0$  the singly occupied adsorbate has a definite spin and so  $M_a=1$ . As  $-V$  increases, the quasimolecule relaxes, causing all  $M_a$ ,  $M_s$ ,  $C_a$ , and  $C_s$  to decrease, except for the saturated ferromagnetic case where the spin-polarized band is either completely full or empty. On the other hand, for  $n=1.88$  the adsorbate is doubly occupied at  $V=0$  and the down-spin band can never be empty. Since at  $V=0$  the adsorbate is nonmagnetic, as  $-V$  increases, the relaxation of the quasimolecule drives the flow of electrons from the quasi-

molecule to the substrate with the corresponding increases of  $M_a$  and  $M_s$ . As the adsorbate plays the dominating role in the quasimolecule, the fluctuations  $F(C_a)$  and  $F(M_a)$  are stronger than the fluctuations  $F(C_s)$  and  $F(M_s)$ .

Similar results are shown in Fig. 5 for  $n=1$  and  $U=10$ , and in Fig. 6 for  $n=1.88$  and  $U=10$ . Here, due to the large value of  $U$ , the adsorbate is always singly occupied at  $V=0$ . We should notice that the range of  $V$  in Figs. 5 and 6 is much larger than that in Figs. 3 and 4 (1.25 against 0.25). Hence for a small value of  $V$  the physical picture of  $U=10$  is similar to that of  $U=1$ . However, when  $-V$  becomes large,  $M_a$ ,  $M_s$ ,  $C_a$ , and  $C_s$  exhibit a complicated structure which reflects the intrinsic properties of the quasimolecule. As the coupling  $V$  gets very strong, the situation simulates a molecule in contact with a particle reservoir. For a given number of electrons in the molecule, the molecular orbitals can be classified according to the spin eigenvalues. Hence as  $-V$  increases, the molecular orbitals are shifted with respect to the mean band energy. At certain values of  $V$  a large number of particles may be transferred between the molecule and the reservoir in the fashion of a "quantum step." It would be very interesting to work out in details the dynamical process underlying the observed structure. Unfortunately, the problem is too difficult to solve at the moment.

Before closing this paper, we should emphasize the large enhancement of the chemisorption energy due to the spin and charge polarization around the adsorbate. If the doubly occupied adsorbate valence level has an energy ( $2E_a+U$ ) higher than the Fermi energy,  $M_a$  and  $M_s$  decrease monotonically with increasing  $-V$ . This conclusion may very likely be relevant to the observed demagnetization of the surface by hydrogen adsorption.<sup>6</sup> Finally, at the large- $U$  limit with a strong coupling within the quasimolecule, the situation corresponding to a molecule in contact with a particle reservoir provides a challenging problem.

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