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Polarization effect on the chemisorption energy on transition metals

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We have investigated the spin- and charge-polarization effect on the chemisorption energy in terms of an Anderson-Newns-type model Hamiltonian with a quasimolecule approach. The quasimolecule consists of the adsorbate and its nearest substrate atoms, and is embedded in the rest of the substrate. Using a quasimolecule projection method, which is a generalization of Schönhammer's single-site projection technique, the trial function for the ground state describes the quasimolecule exactly. Numerical solution indicates a 20−30 % change of the chemisorption energy due to the polarization effect to make the adsorbate bond more strongly to the substrate.

I. INTRODUCTION

Depending on the electronic properties of substrates, various models have been proposed to study chemisorption. For chemisorption on transition metals, the Anderson-Newns model[1-6] and its modified version[7-13] have been extensively used. Besides the chemisorption energy, the overlap effect,[14] the screening and polarization,[7,15] the dissociative process,[8] the nature of the bond,[11] and the core-level spectra in adsorbates[16,17] was also investigated. Recently, this model has been reviewed in detail by Muscat and Newns.[18]

When an adsorbate approaches a surface, the image potential, the charge transfer, and the polarization of the substrate electrons should be considered in a self-consistent calculation of the adsorbate valence levels and the local density of states. To perform such a self-consistent calculation, one needs to know the geometry of the chemisorption site and the effective range of polarization. Sophisticated numerical calculations[19-22] indicate that the exact geometrical position of a single adsorbate on a surface varies with metals and with crystallographic planes. Nevertheless, in most cases the adatom is found to occupy a site of maximum coordination, i.e., a hollow site in the surface.[18] Regarding the effective range of polarization, the ultraviolet photoemission spectra below the bottom of the substrate valence band suggest a picture in which the chemisorbed H on transition-metal surfaces couples strongly to a limited number of substrate atoms in a quasimolecule fashion.

The problem becomes more complicated if the substrate is magnetic.[12] Even for a clean surface, the surface magnetization may not be the same as the bulk magnetization. Furthermore, it has been observed[23] that chemisorbed H on Ni(100) causes surface demagnetization. Although the present work can be generalized without difficulty to cope with a magnetic substrate, we will only consider here nonmagnetic surfaces in order to demonstrate our results in a clear physical picture.

To calculate the absolute chemisorption energy of an adatom is almost impossible. While many authors have calculated the chemisorption energy involving transition metals, very few have treated explicitly the effect of the substrate electron polarization on the adsorbate valence levels. The method of Bell and Madhukar[7] seems unsuitable for quantitative investigation.[9]

The present work will study this polarization effect using a modified Anderson-Newns model. We will extend the single-site projection operator approach of Schöhammer[24] and construct the projection operators for the "quasimolecule." It is then straightforward to calculate the change of chemisorption energy due to the induced polarization around the adsorbate.

II. THE MODEL

The electronic structure of the transition-metal substrate is complicated owing to the strong electron-electron correlation. As a starting point to formulating a solvable model, we assume a nondegenerate narrow band for the clean substrate. In terms of the orthonormal set of localized Wannier orbitals, the Hamiltonian for the substrate is simply

$$H_{s0}=\sum_{ij\sigma} t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}\ . \tag{1}$$

$a^{\dagger}_{i\sigma}$ ($a_{i\sigma}$) is the creation (annihilation) operator corresponding to the orbital localized at i. One may imagine that the exchange and the correlation effects are included in the band calculation, and therefore, t_{ij} is the effective electron transfer integral obtained as the Fourier transform of the band energy. Because we assume a nonmagnetic substrate, t_{ij} is spin independent. We also choose $t_{ii}=0$ as the zero reference energy.

To make the problem simple, we consider a single adsorbate with only one valence level. Far away from the surface the valence-level energy is $E_{0\alpha}$. Let α specify the position of the adsorbate on the surface and $V_{0\alpha}$ the valence-level shift due to the substrate lattice potential. Then the adsorbate can be described by the Hamiltonian

$$H_a=E_\alpha\sum_{\sigma} n_{\alpha\sigma}+Un_{\alpha\uparrow}n_{\alpha\downarrow}\ , \tag{2}$$

where $E_\alpha=E_{0\alpha}+V_{0\alpha}$, $n_{\alpha\sigma}=a^{\dagger}_{\alpha\sigma}a_{\alpha\sigma}$ with $a^{\dagger}_{\alpha\sigma}(a_{\alpha\sigma})$ being the creation (annihilation) operator associated with the adsorbate orbital localized at position α. U is the intra-adsorbate Coulomb energy.

The coupling between the adsorbate and the substrate can be expressed in the general form

$$\begin{aligned}H_{as}=&\sum_{i\sigma}(V_i a^{\dagger}_{i\sigma}a_{\alpha\sigma}+V_i^{*}a^{\dagger}_{\alpha\sigma}a_{i\sigma})\\&+\tfrac{1}{2}\sum_{i\sigma\sigma'} W_{i\sigma\sigma'}n_{i\sigma}n_{\alpha\sigma'}\ .\end{aligned} \tag{3}$$

The presence of the adsorbate potential also modifies the substrate band structure. This effect will be introduced with a set of parameters $\{\gamma_{ij}\}$ to change H_{0s} into

$$H_s=\sum_{ij\sigma}(1+\gamma_{ij})t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}\ , \tag{4}$$

The Hamiltonian of the whole system is then

$$\begin{aligned}H&=H_s+H_a+H_{as}\\&=\sum_{ij\sigma}(1+\gamma_{ij})t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}+E_\alpha\sum_{\sigma}n_{\alpha\sigma}+Un_{\alpha\uparrow}n_{\alpha\downarrow}\\&\quad+\sum_{i\sigma}(V_i a^{\dagger}_{i\sigma}a_{\alpha\sigma}+V_i^{*}a^{\dagger}_{\alpha\sigma}a_{i\sigma})\\&\quad+\tfrac{1}{2}\sum_{i\sigma\sigma'}W_{i\sigma\sigma'}n_{i\sigma}n_{\alpha\sigma'}\ .\end{aligned} \tag{5}$$

This is simply an Anderson-type Hamiltonian in the coordinate space representation.

This general Hamiltonian must be simplified in order to derive an analytical solution. Let us assume a square lattice for the surface and the chemisorption site α at the center of a square. Such geometry is rather common in real systems.[18] We mentioned earlier that the experimental data suggests a short-range coupling between the adsorbate and the substrate. For a practical reason, to be seen in the next section, we only retain the coupling between the adsorbate and its four nearest substrate atoms. For a nonmagnetic substrate assumed here, we further restrict ourselves to spin-independent interaction $W_{i\sigma\sigma'}=W_i$. If we choose real V_i for convenience, the simplified Hamiltonian has the form

$$\begin{aligned}H=&\sum_{ij\sigma'}{}' t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}+(1+\gamma)\sum_{\langle ij\rangle\sigma}t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}\\&+E_\alpha\sum_{\sigma}n_{\alpha\sigma}+Un_{\alpha\uparrow}n_{\alpha\downarrow}+V\sum_{\langle i\rangle\sigma}(a^{\dagger}_{\alpha\sigma}a_{i\sigma}+a^{\dagger}_{i\sigma}s_{\alpha\sigma})\\&+\tfrac{1}{2}W\sum_{\langle i\rangle\sigma\sigma'}n_{i\sigma}n_{\alpha\sigma'}\ .\end{aligned} \tag{6}$$

The primed sum excludes both i and j in the quasimolecule simultaneously, and summations over $\langle ij\rangle$ and $\langle i\rangle$ run over only the four atoms nearest to the adsorbate. Because of the symmetry, we can drop the subscripts of γ, V, and W.

If we rewrite (6) as

$$H=H_m+\sum_{ij\sigma'}{}' t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}\ , \tag{6'}$$

where

$$\begin{aligned}H_m=&\ E_\alpha\sum_{\alpha}n_{\alpha\sigma}+Un_{\alpha\uparrow}n_{\alpha\downarrow}+V\sum_{\langle i\rangle\sigma}(a^{\dagger}_{\alpha\sigma}a_{i\sigma}+a^{\dagger}_{i\sigma}a_{\alpha\sigma})\\&+\tfrac{1}{2}W\sum_{\langle i\rangle\sigma\sigma'}n_{i\sigma}n_{\alpha\sigma'}+(1+\gamma)\sum_{\langle ij\rangle\sigma}t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}\ ,\end{aligned} \tag{7}$$

then the whole system can be visualized as a quasimolecule embedded in a matrix. The quasimolecule consists of the adsorbate and its four nearest substrate atoms, and its Hamiltonian is just H_m. This quasimolecule picture helps to clarify the quasimolecule projection technique in the next section.

Before going further we must point out that the adsorbate-level shift $V_{0\alpha}$ is caused only by the substrate lattice potential since the interaction between the adsorbate and the substrate electrons is included in H_{as}. On the other hand, we have neglected the shift of the Wannier-state energy by the adsorbate ion core in order to reduce the number of parameters in the model Hamiltonian. We will return to this point when we perform the numerical calculation in Sec. IV.

III. QUASIMOLECULE PROJECTION METHOD

For an adsorbate with only one orbital, there are four configurations: doubly occupied by two antiparallel spin electrons, singly occupied by one up-spin electron, singly occupied by one down-spin electron, and empty. If the adsorbate is singly occupied by a σ-spin electron, the lowering of energy owing to the electron hopping between the adsorbate and its nearest substrate atoms enhances the probability of having $-\sigma$-spin electrons occupy these nearest substrate atoms. Similarly, if the number of electrons on the adsorbate deviates from the average number of electrons per atom, the surrounding substrate electrons may relax via a charge redistribution to compensate for the charge fluctuation on the adsorbate and so lower the energy. Besides, the charge redistribution is also driven by the Coulomb interaction between the electrons on adsorbate and on substrate. In other words, there is strong spin and charge polarization within the quasimolecule introduced in the previous section.

The total number of configurations of the quasimolecule is finite. The spin and charge polarization simply means that some of these configurations are energetically more favorable than the others. Therefore, if we neglect the polarization effect and find the lowest energy state of the quasimolecule embedded in the matrix, the ground state of the whole system can be well approximated by properly projecting out partially the unfavored configurations from this lowest energy state. This approach is exactly a generalization of the single-site projection operator method used by Schönhammer.[24]

In practice it is easier to start directly from the trial function based on the concept of the quasimolecule projection operation. Let the total number of electrons of the whole system be N. For a nonmagnetic substrate, we have $N(\uparrow)=N(\downarrow)=N/2$, where $N(\sigma)$ is the number of σ-spin electrons. A configuration can be defined as follows. Let Γ (or Ω) be a set of μ (or ν) substrate atoms within the quasimolecule, and G (or F) a set of $N/2-\mu-1$ [or $(N/2-\nu-1]$ substrate atoms outside the quasimolecule. Then

$$\Phi(pq:\mu\nu:\Gamma\Omega:GF)=a^\dagger_{p\uparrow}a^\dagger_{q\downarrow}\prod_{j\in\Gamma}a^\dagger_{j\uparrow}\prod_{k\in\Omega}a^\dagger_{k\downarrow}\prod_{g\in G}a^\dagger_{g\uparrow}\prod_{f\in F}a^\dagger_{f\downarrow}\,|0\rangle\ , \qquad (8)$$

where p and q are not the substrate atoms inside the quasimolecule, represents one configuration.

The configurations can be separated into four groups: (1) $p=q=\alpha$ for the adsorbate being doubly occupied, (2) $p=\alpha$ and $q\neq\alpha$ for the adsorbate being singly occupied by $\uparrow$-spin electron, (3) $p\neq\alpha$ and $q=\alpha$ for the substrate being singly occupied by a $\downarrow$-spin electron, and (4) $p\neq\alpha$ and $q\neq\alpha$ for the adsorbate being empty. For a given degree of spin and charge polarization within the quasimolecule, the many-electron wave function can be expressed in the general form

$$\Phi_{1\mu\nu}=\sum_{\Gamma\Omega FG}A(\alpha\alpha:\mu\nu:\Gamma\Omega:GF)\times\Phi(\alpha\alpha:\mu\nu:\Gamma\Omega:GF) \qquad (9a)$$

for the adsorbate being doubly occupied,

$$\Phi_{2\mu\nu}=\sum_{q\Gamma\Omega FG}A(\alpha q:\mu\nu:\Gamma\Omega:GF)\times\Phi(\alpha q:\mu\nu:\Gamma\Omega:GF) \qquad (9b)$$

with $q\neq\alpha$ for the adsorbate being singly occupied by $\uparrow$ spin,

$$\Phi_{3\mu\nu}=\sum_{p\Gamma\Omega FG}A(p\alpha:\mu\nu:\Gamma\Omega:GF)\times\Phi(p\alpha:\mu\nu:\Gamma\Omega:GF) \qquad (9c)$$

with $p\neq\alpha$ for the adsorbate being singly occupied by a $\downarrow$ spin, and

$$\Phi_{4\mu\nu}=\sum_{pq\Gamma\Omega FG} A(pq{:}\mu\nu{:}\Gamma\Omega{:}GF)\times\Phi(pq{:}\mu\nu{:}\Gamma\Omega{:}GF) \tag{9d}$$

with $p\neq\alpha$ and $q\neq\alpha$ for the adsorbate being empty.

For the square lattice considered here, both μ and ν can take the values 0, 1, 2, 3, or 4. Therefore, there are 100 wave functions of the form (9a)–(9d) and the trial function for the ground state can be constructed as

$$\Psi=\sum_{i\mu\nu} f_{i\mu\nu}\Phi_{i\mu\nu}\ . \tag{10}$$

The coefficients $A(pq{:}\mu\nu{:}\Gamma\Omega{:}GF)$ in (9a)–(9d) can be determined self-consistently with the quasichemical approximation proposed by Gutzwiller,[25] which is just the single-site approximation in Kikuchi's cluster variational expansion.[26] The reader is referred to the original work for the detailed computation scheme. The coefficients $f_{i\mu\nu}$ are the variational parameters to minimize the energy $E=\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$. The minimization process leads to solving the coupled equations

$$\sum_{j\omega\tau}\langle\Phi_{i\mu\nu}|H-E|\Phi_{j\omega\tau}\rangle f_{j\omega\tau}=0 \tag{11}$$

for all the 100 sets $(i\mu\nu)$.

The matrix elements $\langle\Phi_{i\mu\nu}|H|\Phi_{j\omega\tau}\rangle$ and $\langle\Phi_{i\mu\nu}|\Phi_{j\omega\tau}\rangle$ can also be calculated with the quasichemical approximation. The algebra is straightforward and here we present only the final results. If we define $\bar{\epsilon}$ as the mean band energy per electron of the clean substrate in the absence of the adsorbate, the diagonal matrix elements are

$$\begin{aligned}\langle\Phi_{1\mu\nu}|H|\Phi_{1\mu\nu}\rangle/\langle\Phi_{1\mu\nu}|\Phi_{1\mu\nu}\rangle=&\ (N-1)\bar{\epsilon}+2E_\alpha+U+(\mu+\nu)W\\&-[48-2(1+\gamma)(4\mu+4\nu-\mu^2-\nu^2)]\bar{\epsilon}/9\ ,\end{aligned} \tag{12a}$$

$$\begin{aligned}\langle\Phi_{2\mu\nu}|H|\Phi_{2\mu\nu}\rangle/\langle\Phi_{2\mu\nu}|\Phi_{2\mu\nu}\rangle&=\langle\Phi_{3\mu\nu}|H|\Phi_{3\mu\nu}\rangle/\langle\Phi_{3\mu\nu}|\Phi_{3\mu\nu}\rangle\\&=(N-1)\bar{\epsilon}+E_\alpha+(\mu+\nu)W/2\\&\quad-[48-2(1+\gamma)(4\mu+4\nu-\mu^2-\nu^2)]\bar{\epsilon}/9\ ,\end{aligned} \tag{12b}$$

and

$$\langle\Phi_{4\mu\nu}|H|\Phi_{4\mu\nu}\rangle/\langle\Phi_{4\mu\nu}|\Phi_{4\mu\nu}\rangle=(N-1)\bar{\epsilon}-[48-2(1+\gamma)(4\mu+4\nu-\mu^2-\nu^2)]\bar{\epsilon}/9\ . \tag{12c}$$

For the off-diagonal matrix elements, we first notice that $\langle\Phi_{i\mu\nu}|\Phi_{j\omega\tau}\rangle\propto\delta_{ij}\delta_{\mu\omega}\delta_{\nu\tau}$. The nontrivial off-diagonal elements of the Hamiltonian are connected to the hopping of electrons between the adsorbate and its four nearest neighbors (the intraquasimolecule hopping), and between these four neighbors and the rest of the substrate (the quasimolecule-substrate hopping). For the intraquasimolecule hopping, let us define

$$\bar{V}=2V\sum_{\langle j\rangle}\left[\frac{1}{L}\sum_{\vec{k}}{}'\exp(i\vec{k}\cdot\vec{R}_j)\right]\ , \tag{13}$$

where L is the total number of atoms in the substrate and the primed sum runs over all the $\vec{k}$ states in the Fermi sea of the clean substrate. In terms of $\bar{V}$ we obtain the following elements for the intraquasimolecule hopping:

$$\langle\Phi_{3,\mu+1,\nu}|H|\Phi_{1\mu\nu}\rangle/(\langle\Phi_{3,\mu+1,\nu}|\Phi_{3,\mu+1,\nu}\rangle\langle\Phi_{1\mu\nu}|\Phi_{l\mu\nu}\rangle)^{1/2}=\xi_{31}(\mu\nu)[(\mu+1)(4-\mu)]^{1/2}\bar{V}/2\ , \tag{14a}$$

$$\langle\Phi_{4,\mu+1,\nu}|H|\Phi_{2\mu\nu}\rangle/(\langle\Phi_{4,\mu+1,\nu}|\Phi_{4,\mu+1,\nu}\rangle\langle\Phi_{2\mu\nu}|\Phi_{2\mu\nu}\rangle)^{1/2}=\xi_{42}(\mu\nu)[(\mu+1)(4-\mu)]^{1/2}\bar{V}/2\ , \tag{14b}$$

$$\langle\Phi_{2,\mu,\nu+1}|H|\Phi_{1\mu\nu}\rangle/(\langle\Phi_{2,\mu,\nu+1}|\Phi_{2,\mu,\nu+1}\rangle\langle\Phi_{1\mu\nu}|\Phi_{1\mu\nu}\rangle)^{1/2}=\xi_{21}(\mu\nu)[(\nu+1)(4-\nu)]^{1/2}\bar{V}/2\ , \tag{14c}$$

and

$$\langle\Phi_{4,\mu,\nu+1}|H|\Phi_{3\mu\nu}\rangle/(\langle\Phi_{4,\mu,\nu+1}|\Phi_{4,\mu,\nu+1}\rangle\langle\Phi_{3\mu\nu}|\Phi_{3\mu\nu}\rangle)^{1/2}=\xi_{43}(\mu\nu)[(\nu+1)(4-\nu)]^{1/2}\bar{V}/2\ . \tag{14d}$$

In the above equations, $\xi_{ij}(\mu\nu)$ can be written as the product of the power of N/L and the power of $(2-N/L)$. For the numerical calculation in the next section, we will assume $N/L=1$ and so $\xi_{ij}(\mu\nu)=1$. Therefore, we will not give here the explicit expression of $\xi_{ij}(\mu\nu)$ which is rather complicated.

The off-diagonal matrix elements corresponding to the quasimolecule-substrate hoppings have the similar form as

$$\langle \Phi_{i,\mu+1,\nu} | H | \Phi_{i\mu\nu} \rangle / (\langle \Phi_{i,\mu+1,\nu} | \Phi_{i,\mu+1,\nu} \rangle \langle \Phi_{i\mu\nu} | \Phi_{i\mu\nu} \rangle)^{1/2} = \xi_{i\uparrow}(\mu\nu)[(\mu+1)(4-\mu)]^{1/2}\overline{\epsilon}/2 \tag{15a}$$

and

$$\langle \Phi_{i,\mu,\nu+1} | H | \Phi_{i\mu\nu} \rangle / (\langle \Phi_{i,\mu,\nu+1} | \Phi_{i,\mu,\nu+1} \rangle \langle \Phi_{i\mu\nu} | \Phi_{i\mu\nu} \rangle)^{1/2} = \epsilon_{i\downarrow}(\mu\nu)[(\nu+1)(4-\nu)]^{1/2}\overline{\epsilon}/2 \; . \tag{15b}$$

The other nontrivial elements are the reverse processes of (14a)–(15b).

Before closing this section, we would like to emphasize two points. First, if we know the surface magnetization from experiments, we can empirically determine the number of electrons with ↑ spin and with ↓ spin. The above procedure for constructing the trial function and for calculating the matrix elements can be easily generalized to investigate the chemisorption on magnetic substrate. Of course the matrix elements will be extremely complicated, and some of the parameters in the Hamiltonian should be spin dependent. At the present stage of the theory for a qualitative investigation, it is necessary to understand first the simpler nonmagnetic surface.

The second point is about the effective range of spin and charge polarization. With only the polarization effect on the nearest neighbors of the adsorbate, we already have to diagonalize a 100×100 matrix indicated by (11). If we extend the polarization range, i.e., if we enlarge the size of the quasimolecule, the Hamiltonian matrix will be too large to be diagonalized by computer. Only if one assumes weak polarization will it be possible to use a lesser number of configurations by restricting the values of α and β, and so make the quasimolecule bigger. But then the quasimolecule is no longer specified exactly as we have done in this paper.

IV. POLARIZATION EFFECT

Knowing all the nontrivial matrix elements, (11) can be solved numerically for given values of γ, $\overline{V}$, W, $\overline{\epsilon}$, E_α, and the electron density $n = N/L$. When the adsorbate is far away from the surface, the energy of the whole system is simply $E_{0\alpha} + (N-1)\overline{\epsilon}$. If $\mathscr{E}_p$ is the lowest energy obtained from solving (11), then the chemisorption energy can be calculated as

$$E_{BP} = \mathscr{E}_p - E_{0\alpha} - (N-1)\overline{\epsilon} \; . \tag{16}$$

However, the valence-level shift $V_{0\alpha} = E_\alpha - E_{0\alpha}$ due to the substrate lattice potential is unknown. This is one of the main difficulties one encounters when trying to calculate the absolute value of the chemisorption energy.

This problem does not appear if we are interested only in the change of chemisorption energy owing to the spin and charge polarization. If we neglect the polarization, i.e., we only specify the configuration of the adsorbate but not the whole quasimolecule, then Eq. (9a)–(9d) reduce to

$$\Phi_1 = \sum_{FG} A(\alpha\alpha{:}GF)\Phi(\alpha\alpha{:}GF) \; , \tag{17a}$$

$$\Phi_2 = \sum_{qFG} A(\alpha q{:}GF)\Phi(\alpha q{:}GF), \quad q \neq \alpha \tag{17b}$$

$$\Phi_3 = \sum_{pGF} A(p\alpha{:}GF)\Phi(p\alpha{:}GF), \quad p \neq \alpha \tag{17c}$$

$$\Phi_4 = \sum_{pqGF} A(pq{:}GF)\Phi(pq{:}GF), \quad p \neq \alpha, \quad q \neq \alpha \tag{17d}$$

where

$$\Phi(pq{:}GF) = a^\dagger_{p\uparrow} a^\dagger_{q\uparrow} \prod_{g\epsilon G} a^\dagger_{g\uparrow} \prod_{f\epsilon F} a^\dagger_{f\downarrow} | 0 \rangle \; . \tag{18}$$

In the above equations, G (or F) is a set of $N/2-1$ substrate atoms without any restriction. The trial function (10) becomes

$$\Psi = \sum_{i=1}^{4} f_i \Phi_i \; . \tag{19}$$

Now we only have to solve four coupled equations when we minimize the total energy $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$:

$$\sum_{j=1}^{4} \langle \Phi_i | H - E | \Phi_j \rangle f_j = 0, \quad i = 1,2,3,4 \; . \tag{20}$$

Using the quasichemical approximation, the matrix elements are derived as

$$\langle \Phi_1 | H | \Phi_1 \rangle / \langle \Phi_1 | \Phi_1 \rangle = 2E_\alpha + U + 4W + 2\gamma\overline{\epsilon} + (N-1)\overline{\epsilon} \; , \tag{21a}$$

$$\begin{aligned}\langle\Phi_2|H|\Phi_2\rangle/\langle\Phi_2|\Phi_2\rangle &= \langle\Phi_3|H|\Phi_3\rangle/\langle\Phi_3|\Phi_3\rangle \\ &= E_\alpha+2W+2\gamma\bar{\epsilon}+(N-1)\bar{\epsilon}\,, \qquad (21\text{b})\end{aligned}$$

$$\langle\Phi_4|H|\Phi_4\rangle/\langle\Phi_4|\Phi_4\rangle=2\gamma\bar{\epsilon}+(N-1)\bar{\epsilon}\,, \qquad (21\text{c})$$

for the diagonal elements, and

$$\langle\Phi_i|H|\Phi_j\rangle/(\langle\Phi_i|\Phi_i\rangle\langle\Phi_j|\Phi_j\rangle)^{1/2}=\xi_{ij}\bar{V}\,, \qquad (22)$$

with $(i,j)=(1,2)$, $(2,1)$, $(1,3)$, $(3,1)$, $(2,4)$, $(4,2)$, $(3,4)$, $(4,3)$ for the nontrivial off-diagonal elements. ξ_{ij} again can be expressed as the product of the power of N/L and the power of $(2-N/L)$, and so becomes a unit for the case $N/L=1$ which we will consider here. All the other off-diagonal elements are zero.

For given values of the parameters which appeared in the Hamiltonian, we can solve the coupled equations (20) and let $\mathscr{E}_u$ be the lowest energy. Then, the chemisorption energy without the polarization effect is

$$E_{BU}=\mathscr{E}_u-E_{0\alpha}-(N-1)\bar{\epsilon}\,. \qquad (23)$$

The change of the chemisorption energy due to the polarization effect

$$E_{BP}-E_{BU}=\mathscr{E}_p-\mathscr{E}_u \qquad (24)$$

is independent of the value of $V_{0\alpha}$. Therefore, as far as the polarization effect is concerned, we can conveniently redefine the chemisorption energies

$$E_{BP}=\mathscr{E}_p-E_\alpha-(N-1)\bar{\epsilon}\,, \qquad (16')$$

$$E_{BU}=\mathscr{E}_u-E_\alpha-(N-L)\bar{\epsilon}\,. \qquad (23')$$

In the following numerical results, we use (16′) and (23′) to calculate the chemisorption energies.

We normalize all the energies with respect to U. $\bar{V}/U$ and E_α/U will be treated as two continuously varying parameters in the range $0\leq\bar{V}/U\leq0.5$ and $-1\leq E_\alpha/U\leq0$. In this range of E_α the charge fluctuation on the adsorbate is not very large (less than 25% from the numerical calculation). Hence, the net potential of the adsorbate seen by substrate electrons should be weakly repulsive. We will then set $\gamma=-\bar{V}/U$. At the end of Sec. II we pointed out that in our model Hamiltonian we have neglected the effect of the adsorbate ion core on the substrate Wannier-state energy. Since the charge fluctuation on the adsorbate is not very large, as an approximation we can include this ion-core effect in the Coulomb energy W and make W very small. Since W is a two-particle coupling constant and $\bar{V}$ is a single-particle coupling constant, we will assume $W/U=0.4(\bar{V}/U)^2$.

For a qualitative investigation, we assume a simple square density of states of width 2Δ for the clean substrate. For a given number of electron density n, the mean band energy $\bar{\epsilon}$ can be obtained easily. In this work we assume $n=1$ to study two cases, $\Delta/U=1$ and $\Delta/U=0.1$. The chemisorption energies are shown in Fig. 1 for $\Delta/U=1$ and in Fig. 2 for $\Delta/U=0.1$. In both figures the solid curves are for the cases with the polarization effect, while the dashed curves are for the cases without the polarization effect. We see that the polarization effect reduces the chemisorption energy by an amount of about 20% for $\Delta/U=1$ and 30% for $\Delta/U=0.1$.

To illustrate the connection between the decrease of the chemisorption energy and the spin and charge polarization, we have calculated the quantity which measures the amount of unpaired spin on the adsorbate

$$P_a=\sum_{\mu\nu}(|f_{2\mu\nu}|^2+|f_{3\mu\nu}|^2)\,, \qquad (25)$$

the quantity which measures the amount of unpaired spin in the quasimolecule

$$P_t=\sum_{\mu\nu}[(1+\mu-\nu)|f_{2\mu\nu}|^2+(1+\nu-\mu)|f_{3\mu\nu}|^2]\,, \qquad (26)$$

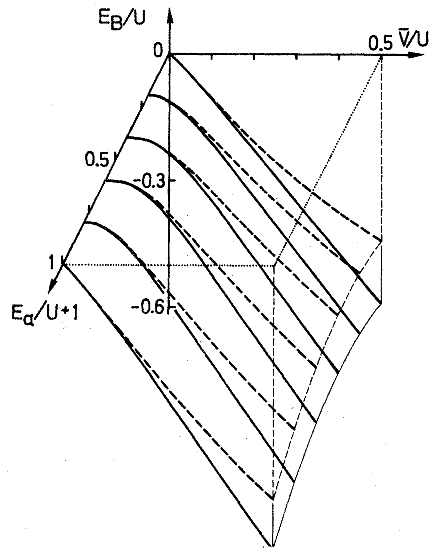

FIG. 1. Chemisorption energy for $\Delta/U=1$. Solid curves include the polarization effect but dashed curves do not.

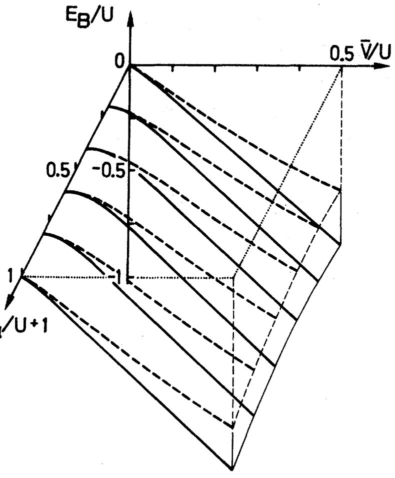

FIG. 2. Chemisorption energy for $\Delta/U=0.1$. Solid curves include the polarization effect but dashed curves do not.

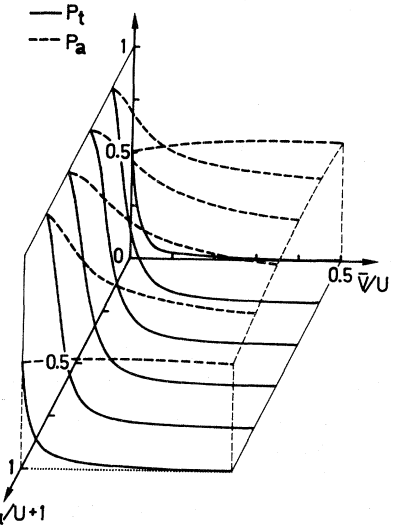

FIG. 4. Spin polarization of the adsorbate P_a and of the quasimolecule P_t for $\Delta/U=0.1$.

the amount of charge fluctuation on the adsorbate

$$Q_a=\sum_{\mu\nu}(|f_{1\mu\nu}|^2-|f_{4\mu\nu}|^2)\,, \tag{27}$$

and the amount of charge fluctuation on the substrate atoms in the quasimolecule

$$Q_{nn}=\sum_{i\mu\nu}(\mu+\nu-4)|f_{i\mu\nu}|^2\,. \tag{28}$$

P_a and P_t are shown as dashed curves and solid surves, respectively, in Fig. 3 for $\Delta/U=1$ and in Fig. 4 for $\Delta/U=0.1$. P_a in both figures are almost the same but P_t are very different, indicating a stronger spin polarization with increasing U/Δ ratio.

In Figs. 5 and 6 we plot Q_a (solid curves) and Q_{nn} (dashed curves) for $\Delta/U=1$ and $\Delta/U=0.1$, respectively. Again we see that the charge fluctuation on the adsorbate is rather insensitive to the variation of Δ/U. On the other hand, the charge fluctuation on the substrate atoms nearest to the adsorbate increases with decreasing Δ/U.

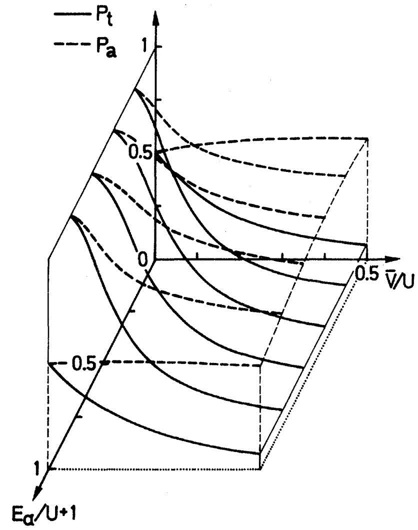

FIG. 3. Spin polarization of the adsorbate P_a and of the quasimolecule P_t for $\Delta/U=1$.

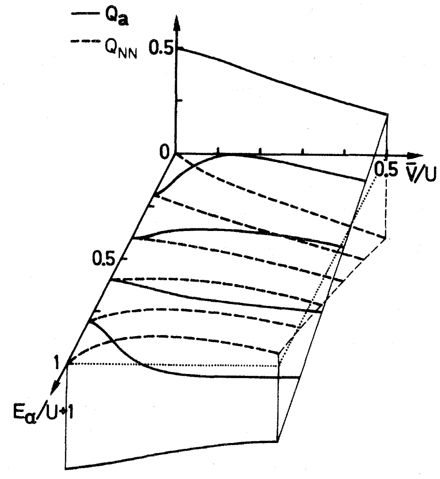

FIG. 5. Charge fluctuation of the adsorbate Q_a and of its nearest substrate atoms Q_{nn} for $\Delta/U=1$.

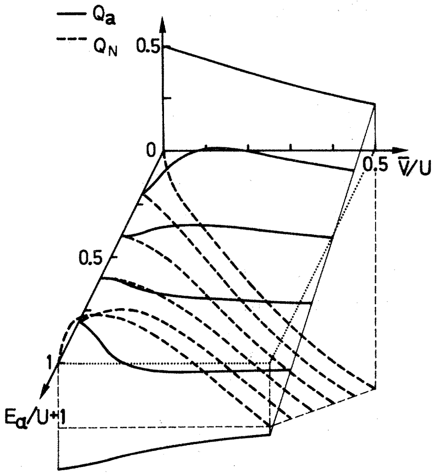

FIG. 6. Charge fluctuation of the adsorbate Q_a and of its nearest substrate atoms Q_{nn} for $\Delta/U=0.1$.

The reason that both P_a and Q_a are insensitive to the change of Δ/U is simply because we have restricted E_α/U in a range where the adsorbate is most likely singly occupied. The variation of (P_t-P_a) with Δ/U is characteristically different from the variation of Q_{nn} with Δ/U. This is owing to the fact that the Coulomb interaction W also drives the charge fluctuation Q_{nn} but not the spin fluctuation (P_t-P_a). We notice that at $\bar{V}/U=0$, i.e., when the adsorbate is not coupled to the substrate, our solutions are exact. However, for P_a, P_t, and Q_a, the exact solutions have discontinuities at $E_\alpha/U=0$ and $E_\alpha/U=-1$. Such behavior can also be seen in Figs. 3–6.

Since within the quasimolecule only the spin and charge fluctuation on the substrate atoms (which are nearest neighbors to the adsorbate) varies with Δ/U systematically in the same fashion as the reduction of the chemisorption energy varies with Δ/U, it is reasonable to draw the conclusion that such spin and charge polarization is responsible for the change of the chemisorption energy.

Although the numerical results are based on the special assignment of the values of the parameters, in our calculation we have covered a large range of parameter values. For all such parameter values we have discovered a large polarization effect. Therefore, the spin and charge polarization effect should be a generally important phenomena in the theory of chemisorption.

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