PHYSICAL REVIEW B VOLUME 8, NUMBER 10 15 NOVEMBER 1973

Chemisorption on Transition-Metal Surfaces: Electronic Structure

Anupam Madhukar
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 15 March 1973; revised manuscript received 18 July 1973)

A simple phenomenological model is used to develop a formalism for chemisorption on transition-metal surfaces. The model includes the Coulomb correlation on both the substrate atoms and the adatom. Nonorthogonality of the metal and adatom wave functions is allowed for through overlap integrals. The analysis provides condition for the existence of local moment on the adatom and can thus distinguish between the applicability of the existing molecular-orbital and Heitler-London approaches. In view of the growing wealth of reliable photoemission data, emphasis is laid on the electronic structure of the chemisorbed atom and substrate, rather than the binding energy. Though a detailed analysis of the data at the moment is hindered due to the unavailability of surface density of states of the clean substrate, simple use of the experimental value of the center of the occupied narrow *d* band leads to self-consistent values of various parameters. This reflects on the importance of the substrate correlation effects in chemisorbtion on narrow-band-metal surfaces.

I. INTRODUCTION

The term "electronic structure" of chemisorbed atoms on metallic surfaces refers to the self-consistently adjusted energy level, density of states, and occupation number of the adatom participating in the "molecule" it forms with the atoms of the substrate. Much experimental work has been done on the adsorbate configuration and binding energies on metallic surfaces but only recently have we obtained reliable data on the electronic structure of adsorbed gases on transition-metal surfaces. This long-felt gap has been filled by the use of ultraviolet photoemission spectroscopy techniques in studying systems such as hydrogen on palladium,[1] oxygen, carbon monoxide, etc., on nickel,[2] titanium,[3] etc. The growing wealth[4] of quite reliable experimental data on the electronic structure of chemisorbed gases on transition-metal surfaces needs to be understood in terms of a simple model that takes into account the important features of the substrate, adsorbate, and their interaction. In this paper we present such a model and its results. A detailed comparison of the results with experiments at this stage must, unfortunately, await the availability of calculated substrate surface density of states. However, as a check on the reasonableness and potentiality of this simple model and approach, we compare the theoretical results under the admittedly drastic assumptions of a δ-function density of states of the substrate surface. Even with this assumption we find that the results give a self-consistent account of the various physical quantities which play an important role in chemisorbtion on narrow-band metals.

Three main theoretical models for adsorption of hydrogen on metal surfaces have appeared. The Anderson model, given in the context of dilute magnetic alloys was used by Newns[5]; one-electron augumented-plane-wave (APW) energy-band calculations by Switendick[6]; and the induced-covalent-bond mechanism put forth by Schrieffer and Gomer.[7] Of these, the first one has been in most prevalent use, even though one recognizes that the free-electron descritpion of the substrate in the Anderson model, while being a reasonably good description of alkali substrates, is not justifiable for transition metal substrates. In this respect, the Schrieffer-Gomer approach is more realistic in describing the localized nature of the substrate. Even though both these approaches consider the substrate within Hartree-Fock approximation, the inclusion of nonorthogonality of the metal-adatom wave functions in the latter leads to a Heitler-London bonding mechanism as opposed to molecular-orbital view taken in the former. In particular, whereas the former gives a nonmagnetic state of the chemisorbed hydrogen (in the sense that spin-up and spin-down hydrogen states are equally occupied), the latter maintains that hydrogen retains its full spin, this spin being coupled antiferromagnetically to an induced spin density on the surface. Thus, even though the surface molecule formed by the adsorbate with the surface atoms is in a net spin zero state, hydrogen by itself remains magnetic. The simple model considered here is capable of discriminating between these two approaches and allows us to comment on the validity and limitations of the molecular-orbital and Heitler-London approaches.

To understand the electronic structure of chemisorbed atoms on transition metal surfaces, we describe the narrow *d* band of the substrate by a tight-binding *s*-band Hubbard[8] model. We include the nonorthogonality of the metal-adatom wave functions through overlap integrals. This then allows us to study the electronic structure of the chemisorbed atom as a function of the relative strength of the adatom-metal transfer matrix element V and the overlap D. The electronic structure is found to be sensitive to the overlap, going from a nonmagnetic state to magnetic state with increasing D. Thus, earlier contentions[9] that the nonorthogonality of the metal-adatom wave function does not play an important role are found to be erroneous. The model provides us with a criterion for the existence of localized moments on the surface, as opposed to the bulk. As such, the analysis can be used to predict and check the magnetic nature of the chemisorbed atoms. Of course, to make such a prediction from first principles would require knowledge of the self-consistent metal-adatom wave functions and their interaction. Even though an attempt has been made in this direction such first principles calculations are difficult, tedious and require utmost care. Indeed, for each given substrate-adatom system a separate calculation is needed. While development of such methods is not only desired, but essential to our realistic understanding of the chemisorption phonomenon, a simple model which can coherently classify the fast growing wealth of data without requiring a detailed knowledge of the fundamental wave functions and interactions is equally needed. We believe that the present work fills in this gap.

In this connection it seems appropriate to mention that in the past, most theoretical attempts have been aimed towards calculating the chemisorption binding energy to make contact with experiment. Thus, either theoretical expressions for chemisorption energy have been compared with the experiments to estimate the metal-adatom coupling strength, as in Ref. 5 within the Anderson model or some estimates of this coupling strength have been made under assumed parametrized form of the wave function and then the parameters varied to fit the theoretically calculated chemisorption energy to the experiment. Two points are to be noted with regard to such approaches; (i) the experimental values of chemisorption energy are fraught with doubt due to uncertainty in the cleanliness of the substrate, presence of defects, etc. Thus, it is generally not clear what part of the measured binding energy is truly due to the substrate atom-adatom binding. (ii) The theoretically calculated binding energy is not very sensitive to the metal-adatom coupling strength. As such, estimates of this coupling based on comparison with chemisorption energy do not provide any reliable information when used to estimate other important physical quantities such as charge transfer, the associated nature of bonding, magnetic behavior, etc. Indeed, in Ref. 5, if the estimated values of metal-adatom coupling V are used to estimate the level width of the chemisorbed level one finds that the level width is as large as, if not larger than, the distance of the level from the Fermi surface of the metal itself. This shows the lack of self-consistency in such attempts and makes the very concept of a chemisorbed atom level meaningless.

Fortunately, with the availability of very reliable ultra-high-vacuum data from ultraviolet spectroscopy, we have now a means of estimating the metal-adatom coupling V directly from the observed photoemission data, and then checking the reliability of this estimate by calculating parameters such as charge transfer, metal-adatom separation which are extremely sensitive to V. We shall, therefore, take this approach and develop a formalism to accomplish this goal.

II. HAMILTONIAN AND FORMALISM

The model Hamiltonian describing the narrow band substrate, the adatom and their interaction is

$$\mathcal{H}=\Bigg(\sum_{ij\sigma} t_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}+\frac{I}{2}\sum_{i\sigma} n_{i\sigma}n_{i-\sigma}+\sum_{\sigma}\epsilon_{\alpha}a^{\dagger}_{\alpha\sigma}a_{\alpha\sigma} + \frac{U}{2}\sum_{\sigma} n_{\alpha\sigma}n_{\alpha-\sigma}+\sum_{i\sigma}\{v_{i\alpha}a^{\dagger}_{i\sigma}a_{\alpha\sigma}+\mathrm{H.\,c.}\}\Bigg), \tag{1}$$

where the subscripts i and α refer to the substrate atoms and the assumed single valence orbital of the adatom participating in the substrate adatom bond respectively. $a^{\dagger}$ and a are the usual electron creation and annihilation operators and $n_{i\sigma}, n_{\alpha\sigma}$ are the number operators. t_{ij} and $v_{i\alpha}$ are the hopping and transfer matrix elements for the substrate atoms and between the substrate atoms and adatom, respectively. I and U are the intra-atomic Coulomb repulsions at the substrate atom and adatom sites, respectively. We present unrestricted Hartree-Fock solutions of Eqs. (1), allowing for nonorthogonality of the metal-adatom wave functions through the following commutation relations:

$$\begin{aligned}&[a^{\dagger}_{i\sigma},\ a_{j\sigma'}]_{+}=\delta_{ij}\delta_{\sigma\sigma'}\ ,\\&[a^{\dagger}_{i\sigma}, a_{\alpha\sigma'}]_{+}=(\delta_{i\alpha}+D_{i\alpha})\delta_{\sigma\sigma'}\ .\end{aligned} \tag{2}$$

Thus, Hamiltonian (1) coupled with relation (2) has two very important features built into it: (a) the inclusion of I, the intra-atomic Coulomb repulsion on substrate atom sites, leads to the dependence of the narrow d-band energy levels on its occupancy. This in turn couples the occupancy of the adatom level to the substrate atom occupancy, since the self-consistent energy level of the adatom depends upon the energy of the d-band levels. Thus, we find that an additional self-consistency relation must be satisfied for transition metal surfaces and is totally missed in a free-electronlike description of these substrates.[5] This self-consistency is essential to obtain the correct charge transfer values and metal-atom bond lengths. (b) Nonvanishing overlap, which would definitely be the case for narrow d band substrate electron and the adatom electron wave functions for observed metal-adatom separations of ~1 Å, leads to important exchange energy contributions. This contribution is important in considering the magnetic state of the chemisorbed atom.[7]

In the Hartree-Fock HF approximation, Hamiltonian (1) written in Bloch representation[8] reads

$$\mathcal{H}_{\mathrm{HF}}=\Big(\sum_{d\sigma}\epsilon_d n_{d\sigma}+\frac{I}{2}\sum_{d\sigma} n_{d\sigma}\langle n_{d-\sigma}\rangle+\sum_{\sigma}\epsilon_\alpha n_{\alpha\sigma} + \frac{U}{2}\sum_{\alpha\sigma} n_{\alpha\sigma}\langle n_{\alpha-\sigma}\rangle+\sum_{d}\{v_{d\alpha}a^\dagger_{d\sigma}a_{\alpha\sigma}+\mathrm{H.\,c.}\}\Big), \tag{3}$$

where the suffix d refers to the states of the narrow d band. Employing the standard technique of Green's functions,[10] we obtain from Eqs. (1) and (2) the following equations for the single-particle Green's function $G^{\sigma\sigma}_{\alpha\alpha}(\omega)$, $G^{\sigma\sigma}_{\alpha d}(\omega)$, and $G^{\sigma\sigma}_{dd}(\omega)$:

$$\Big\{\omega-\epsilon_\alpha-U\langle n_{\alpha-\sigma}\rangle-\sum_d V_{\alpha d}D_{d\alpha}\Big\}G^{\sigma\sigma}_{\alpha\alpha}(\omega) = \frac{1}{2\pi}\delta_{\alpha\alpha}+\sum_d[\{\epsilon_d+I\langle n_{d-\sigma}\rangle\}D_{d\alpha}+V_{\alpha d}]G^{\sigma\sigma}_{\alpha d}(\omega), \tag{4}$$

$$\{\omega-\epsilon_d-I\langle n_{d-\sigma}\rangle\}G^{\sigma\sigma}_{\alpha d}(\omega) = \frac{D_{\alpha d}}{2\pi}+[\{\epsilon_\alpha+U\langle n_{\alpha-\sigma}\rangle\}D_{\alpha d}+V_{\alpha\alpha}] \times G^{\sigma\sigma}_{\alpha\alpha}(\omega)+D_{\alpha d}\sum_{d'}V_{\alpha d'}G^{\sigma\sigma}_{\alpha d'}(\omega), \tag{5}$$

$$\{\omega-\epsilon_d-I\langle n_{d-\sigma}\rangle\}G^{\sigma\sigma}_{dd'}(\omega) = \frac{D_{\alpha d}}{2\pi}+[\{\epsilon_\alpha+U\langle n_{\alpha-\sigma}\rangle\}D_{\alpha d}+V_{\alpha d}] \times G^{\sigma\sigma}_{\alpha d'}(\omega)+D_{\alpha d}\sum_{d''}V_{d''\alpha}G^{\sigma\sigma}_{d''d'}(\omega). \tag{6}$$

Defining

$$E_{\alpha\sigma}=\epsilon_\alpha+U\langle n_{\alpha-\sigma}\rangle, \qquad E_{d\sigma}=\epsilon_d+I\langle n_{d-\sigma}\rangle; \tag{7}$$

we obtain the following for $G^{\sigma\sigma}_{\alpha\alpha}(\omega)$ from Eqs. (4) and (5):

$$G^{\sigma\sigma}_{\alpha\alpha}(\omega)=(1/2\pi)\{1+\chi_3(\omega)\} \times[\{\omega-E_{\alpha\sigma}-\Lambda_\alpha-\chi_2(\omega)-E_{\alpha\sigma}\chi_3(\omega)\} \times\{1-\chi_3(\omega)\}-\{1+\chi_3(\omega)\}\{\chi_0(\omega) +E_{\alpha\sigma}\chi_1(\omega)\}]^{-1}; \tag{8}$$

and from Eqs. (5) and (6), we obtain the following for $G^{\sigma\sigma}_{dd}(\omega)$:

$$G^{\sigma\sigma}_{dd}(\omega)=\{(\omega-E_{d\sigma})(1-\chi_1)\}^{-1} \times[(1/2\pi)\{(1-\chi_1)+D_{\alpha d}(2V_{\alpha d}+D_{\alpha d}E_{\alpha\sigma}+\chi_1E_{\alpha\sigma}\} +(D_{\alpha d}E_{\alpha\sigma}+V_{\alpha d}+\chi_0+\chi_1E_{\alpha\sigma}) \times\{D_{\alpha d}E_{\alpha\sigma}+V_{\alpha d}(1-\chi_1)+D_{\alpha d}\chi_0\}G^{\sigma\sigma}_{\alpha\alpha}(\omega)], \tag{9}$$

where

$$\begin{aligned}\Lambda_\alpha&=\sum_d V_{\alpha d}D_{\alpha d},\\ \chi_0(\omega)&=\sum_d|V_{\alpha d}|^2(\omega-E_{d\sigma}+i\eta)^{-1},\\ \chi_1(\omega)&=\sum_d V_{d\alpha}D_{d\alpha}(\omega-E_{d\sigma}+i\eta)^{-1},\\ \chi_2(\omega)&=\sum_d E_{d\sigma}V_{\alpha d}D_{d\alpha}(\omega-E_{d\sigma}+i\eta)^{-1},\\ \chi_3(\omega)&=\sum_d E_{d\sigma}|D_{\alpha d}|^2(\omega-E_{d\sigma}+i\eta)^{-1}.\end{aligned} \tag{10}$$

We note that for $D_{\alpha d}=0$, expression (8) for $G^{\sigma\sigma}_{\alpha\alpha}(\omega)$ reduces to the standard form of result with only $\chi_0(\omega)$ surviving. However, note that $\chi_0(\omega)$ involves summation over $E_{d\sigma}=(\epsilon_d+I\langle n_{d\sigma}\rangle)$ and not just ϵ_d. This shows the additional self-consistency coming through $\langle n_{d-\sigma}\rangle$. For nonvanishing $D_{\alpha d}$, the other terms contribute significantly. Starting from values $D_{\alpha d}$ of the order of a tenth of $V_{\alpha d}$ we find that $\chi_2(\omega)$ shall be of the same order of magnitude as χ_0 since $E_{d\alpha}$ is generally of the order of 10 eV. χ_1 and χ_3 are of the same order, being an order of magnitude smaller than χ_0 and χ_2 in this region. As the overlap becomes larger, $\chi_m(\omega)$, $m=0,1,2,3$ all become equally important and must be included in determining the chemisorbed atom energy level, given by the poles of $G^{\sigma\sigma}_{\alpha\alpha}(\omega)$; the density of states at this level, given by

$$\rho^\sigma_\alpha(\omega)=-\mathrm{Im}\,G^{\sigma\sigma}_{\alpha\alpha}(\omega) \tag{11}$$

and the occupancy of this level given by

$$\langle n_{\alpha\sigma}\rangle=\int_{-\infty}^{\epsilon_F}\rho^\sigma_\alpha(\omega)\,d\omega. \tag{12}$$

The density of states of the substrate is calculated from

$$\rho^\sigma_d(\omega)=-\sum_d\mathrm{Im}\,G^{\sigma\sigma}_{dd}(\omega) \tag{13}$$

and occupation of the substrate levels from

$$\langle n_{d\sigma}\rangle=\int_{-\infty}^{\epsilon_F}\rho^\sigma_d(\omega)\,d\omega. \tag{14}$$

The general form of the functions $\chi_m(\omega)$, $m=0,1,2,3$ is

$$\chi_m(\omega)=\int_{D_1}^{D_2}\frac{\rho_s(\epsilon_d)F_m(\epsilon_d)\,d\epsilon_d}{\omega-\epsilon_d-I\langle n_{d-\sigma}\rangle+i\eta} =\Delta^\sigma_m(\omega)+i\Gamma^\sigma_m(\omega), \tag{15}$$

$$\Delta^\sigma_m(\omega)=\mathcal{P}\int_{D_1}^{D_2}\frac{\rho_s(\epsilon_d)F_m(\epsilon_d)\,d\epsilon_d}{\omega-\epsilon_d-I\langle n_{d-\sigma}\rangle}, \tag{16a}$$

$$\Gamma^{\sigma}_{m}(\omega) = -\pi \int_{D_1}^{D_2} \rho_s(\epsilon_d) F_m(\epsilon_d) \times \delta(\omega - \epsilon_d - I\langle n_{d-\sigma}\rangle)\, d\epsilon_d \;, \qquad (16b)$$

where $F_m(\epsilon_d)$ is the corresponding numerator in Eq. (10) for χ_m, $m=0, 1, 2, 3$; $\rho_s(\epsilon_d)$ is the surface density of states of the clean substrate and D_1, D_2 are the lower and upper limits of the d band of the substrate. Even though the expressions for the quantities of interest to us, $\rho^{\sigma}_{\alpha}(\omega)$ and $\langle n_{\alpha\sigma}\rangle$ look cumbersome, a numerical analysis is straightforward and quite simple on the computer. However, any attempt at this analysis at this stage is hindered because of our lack of knowledge of the surface density of states of the clean substrate, $\rho_s(\epsilon_d)$. Consequently, in Sec. III we derive certain simpler expressions in the limit of a narrow band to obtain some insight qualitatively.

III. NARROW BANDWIDTH LIMIT

For a narrow-d-band substrate, a localized adatom level exists if the pole of $G^{\sigma\sigma}_{\alpha\alpha}(\omega)$ lies outside the band. Only in this case can we talk of an electronic structure of the chemisorbed atom in a meaningful way. In this case $\Gamma^{\sigma}_{m}(\omega_{\alpha\sigma}) \approx 0$ and the self-consistent adatom level, $\omega_{\alpha\sigma}$ is given by

$$\begin{aligned}[\{\omega_{\alpha\sigma} - E_{\alpha\sigma} - \Lambda_{\alpha} - \Delta_2(\omega_{\alpha\sigma}) - E_{\alpha\sigma}\Delta_3(\omega_{\alpha\sigma})\}& \\ \times\{1 - \Delta_1(\omega_{\alpha\sigma})\} - \{1 + \Delta_3(\omega_{\alpha\sigma})\}& \\ \times\{\Delta_0(\omega_{\alpha\sigma}) + E_{\alpha\sigma}\Delta_1(\omega_{\alpha\sigma})\}\,] = 0 \;.& \qquad (17)\end{aligned}$$

Now, $\Delta_m(\omega_{\alpha\sigma})$ may be approximated by

$$\begin{aligned}\Delta_m(\omega_{\alpha\sigma}) &\simeq N_m/(\omega_{\alpha\sigma} - E^{c}_{d\sigma}) \;, \\ N_m &= \int_{D_1}^{D_2} \rho_s(\epsilon_d) F_m(\epsilon_d)\, d\epsilon_d \;. \qquad (18)\end{aligned}$$

In the above $E^{c}_{d\sigma}$ is the center of the occupied narrow d band and use has been made of the fact that for $\omega_{\alpha\sigma}$ removed from the narrow d band, $E_{d\sigma} - E^{c}_{d\sigma} \ll \omega_{\alpha\sigma} - E^{c}_{d\sigma}$. Thus, the self-consistent adatom level is given by

$$\begin{aligned}[(\omega_{\alpha\sigma} - E^{c}_{d\sigma}) - (\omega_{\alpha\sigma} - E^{c}_{d\sigma})^2 (E,_{\alpha\sigma} - E^{c}_{d\sigma} + \Lambda_{\alpha} + N_1)& \\ + (\omega_{\alpha\sigma} - E^{c}_{d\sigma})\{N_1(\Lambda_{\alpha} - E^{c}_{d\sigma}) - N_0 - N_2 - E_{\alpha\sigma}N_3\}& \\ + (N_1N_2 - N_0N_3)\,] = 0& \qquad 19)\end{aligned}$$

and from (12), we find

$$\langle n_{\alpha\sigma}\rangle = \int_{-\infty}^{\epsilon_F} \sum_{\omega\gamma} \left| 1 - \frac{N_1\Lambda_{\alpha} - E^{c}_{d\sigma} - N_2 - N_0 - E_{\alpha\sigma}N_3}{(\omega - E^{c}_{d\sigma})^3} - \frac{2(N_1N_2 - N_0N_3)}{(\omega - E^{c}_{d\sigma})^2} \right|^{-1} \delta(\omega - \omega_{\gamma})\, d\omega \;, \qquad (20)$$

where ω_{γ} are the roots of (19). Note that within the above made approximation, the additional full self-consistency of the occupation of the substrate levels has been replaced by a partial consistency if we rely on the experimental value of $E^{c}_{d\sigma}$, as obtained from photoemission data.

IV. DISCUSSION

The electronic structure of the chemisorbed atom is characterized by Eqs. (11) and (12) for the density of states and occupancy of the chemisorbed atom level, respectively. Within the unrestricted Hartree-Fock scheme of the present work expression (12) for $\langle n_{\alpha\sigma}\rangle$ always has a nonmagnetic solution $\langle n_{\alpha\sigma}\rangle = \langle n_{\alpha-\sigma}\rangle$ for the occupancy of the spin states of the adatom. However, in certain regions of the values of V and D, there exists a magnetic solution, i.e., $\langle n_{\alpha\sigma}\rangle \neq \langle n_{\alpha-\sigma}\rangle$, as well. Whenever a magnetic solution exists, it has a lower-energy state as compared to the nonmagnetic state. Solutions of (12) thus provide a criterion for the existence of localized moments on the chemisorbed atoms. In this context it is well to recall that in the Anderson model, which provided a criterion, within the unrestricted Har-

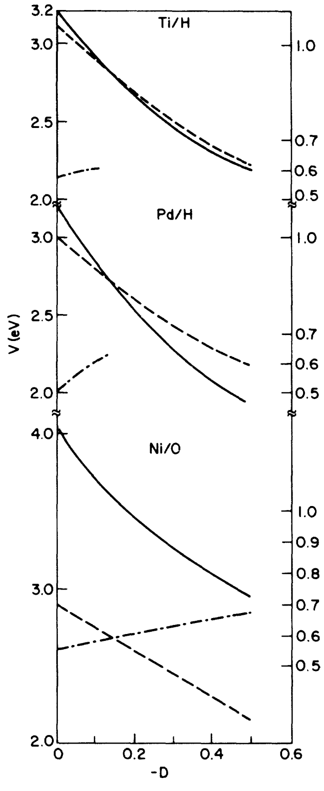

FIG. 1. Adatom-metal coupling strength vs overlap. Broken line gives the theoretical limit for magnetic state of adatom, the nonmagnetic region being above the line. Solid curve is obtained by fitting theory with photoemission data, on the assumption of nonmagnetic state of the adatom. The dash-dot curve gives the occupancy of one spin state of the adatom in the region where the above-mentioned assumption is consistent with experiment. $U = 12.895$ and 12.134 eV for H and O, respectively. Reduction by 20% to take account of screening does not alter the nature of the results.

tree-Fock, for the existence of localized moments in the bulk of the metal, as indeed in general virtual level problems, it is the ratio of the intra-atomic Coulomb repulsion on the "impurity" atom U (here the adatom) and the level width of the virtual level which essentially determines the boundary between nonmagnetic and magnetic regions. In the chemisorption problem, this is determined by essentially the ratio of V and the splitting of the bonding and antibonding levels. For adatoms such as hydrogen, oxygen, etc., on transition metals such as Pd, Ti, Ni, etc., we are essentially in the region where V and splitting of the bonding-antibonding levels are comparable. The theoretical problem is thus a complicated one and the validity of the unrestricted Hartree-Fock scheme becomes doubtful due to its neglect of the correlation effects. This fundamental short coming is faced in all applications of the approach of Ref. 5 when applied to chemisorption of gases on transitional metal surfaces.[11] On the other hand, a description in terms of a totally Heitler-London picture of bonding over emphasizes the role of correlation. We have, therefore, made an attempt to provide a formalism which includes the dominant contribution of the correlations, namely the strong correlation energy I on the substrate atom and the exchange-correlation contributions due to the overlap of the metal-adatom wave functions. The formalism is not subject to restrictions on the magnitudes of the bandwidth, overlap, etc. It is true though that for strong overlap a clear distinction between Coulomb and exchange energies is very obscure. Nonetheless, in the important region of intermediate amounts of overlap the formalism would be quite reliable and provides a criterion for the justification of the *ad hoc* assumption of a magnetic state of the adatom built into the induced covalent bond mechanism of chemisorption. As mentioned before, a lack of knowledge of the clean substrate density of states has not allowed us to apply the formalism to experiments. However, work is in progress in this direction and we hope to be able to put the formalism to test in the near future. In the meantime to illustrate the sensitivity of the results to directly observable quantities and to show the importance of the correlation on the substrate atom site in the transitional metals, we present an almost trivial analysis of some recent photoemission data, under the assumption of a δ-function substrate density of states.

In this limit from Eqs. (19) and (20), one obtaines the result

$$\omega^{\pm}_{\alpha\sigma} = \tfrac{1}{2}\big[(E_{\alpha\sigma} + E^{c}_{d\sigma} + 2VD) \pm \{(E_{\alpha\sigma} - E^{c}_{d\sigma})^2 + 4(E^{c}_{d\sigma}D + V)(E_{\alpha\sigma}D + V)\}^{1/2}\big] , \quad (21)$$

$$\langle \eta^{\pm}_{\alpha\sigma} \rangle = \begin{cases} \left| 1 + \dfrac{V^2(1 - D^2) + 2VDE^{c}_{d\sigma} + E_{\alpha\sigma}E^{c}_{d\sigma}D^2}{(\omega^{\pm}_{\alpha\sigma} - E^{c}_{d\sigma})^2} \right|^{-1} , & \omega^{\mp}_{\alpha\sigma} > 0 \\ 0, & \omega^{\pm}_{\alpha\sigma} > 0 \ . \end{cases} \quad (22)$$

Indeed under this drastic assumption, the problem reduces to a two-level problem and the results could trivially be derived from

$$\det |H - \omega D| = 0 ,$$

where

$$H \equiv \begin{pmatrix} E_{\alpha\sigma} & V \\ V & E^{c}_{d\sigma} \end{pmatrix} , \quad D \equiv \begin{pmatrix} 1 & D \\ D & 1 \end{pmatrix} .$$

Equations (21) and (22) are identical to Ref. 5 if we neglect the overlap and replace $E^{c}_{d\sigma}$, the center of the *occupied* part of the d band, by the center of the *entire* band. However, in Ref. 5 and subsequent such approaches, use of the center of the entire d band led to estimates of metal-adatom separation lengths an order of magnitude or more smaller than observed and expected, and the estimated values of V when used to estimate the level width give widths as large as the substrate band itself, totally inconsistent with experiments, as mentioned before. However, when the correlation on the substrate atom I is taken into account from the very beginning, then even within the drastic approximation of a two-level system one arrives at the result, which one would have expected intuitively even without a detailed analysis, that it is the center of the occupied part of the d band which plays an important role. Thus, mere use of $E^{c}_{d\sigma}$ provides results shown in Figs. 1 and 2 and Table I which are fully self-consistent. Using observed values of $\omega_{\alpha\sigma}$ and $E^{c}_{d\sigma}$ from photoemission data (see Table I), Eqs. (21) and (22) lead to values

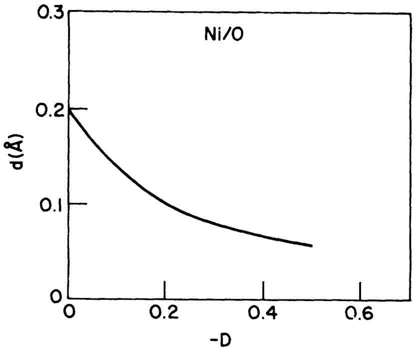

FIG. 2. Metal-adatom separation estimated from know work function change ($\Delta\phi = 0.2$ eV for one-half Langmuir coverage) and calculated charge transfer, as a function of overlap.

TABLE I. Shows photoemission experimental data and theoretically calculated values for zero overlap. N stands for number of substrate nearest neighbors of the adatom. Actual metal-adatom coupling strength equal to $(1/\sqrt{N})V$, where V is the calculated value.

	Experiment			Theoretical calculations			
System	$\omega_{\alpha\sigma}$ (eV)	E_d^c (eV)	Width (eV)	$\langle n_{\alpha\sigma}\rangle = \langle n_{\alpha-\sigma}\rangle$	$V(N=1)$ (eV)	$V(N=4)$ (eV)	Width (eV)
Ti/H	−4.0	−2.2	~2.0	0.57	3.2	1.6	~2.0
Pd/H	−5.4	−1.3	2.0	0.51	3.2	1.6	~2.0
Ni/O	−5.5	−1.0	2.0	0.55	4.0	2.0	~2.0

of V as a function of D (solid curve, Fig. 1), assuming a nonmagnetic state of the adatom. The broken curve gives the theoretical limit for occurrence of a magnetic state, the upper region being the nonmagnetic region. We find that beyond $D \sim 0.1$, the assumption of a nonmagnetic state of hydrogen on Pd and Ti is inconsistent with the observed electronic structure. The dash-dot curve gives the occupancy of the chemisorbed atom level in the nonmagnetic region. The values of charge transfer provide reasonable estimates of metal-adatom separation as a function of D (Fig. 2). Furthermore, estimated values of V give values of the width of the chemisorbed atom level, consistent with the observed widths (Table I). Oxygen on nickel shows a very different behavior than hydrogen on padladium or titanium. We find that oxygen remains nonmagnetic for large values of overlap and the charge transfer is much larger, the bonding thus being significantly ionic. Hydrogen on Pd and Ti on the other hand is border line between magnetic and nonmagnetic and the charge transfer is extremely small, the bonding thus being primarily covalent.

This trivial analysis illustrates the importance of the correlation effects on the narrow-band substrates. The role of these correlation energies has been emphasized in this paper. Indeed it is clear from the trivial analysis discussed above that any realistic attempt to understand chemisorption phenomenon on narrow-band substrates must have at least the ingredients of the formalism presented here. Work is under progress in certain quarters to calculate the surface density of states for bcc, fcc, and hcp structures needed to evaluate the quantities χ_m. With the availability of these surface density of states we hope to provide a coherent picture of chemisorption on narrow-band substrates. Since the evaluation of V and D from first principles is a very difficult problem, we suggest that experiments that probe the magnetic state of the adatom (e.g., resonance tunneling, NMR) will yield information which in conjunction with photoemission data, would allow us to estimate V and D using the formalism presented here.

ACKNOWLEDGMENTS

The author is grateful to Dr. D. E. Eastman for helpful discussions of his data and to Dr. D. Spanjaard for his help in computational work.

---

[1] D. E. Eastman, J. K. Cashion, and A. C. Switendick, Phys. Rev. Lett. **27**, 35 (1971).

[2] D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. **27**, 1520 (1971).

[3] D. E. Eastman, Solid State Commun. **10**, 933 (1972).

[4] B. J. Waclawski and E. W. Plummer, Phys. Rev. Lett. **29**, 783 (1972); B. Feuerbacher and B. Fitton, Phys. Rev. Lett. **29**, 786 (1972).

[5] D. Newns, Phys. Rev. **178**, 1123 (1969).

[6] J. R. Schrieffer and R. Gomer, Surf. Sci. **25**, 315 (1971).

[7] J. R. Schrieffer and R. H. Paulson (unpublished).

[8] J. Hubbard, Proc. R. Soc. A **276**, 238 (1963).

[9] T. B. Grimley, J. Phys. C **3**, 1934 (1970).

[10] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [Sov. Phys.-Usp. **3**, 320 (1960)].

[11] J. R. Schrieffer, J. Vac. Sci. Technol. **9**, 561 (1971).