Chemisorption on Transition-Metal Surfaces: Screening and Polarization versus the Intra-adsorbate Coulomb Interaction*

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It is shown that a correct interpretation of the spectroscopic data for most chemisorbed systems implies the existence of considerable screening and polarization effects. A specific view of chemisorption on transition metals is suggested, incorporating the importance of the metallic nature of the substrate as well as the effect of the local environment of the adsorbate.

An important distinction between ordinary chemical bonding in molecules and the chemical bonding of an adsorbate on a metallic surface is the presence of the large number ($\sim 10^{23}$) of electrons in the latter which may cause significant screening effects, absent in the former. However, the relative importance and significance of these screening effects and the intra-adsorbate Coulomb interaction (usually denoted by U) has as yet remained unclear. Recent successes of spectroscopic techniques have provided us with considerable data on the electronic structure of chemisorbed systems. Among the varied[1-3] attempts to interpret this data, a widespread approach has been based on phenomenological model Hamiltonians which require that certain energies be specified as input values and others parametrized to achieve agreement with experiment. The aim of this Letter is to demonstrate that theoretical analyses which neglect screening and polarization effects and retain only U cannot explain the spectroscopic data. A correct interpretation of this data requires significant screening and polarization effects. In addition, most adsorbates (e.g., H, O, CO, C_2H_4, etc.) on transition metals exhibit primarily covalent bonds, implying that U, whatever its adjusted value in the chemisorbed system, must still remain a dominant interaction energy. We note that the Hartree-Fock (HF) approximation of U in describing such a situation is inadequate for a meaningful interpretation of spectroscopic data and obscures the importance of the above-mentioned screening effects.

The phenomenological model most widely used to describe the interacting adsorbate substrate system is the Anderson model[4] which takes the following form, written here in the site representation[5]:

$$H=\sum_{ij\sigma} T_{ij}\mathfrak{a}_{i\sigma}{}^{\dagger}\mathfrak{a}_{j\sigma}+\sum_{\sigma} E_{\alpha}\mathfrak{a}_{\alpha\sigma}{}^{\dagger}\mathfrak{a}_{\alpha\sigma}+\tfrac{1}{2}U\sum_{\sigma} n_{\alpha\sigma}n_{\alpha-\sigma}+\sum_{i\sigma}\{V_{\alpha i}\mathfrak{a}_{\alpha\sigma}{}^{\dagger}\mathfrak{a}_{i\sigma}+\text{H.c.}\}. \tag{1}$$

In (1), $|\alpha\rangle$ denotes the adsorbate bonding orbital and $|i\rangle$ denotes the orbitals (e.g., s and d) associated with the ith substrate site.[6] T_{ij} and $V_{\alpha i}$ are the electron-transfer integrals between the substrate atoms, and between the adsorbate and substrate atoms. E_α is an assumed effective energy level for $|\alpha\rangle$ which, in the absence of screening and polarization effects, reduces to its free ionization potential, E_I. The density of states of (1) is obtained from the single-particle Green's function. Following Zubarev,[7] the equation of motion for the Green's function $G_{AB}(\omega)=\langle\langle A;B\rangle\rangle_\omega$, for two operators A and B, is given by

$$\omega G_{AB}(\omega)=(2\pi)^{-1}[A,B]_{-}+\langle\langle [A,H]_{-};B\rangle\rangle_{\omega}. \tag{2}$$

From (1) and (2) we obtain the following equations for the single-particle propagators:

$$\omega G_{\alpha\alpha}{}^{\sigma}(\omega)=(2\pi)^{-1}+E_{\alpha}G_{\alpha\alpha}{}^{\sigma}(\omega)+\textstyle\sum_i V_{\alpha i}G_{i\alpha}{}^{\sigma}(\omega)+U\Gamma_{\alpha\alpha}{}^{\sigma}(\omega), \tag{3}$$

$$\omega G_{i\alpha}{}^{\sigma}(\omega)=\textstyle\sum_j T_{ij}G_{j\alpha}{}^{\sigma}(\omega)+V_{i\alpha}G_{\alpha\alpha}{}^{\sigma}(\omega), \tag{4}$$

where $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)=\langle\langle n_{\alpha-\sigma}\mathfrak{a}_{\alpha\sigma};\mathfrak{a}_{\alpha\sigma}{}^{\dagger}\rangle\rangle_{\omega}$ is a two-particle propagator. Defining $[\mathcal{G}^{-1}]_{ij}=(\omega\delta_{ij}-T_{ij})$, which corresponds to electron propagation in the substrate, we obtain from (2) and (3)

$$[\omega-\epsilon_{\alpha}-\Sigma_I(\omega)]G_{\alpha\alpha}{}^{\sigma}(\omega)=(2\pi)^{-1}+U\Gamma_{\alpha\alpha}{}^{\sigma}(\omega), \tag{5}$$

where $\Sigma_I(\omega)=\sum_{ij}V_{\alpha i}\mathcal{G}_{ij}V_{j\alpha}$ is the self-energy of the adsorbate ionization level. To determine $G_{\alpha\alpha}{}^{\sigma}(\omega)$, we need to know $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)$.

Now, in the Hartree-Fock approximation one closes Eq. (4) by putting $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)\approx\langle n_{\alpha-\sigma}\rangle G_{\alpha\alpha}{}^{\sigma}(\omega)$. This introduces an upward shift by $U\langle n_{\alpha-\sigma}\rangle$ in the bonding level E_α.[8-11] As shown below, such a decoupling procedure can introduce erroneous structure in the density of states. It is precisely information on the density of states that is provided by spectroscopic data (e.g., photoemission). Hence for a meaningful interpretation of this data it is essential to retain, as far as possible, the correct structure of the density of states.

The structure of the single-particle density of states can be seen from a consideration of the equation of motion of $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)$. From (1) and (2) it may be seen[12] that this equation will not contain any single-particle Green's function. Hence whatever the structure of $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)$, it cannot be proportional to $G_{\alpha\alpha}{}^{\sigma}(\omega)$ as the HF approximation assumes. We have performed a detailed analysis of $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)$ that will be published elsewhere[13] and find that its exact form must have the structure

$$\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)=(2\pi)^{-1}n_\alpha{}^{-\sigma}(\omega)/[\omega-E_\alpha-U-\Sigma_A(\omega)], \tag{6}$$

where $\Sigma_A(\omega)$ is the self-energy of the electron-affinity level and $n_\alpha{}^{-\sigma}(\omega)$ is the (frequency dependent) effective occupation probability. It is to be appreciated that the exact $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)$ does not have poles at the same location as $G_{\alpha\alpha}{}^{\sigma}(\omega)$. Hence $\Gamma_{\alpha\alpha}{}^{\sigma}(\omega)$ cannot produce a shift of the type $U\langle n_\alpha{}^{-\sigma}\rangle$ in the position of the poles of $G_{\alpha\alpha}{}^{\sigma}(\omega)$ arising from the ionization level, E_α. Inserting (6) into (5) we obtain

$$G_{\alpha\alpha}{}^{\sigma}(\omega)=\frac{1}{2\pi}\left\{\frac{1}{\omega-E_\alpha-\Sigma_I(\omega)}+\frac{Un_\alpha{}^{-\sigma}(\omega)}{[\omega-E_\alpha-\Sigma_I(\omega)][\omega-E_\alpha-U-\Sigma_A(\omega)]}\right\}. \tag{7}$$

This structure for $G_{\alpha\alpha}{}^{\sigma}(\omega)$ is valid for both small and large U (the result is exact for $V=0$, $U\neq0$ and for $U=0$, $V\neq0$ and provides a smooth interpolation between these two limits).

The physical content of (7) can be appreciated from the following considerations. In the absence of $V_{\alpha i}$, $G_{\alpha\alpha}{}^{\sigma}(\omega)$ has two poles, one at E_α and the other at $(E_\alpha+U)$. These correspond to the adsorbate-ionization and electron-affinity levels, respectively.[13]

As the interaction $V_{\alpha i}$ is allowed to build up, we would expect the two levels E_α and $E_\alpha+U$ to shift and acquire a width, nevertheless maintaining the character that there is no contribution from U to the shift in the peak of the derived level E_α. The correction U in the level $(E_\alpha+U)$ is purely a consequence of the fact that it is the electron-affinity level which contains two electrons. However, the HF approximation replaces the ionization and electron-affinity levels by a single level at an appropriate mean energy between the two. It compensates for this error by giving equal weight to the neutral and ionic contributions to the system ground-state wave function. (Note that the HF scheme is equivalent to the well-known molecular-orbital scheme of quantum chemistry.) Our result (7) *always* gives two poles (in contrast to the single-pole HF approximation); however as U becomes small the peaks associated with the ionization and affinity levels merge into a single peak at some intermediate energy—the situation described by Hartree-Fock. Thus by its very nature the HF scheme is incapable of providing the correct spectral function, *unless* the separation of the two bonding levels is completely dominated by their widths, giving rise to a single peak in the spectral function. In its essence, our result (7) for $G_{\alpha\alpha}{}^{\sigma}(\omega)$ is equivalent to the valence-bond picture in which one attempts to retain the correct energies of the neutral and ionic configurations and calculates their relative weights as accurately as the presence of Coulomb interactions will allow.

Returning to (7), we note that the poles derived from the ionization level, E_α, are given by the solutions of $\omega=E_\alpha+\Lambda_I(\omega)$, where $\Sigma_I(\omega)=\Lambda_I(\omega)-i\Delta_I(\omega)$. For any reasonable density of states of the substrate, $\Lambda_I(\omega)$ is negative for $\omega<\omega_c$, where ω_c is usually near the center of the band.[14] Thus if screening and polarization effects are completely neglected, E_α reduces to the free-adsorbate ionization potential, E_I, and the bonding level would occur at $\omega_\alpha=E_I-|\Lambda_I(\omega_\alpha)|$. As we see, this is *below* the ionization level E_I.

In contrast, for all adsorbates with E_I below the substrate ϵ_F and ω_c, the experimentally determined bonding level is always found to be *above* E_I. For example, E_I for hydrogen and oxygen is about -13.6 eV and the observed bonding level of these adsorbates on transition metals is observed about 4 eV above this value.[15,16] Four possible explanations for this discrepancy come to mind: (1) The observed level is not the bonding level of the adsorbate but some other level, the actual bonding level being below E_I. As far as we know no such level has so far been observed. We therefore discount this explanation. (2) The bonding level is indeed below E_I but photoemission gives an apparent energy above E_I due to contribution of relaxation effects. However, other spectroscopic measurements (e.g., ion-neutralization spectroscopy) give values close to the photoemission values. In addition, for most systems the required relaxation shift would be $\gtrsim 5$ eV which seems too large and unexpected. (3) The value of the Coulomb energy, U, is so small that the distinction between the ionization level and the affinity level has become obscured. Their separation is dominated by their widths giving rise to a single peak between E_I and $E_I + U$ (the conventional Hartree-Fock picture). However, the observed upward shift ~ 5 eV would require a value of $U \sim 10$ eV (if we take $\langle n_{\alpha}{}^{-\sigma} \rangle \sim \frac{1}{2}$) inconsistent with the above assumption. Thus this cannot be the explanation. (4) From the above we are led to the inevitable conclusion that the observed level is indeed associated with the adsorbate ionization level. For this to be so, the free-ionization level must have been shifted upwards by an amount which we denote by $V_{\alpha\alpha}$. This gives rise to an effective level at $E_I + V_{\alpha\alpha}$ which is the appropriate identification of E_{α} in (1). Contributions to $V_{\alpha\alpha}$ arise primarily from the Coulomb interaction of the metal electrons with the adsorbate electron and with the adsorbate ion core. The details of these individual contributions, which are conventionally viewed as screening and polarization effects, have been discussed elsewhere.[5] The important point to be noted is that the *upward shift due to* $V_{\alpha\alpha}$ *must be large enough to overcompensate for the downward shift due to the "chemical bonding" interaction* $V_{\alpha i}$, thus giving a chemisorbed adsorbate ionization level at the observed position.

It has long been recognized that screening and polarization effects must be an integral part of the chemisorption phenomenon.[17] However, the relative significance and importance of the screening and electron-electron interaction U has escaped meaningful analysis because of the complex nature of the problem. We believe that comparison of our results with spectroscopic data for the first time demonstrates the true importance of the screening and polarization effects arising from the metal electrons. (It would also appear that the screening of the adsorbate ion core and the consequent delocalization of the adsorbate valence electron would tend to reduce U considerably from its free adsorbate value. However, the bonding localization on the other hand will tend to oppose this effect. A rough estimate[18] for hydrogen, neglecting the localization due to bonding, indicates that $U \sim 3$–6 eV.) In view of our results we are led to propose the following picture for chemisorption on transition metal surfaces.

The relevant bands of the transition metal are primarily of s and d character. The chemical bonds formed by adsorbates on these metal surfaces may be viewed as involving two kinds of contributions. (1) The presence of the adsorbate ion-core potential induces a significant modification of the substrate s and d densities of states and may cause significant s-d hybridization as well.[5] The repulsive Coulomb interaction between the substrate and adsorbate electrons gives rise to considerable screening effects, thus raising the energy of the adsorbate valence electrons. Because of the mobile nature of the s-like electrons and their ability to adjust and accommodate, these screening and polarization effects may be relatively insensitive to the crystallographic face of the substrate. (2) The relatively localized d-like electrons with their associated directed orbitals form bonds via electron sharing with the charge associated with the adsorbate valence level. This contribution to the bonding is expected to be sensitive to the local environment (geometry, size effects, etc.) of the adsorbate. Thus variations in the properties of the adsorbate-substrate system for different crystallographic faces arise primarily from the variations in this contribution. Of course these two contributions are intimately interrelated.[5, 12] We have made the demarcation only for conceptual simplicity in presentation.

We conclude by mentioning the work of Demuth and Eastman[19] on chemisorption of ethylene on Ni(111) which, to our knowledge, is the only system for which one has an experimental estimate of the "screening" and "bonding" contribution. They find an initial constant upward shift for *all* the levels. This has been associated with screening and relaxation effects. However, the bonding π level then has a downward shift with respect to the σ levels, this being a consequence of the π-d bonding. Finally, in a very recent paper, Lang and Williams[20] have reported a fully self-consistent calculation for hydrogen on a semi-infinite jellium substrate (of $\gamma_s = 2$) and find the chemisorbed ionization level at 1.5 eV below the Fermi level. This is ~ 3 eV *above* the observed level on most transition metals. We suggest that including the bonding with *d* orbitals (along with adjustment to an appropriate γ_s value) will provide the required downward shift.

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Scaling Axes and the Spin-Flop Bicritical Phase Boundaries

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The orientation of the scaling axes at nonsymmetric critical and multicritical points is discussed. Although nonuniversal, the orientations at a spin-flop bicritical point may be found to leading order in the magnetic anisotropy and in $\epsilon = 4 - d$ (where d is the dimensionality). The resulting geometry of the antiferromagnetic phase boundaries accords well with new experimental data.

A scaling theory[1] has been advanced to describe the *spin-flop bicritical point* which arises when a magnetic field H is imposed on a weakly anisotropic antiferromagnet [see Fig. 1(a)]. The theory predicts[1] that the critical lines $T_c^{\parallel}(H)$ (paramagnetic to antiferromagnetic) and $T_c^{\perp}(H)$ (paramagnetic to spin flop) should meet the spin-flop line *tangentially* at the bicritical point [see Fig. 1(a)] with a curvature characterized[2,3] by the Heisenberg crossover exponent ϕ. Recent precise experiments by Rohrer[4,5] on GdAlO$_3$ should allow the first sensitive test of the prediction but reveal that this is feasible only if the *orientations* of both *linear scaling axes* (for H *and* T) are known or determined. In this note we show how these (nonuniversal) orientations can be esti-