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Theory of chemisorption on metallic surfaces: Role of intra-adsorbate Coulomb correlation and surface structure*

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A theory of chemisorption on metallic surfaces is formulated in the site representation. The influence of the intra-adsorbate Coulomb correlations is investigated and is found to lead to significant changes in the single-particle spectral function as compared to the Hartree-Fock result. Comparison with spectroscopic data is shown to imply the existence of large upwards shift in the adsorbate ionization potential due to screening effects arising from the adsorbate-substrate e-e interaction. Thus the relative importance of screening and polarization effects and the intra-adsorbate Coulomb correlation is for the first time extracted **unambiguously** from spectroscopic data. The use of the site representation allows for a natural introduction of the concept of a "surface cluster" without any need for detaching it from the rest of the metallic substrate. Thus the issue of rebonding the surface cluster to the "indented surface" does not arise, the entire system being treated on the same footing self-consistently. We are able to explicitly exhibit **the local** nature of bonding and incorporate the influence of the surface geometry without disregard of the important screening and polarization effects characteristic of the substrate. The theory is generalized to take account of the nonorthogonality of the adsorbate-substrate wave functions.

I. INTRODUCTION

The phenomenon of chemisorption is known to be strongly dependent upon the electronic structure of the free adsorbate and the free substrate.[1] In particular, chemisorption on transition-metal substrates tends to exhibit a rather local nature of the chemical interaction. Theoretical attempts to correlate the behavior of the chemisorbed system with the properties of the free adsorbate and substrate have, in the main, taken two directions, each emphasizing a particular aspect of the problem. One view relies on the local nature of the adsorbate-substrate bonding and thus attempts to describe it as a bonding of the adsorbate with a few neighboring substrate atoms.[2,3] Conventional quantum molecular methods are employed and the presence of the rest of the metallic surface is considered of secondary importance. The other view emphasizes the metallic nature of the surface and describes the metal electrons within the conventional band picture.[4-8] However, the chemical interaction with the adsorbate has most often been considered in terms of phenomenological models describing the interaction of the valence level of the adsorbate with the substrate band. Most theoretical work[5-8] along this line has been within the Hartree or Hartree-Fock approximation. While both the above-mentioned approaches have their qualitative merits, neither of them is separately able to provide a satisfactory description of the observed phenomenon.

It is perhaps widely recognized that a reasonable description of chemisorption on transition-metal surfaces must contain the essentials of both the above-mentioned aspects of the problem. A microscopic Hartree-Fock theory incorporating this point of view is provided elsewhere.[9] In this paper we develop the theory in three significant directions; (i) the role of Coulomb correlations on the adsorbate is investigated and (ii) an explicit development of the formalism in the site representation is presented. This allows us to exhibit the role of the local environment of the adsorbate. (iii) The nonorthogonality of the adsorbate-substrate wave functions is taken into account.

An issue of long standing in chemisorption is the relative significance and importance of screening and polarization effects on one hand and the Coulomb correlations on the adsorbate on the other. A discussion of these effects starting from the full microscopic Hamiltonian of the adsorbate-substrate system very quickly leads to intractable mathematical equations. Thus to meaningfully discuss the significance of the above-mentioned effects it is not only desirable, but appears essential to discuss one effect at a time so that controlled and meaningful approximations can be introduced. As such, of the many Coulomb interactions present in the system, we consider, in this paper, the situation where the intra-adsorbate Coulomb interaction, U, is most dominant. Other Coulomb interactions are assumed to be described fairly well within a Hartree-Fock approximation. An effective Hamiltonian which describes such a situation has been derived from the microscopic theory.[9] We take this effective Hamiltonian as the starting point for a discussion of the consequences of correlation effects arising from U. It is shown that such correlations can have a profound effect upon the spectral function (and hence the density of states) of the chemisorbed system. Except for very small values of U, the results obtained by a standard Hartree-Fock analysis are shown to be even qualitatively inadequate, producing erroneous structure in the density of states. It is precisely information on the density of states that is provided by spectroscopic measurements (e.g., photoemission, ion-neutralization spectroscopy, etc.) and we show that for most adsorbates with relatively large ionization potentials (e.g., H, O, CO, C_2H_4, etc.) the Hartree-Fock approximation of U is incapable of providing a meaningful analysis of the spectroscopic data.

Another important aspect of the chemisorption phenomenon on transition-metal substrates is its dependence upon the crystallographic face (or surface structure), reflecting the influence of the local and directed nature of the d orbitals of the substrate.[10,11] To bring this feature out explicitly we find it desirable to further develop the formalism in a site representation. We find that the concept of a substrate group and a surface cluster emerges naturally and allows for a connection with the usual notions of molecular calculations. We note that this substrate group (consisting of an arbitrary, finite number of substrate atoms surrounding the adsorbate) is never considered detached from the rest of the solid. Thus the metallic nature of the substrate is not ignored and the resulting adjustment of charge etc. can be calculated in a self-consistent manner.

In Sec. II we present the effective Hamiltonian and its relationship to the chemisorption phenomenon on transition-metal surfaces. In Sec. III we discuss its solution employing the equation-of-motion method of Zubarev.[12] The results for the adsorbate single-particle propagator are cast in a form that explicitly reveals the self-consistent adjustment of the free adsorbate ionization and electron affinity levels. It is shown that the contributions of spin fluctuations on the adsorbate are as important as those arising from direct scattering processes (the only ones considered in a Hartree-Fock treatment of the problem).

In Sec. IV we discuss our results in the limit of the standard Newns[5] model for chemisorption. In this limit, one neglects the screening and polarization effects of the metal induced by the presence of the adsorbate. We show that such effects are essential to the chemisorption process and must be included for a meaningful discussion of the phenomenon. In Sec. V the concept of a "substrate group" and a "surface cluster" is discussed. Section VI generalizes the results to take account of the nonorthogonality of the adsorbate-substrate wave functions. The results of this paper are summarized in Sec. VII.

II. HAMILTONIAN

To simplify the problem we consider only adsorbates having a single level available for bonding. We also consider substrates that are describable in terms of a tight-binding band arising from site orbitals.[13] The electronic structure at the surface of such a metal is a subject of active investigation.[14] Therefore we will assume that this is known, i.e., the electronic structure of the clean surface is one of the inputs in our treatment of chemisorption. To describe the chemisorbed system we adopt the following model Hamiltonian whose quantum-mechanical basis has been discussed by one of us[9]:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3,$$

where

$$\begin{aligned} \mathcal{H}_1 &= \sum_{ij\sigma} (T^0_{ij} + V^0_{ij}) c^\dagger_{i\sigma} c_{j\sigma} + \tfrac{1}{2} I \sum_{i\sigma} n_{i\sigma} n_{i\,-\sigma}, \\ \mathcal{H}_2 &= \sum_{\sigma} (E^0_\alpha + V^0_{\alpha\alpha}) n_{\alpha\sigma} + \tfrac{1}{2} U \sum_{\sigma} n_{\alpha\sigma} n_{\alpha\,-\sigma}, \qquad (2.1) \\ \mathcal{H}_3 &= \sum_{i} (V^0_{\alpha i} c^\dagger_{\alpha\sigma} c_{i\sigma} + \text{H.c.}) + \tfrac{1}{2} W \sum_{i\sigma\sigma'} n_{\alpha\sigma} n_{i\sigma'} . \end{aligned}$$

$\mathcal{H}_1$ is a Hamiltonian for the substrate in the presence of the adsorbate. The term V^0_{ij} describes the additional hopping from site j to site i induced by the presence of the adsorbate core potential. I is the Coulomb interaction within the metal for two electrons on the same metal site. If $V^0_{ij} \equiv 0$, $\mathcal{H}_1$ would describe the clean metal surface. $\mathcal{H}_2$ is a Hamiltonian for the adsorbate in the presence of the substrate, E^0_α being the energy of the ionization level and $E^0_\alpha + U$ being the energy of the affinity level of the free adsorbate. $V^0_{\alpha\alpha}$ is the level shift caused by the ion core potential of the substrate atoms.

$\mathcal{H}_3$ is the "interaction" part that couples the two components. We have explicitly included a Coulomb interaction, W, between an electron in the substrate and one on the adsorbate.[15] The lowest-order contribution of this term is obtained by making a Hartree-Fock decoupling of the operator $n_{\alpha\sigma} n_{i\sigma}$. Higher-order contributions arise because of correlations between electrons on the adsorbate and those in the substrate. Since we expect W, $I < U$, these correlations may be unimportant compared to others in the problem. We therefore concentrate on correlations arising from U, postponing the other correlations to subsequent papers. The term in W serves to "renormalize" the one-body interaction potential V, e.g., $V_{\alpha\alpha} \rightarrow V^0_{\alpha\alpha} + \frac{1}{2} W \sum_{i\sigma} \langle n_{i\sigma} \rangle$, etc. A completely self-consistent calculation should take into account the dependence of V on the occupation numbers and bond charges. This will be important if there is significant charge build-up in the region of the adsorbate.

In the Hamiltonian for the metal we can also make a Hartree-Fock decoupling on the Coulomb term I. That this may be reasonable can be seen from the following argument: In the absence of the adsorbate there are already Coulomb interactions between the substrate electrons. In any reasonable description of the clean metal surface these should already have been taken into account. The Coulomb term, I, will then affect the chemisorption process only if there is significant charge redistribution brought about by the presence of the adsorbate. In that case the Hartree-Fock contribution of electron-electron interaction in the metal is $\sim I(\langle n_{i\sigma} \rangle - \langle n^0_{i\sigma} \rangle)$, where $\langle n_{i\sigma} \rangle$ is the occupation of the ith site in the presence of the adsorbate and $\langle n^0_{i\,-\sigma} \rangle$ is the occupation for the clean substrate. Again we will include this term in a Hartree-Fock decoupling scheme; but if the results indicate significant charge redistribution, we will have to explicitly include correlations in the substrate.

Within our approximations the Hamiltonian for the metal $\mathcal{H}_1$ has been reduced to a sum of one-body terms. It differs from the Hamiltonian for the clean substrate because of the terms V^0_{ij} and $I(\langle n_{i\sigma} \rangle - \langle n^0_{i\sigma} \rangle)$. This difference is important in that these terms alter the response of the substrate when the "bonding" interactions $V_{\alpha i}$ are included.[9] This response is determined by the Green's function of the substrate which is now *not the same* as the Green's function for the clean substrate. This difference invalidates previous[16,17] discussions that consider the applicability of a "group orbital" concept without considering the very important modification of metal states brought about by the presence of the adsorbate.[18]

Within the above approximations our Hamiltonian is now:

$$\mathcal{H} = \sum_{ij\sigma} T_{ij,\sigma} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{\sigma} E_\alpha n_{\alpha\sigma} + \frac{1}{2} U \sum_{\sigma} n_{\alpha\sigma} n_{\alpha-\sigma} + \sum_{i\sigma} (V_{\alpha i} c^\dagger_{\alpha\sigma} c_{i\sigma} + \text{H.c}). \tag{2.2}$$

This looks similar to the standard Anderson Hamiltonian[19] but now the effective interaction strengths can be related to the properties of the clean substrate and free adsorbate viz.:

$$T_{ij,\sigma} = T^0_{ij} + V^0_{ij} + \delta_{ij} \left(I(\langle n_{i\,-\sigma} \rangle - \langle n^0_{i\,-\sigma} \rangle) + \frac{1}{2} W \sum_{\sigma'} \langle n_{\alpha\sigma'} \rangle \right), \tag{2.3}$$

$$V_{\alpha i} = V^0_{\alpha i} + W \sum_{\sigma} \langle c^\dagger_{\alpha\sigma} c_{i\sigma} \rangle$$

$$E_\alpha = E^0_\alpha + V^0_{\alpha\alpha} + W \sum_{i\sigma} \langle n_{i\sigma} \rangle .$$

In standard treatments of the Anderson Hamiltonian as applied to chemisorption[5-8] the dependence of the matrix elements on occupation number and bond charges is neglected. For significant charge transfer or redistribution this is obviously not correct and the problem has to be solved completely self-consistently. In Sec. IV, we show that charge redistribution is an integral part of chemisorption and must be included for a meaningful description of the phenomenon. We now go on to discuss the effects of the Coulomb interaction U and the correlations introduced by it.

III. EFFECTS OF CORRELATION

The electronic properties of the system are given by the appropriate Green's function. We will use the double-time Green's function of Zubarev.[12] For two operators A and B we define the Green's function:

$$\mathcal{G}_{AB}(t-t') \equiv \langle\langle A(t); B(t') \rangle\rangle = -i\Theta(t-t') \langle [A(t), B(t')]_+ \rangle . \tag{3.1a}$$

Its Fourier transform satisfies the equation of motion:

$$\omega \mathcal{G}_{AB}(\omega) = (1/2\pi) \langle [A, B]_+ \rangle_\omega + \langle\langle [A, H]_-; B \rangle\rangle_\omega , \tag{3.1b}$$

where H is the Hamiltonian for the system. Using this, we write down the equations of motion for the single-particle Green's functions,[20] $\mathcal{G}^\sigma_{\mu\nu}(\omega) \equiv \langle\langle c_{\nu\sigma}; c^\dagger_{\mu\sigma} \rangle\rangle_\omega$, where ν and μ can be the substrate site orbitals $\{|i\rangle\}$ and/or the adsorbate orbital, $|\alpha\rangle$. (We will neglect overlap at this stage, by assuming $\langle \alpha | i \rangle$ is zero for all $|i\rangle$. These effects are discussed in Sec. VI). From Eqs. (2.2) and (3.1) we obtain,

$$\omega \mathcal{G}^\sigma_{\alpha\alpha}(\omega) = \frac{1}{2\pi} + E_\alpha \mathcal{G}^\sigma_{\alpha\alpha}(\omega) + \sum_i V_{\alpha i} \mathcal{G}^\sigma_{i\alpha}(\omega) + U \Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega), \tag{3.2}$$

where

$$\Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) = \langle\langle n_{\alpha-\sigma} c_{\alpha\sigma}; c^\dagger_{\alpha\sigma} \rangle\rangle_\omega .$$

Similarly we have

$$\omega \mathcal{G}^{\sigma}_{i\alpha}(\omega) = \sum_{ij} T_{ij}\, \mathcal{G}^{\sigma}_{j\alpha}(\omega) + V_{i\alpha} \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega). \qquad (3.3)$$

We can define the substrate Green's function by $G = (\omega - H_1)^{-1}$ corresponding to propagation in the renormalized metal states. Inserting this into Eq. (3.3) we obtain

$$\mathcal{G}^{\sigma}_{i\alpha}(\omega) = \left(\sum_{j} G^{\sigma}_{ij}(\omega)\, V_{j\alpha}\right) \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega). \qquad (3.3a)$$

Inserting (3.3) into (3.2) gives

$$\omega \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega) = \frac{1}{2\pi} + E_{\alpha} \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega) + \Sigma_0(\omega)\, \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega) + U\, \Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega), \qquad (3.4)$$

where

$$\Sigma_0(\omega) = \sum_{ij} V_{\alpha i}\, G^{\sigma}_{ij}(\omega)\, V_{j\alpha}. \qquad (3.5)$$

It is seen that one effect of the interaction is to introduce a self-energy, $\Sigma_0(\omega)$, into the adsorbate Green's function. The effects of surface geometry and local electronic response of the metal are contained in G_{ij}.

The effects of correlation in the problem are contained in the two-particle Green's function $\Gamma^{\alpha\alpha}_{\alpha\alpha} = \langle\langle n_{\alpha-\sigma} c_{\alpha\sigma} ; c^{\dagger}_{\alpha\sigma}\rangle\rangle_{\omega}$. In a simple decoupling scheme this is replaced by $\langle n_{\alpha-\sigma}\rangle \mathcal{G}^{\sigma}_{\alpha\alpha}$, thus giving the result,

$$\mathcal{G}^{\mathrm{HF}\sigma}_{\alpha\alpha}(\omega) = (1/2\pi)[\omega - E_{\alpha} - U\langle n_{\alpha-\sigma}\rangle - \Sigma_0(\omega)]^{-1}.$$

This is the standard Hartree-Fock result which gives rise to a single pole at $\omega = [E_{\alpha} + U\langle n_{\alpha-\sigma}\rangle + \Sigma_0(\omega)]$. However, such a decoupling eliminates the very correlations that are important if U is large. To include them we must, instead, calculate the equation of motion for $\Gamma^{\alpha\alpha}_{\alpha\alpha}$.

$$\omega \Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) = \frac{1}{2\pi}\langle n_{\alpha-\sigma}\rangle + (E_{\alpha} + U)\Gamma^{\alpha\alpha}_{\alpha\alpha} + \sum_{i} V_{\alpha i}(\Gamma^{\alpha\alpha}_{\alpha i} + \Gamma^{\alpha\alpha}_{i\alpha} - \Gamma^{i\alpha}_{\alpha\alpha}), \qquad (3.6)$$

where we have used $n^2_{\alpha-\sigma} = n_{\alpha-\sigma}$ and defined the general two-particle Green's function via

$$\Gamma^{il}_{jk}(\omega) = \langle\langle c^{\dagger}_{i-\sigma} c_{j-\sigma} c_{k\sigma} ; c^{\dagger}_{l\sigma}\rangle\rangle_{\omega}.$$

It is seen that, in the equation for $\Gamma^{\alpha\alpha}_{\alpha\alpha}$ the transfer integral $V_{\alpha i}$ has introduced three additional two-particle Green's functions.

(i) $\Gamma^{\alpha\alpha}_{\alpha i} = \langle\langle n_{\alpha-\sigma} c_{i\sigma} ; c^{\dagger}_{\alpha\sigma}\rangle\rangle$: this describes the following process: at some time we have a σ spin on the adsorbate. This Green's function then gives the amplitude for excitation to an intermediate state in which the σ spin is now in the metal, the motion being correlated with the presence of a $-\sigma$ spin on the adsorbate. We will refer to this as "direct" scattering.

(ii) $\Gamma^{\alpha\alpha}_{i\alpha} = \langle\langle c^{\dagger}_{\alpha-\sigma} c_{i-\sigma} c_{\alpha-\sigma} ; c^{\dagger}_{\alpha\sigma}\rangle\rangle$. The intermediate state involved here is one having a σ spin propagating in the presence of a $-\sigma$ hole. This corresponds to a spin flip on the adsorbate and we will refer to this as "spin-flip" scattering.

(iii) $\Gamma^{i\alpha}_{\alpha\alpha} = \langle\langle c^{\dagger}_{i-\sigma} c_{\alpha-\sigma} c_{\alpha\sigma} ; c^{\dagger}_{\alpha\sigma}\rangle\rangle$. This intermediate state has two electrons on the adsorbate at the same time. For very large U this term is ~$1/U$ and is usually neglected.[21,22] If we wish to discuss intermediate U it obviously has to be retained. We will refer to this process as "charge-transfer" scattering.

These three additional two-particle Green's functions involve the correlated motion of electrons and holes on the adsorbate mediated by the metal. As we shall see, it is exactly these correlations that are important in the large U limit. Thus it is not admissible to decouple these and we must evaluate their equations of motion.

$$\omega \Gamma^{\alpha\alpha}_{\alpha i} = \sum_{ij} T_{ij}\, \Gamma^{\alpha\alpha}_{\alpha j} + V_{i\alpha}\Gamma^{\alpha\alpha}_{\alpha\alpha} + \sum_{j} V_{\alpha j}(\Gamma^{\alpha\alpha}_{ji} - \Gamma^{j\alpha}_{\alpha i}), \qquad (3.7a)$$

$$\omega \Gamma^{\alpha\alpha}_{i\alpha} = \frac{\langle n^{-\sigma}_{\alpha i}\rangle}{2\pi} + \sum_{ij} T_{ij}\, \Gamma^{\alpha\alpha}_{j\alpha} + V_{i\alpha}\Gamma^{\alpha\alpha}_{\alpha\alpha} + \sum_{j} V_{\alpha j}(\Gamma^{\alpha\alpha}_{ij} - \Gamma^{j\alpha}_{i\alpha}), \qquad (3.7b)$$

$$\omega \Gamma^{i\alpha}_{\alpha\alpha} = \frac{\langle n^{-\sigma}_{i\alpha}\rangle}{2\pi} + (2E_{\alpha} + U)\Gamma^{i\alpha}_{\alpha\alpha} - \sum_{j} T_{ij}\, \Gamma^{j\alpha}_{\alpha\alpha} + \sum_{j} V_{\alpha j}(\Gamma^{i\alpha}_{\alpha j} + \Gamma^{i\alpha}_{j\alpha}) - V_{i\alpha}\Gamma^{\alpha\alpha}_{\alpha\alpha}. \qquad (3.7c)$$

As expected we have encountered additional two-particle Green's functions, for example,

$$\Gamma^{i\alpha}_{\alpha i} = \langle\langle c^{\dagger}_{j-\sigma} c_{\alpha-\sigma} c_{i\sigma} ; c^{\dagger}_{\alpha\sigma}\rangle\rangle.$$

These involve the correlated motion of two electrons *in* the substrate mediated by the adsorbate.

Consistent with the spirit of our model Hamiltonian [Eq. (2.2)], which retains correlations arising from two electrons on the adsorbate only and neglects correlations in the metal, we decouple these additional two-particle Green's functions, involving two electrons in the metal, in the Hartree approximation. The equations of motion of these two-particle Green's functions are provided in Appendix A where it is shown that such a decoupling is exact to order V^2 and to all orders in U. It appears worth noting that the terms arising from such a decoupling of these two-particle Green's functions are of the same order as other terms that we have retained and therefore must be included to obtain results exact to order V^2. We also point out that the deficiency in completely neglecting the two-particle Green's functions involving two electrons in the metal manifests itself by giving a negative spectral weight function for the single-particle Green's function $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$. However, approximating them in the Hartree approximation does not lead to such inconsistency in the solution for $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$.

Thus replacing all two-particle Green's functions of the form $\Gamma^{j\alpha}_{i\alpha}$ by $\langle c^{\dagger}_{j-\sigma} c_{i-\sigma}\rangle \mathcal{G}^{\sigma}_{\alpha\alpha}$, etc., we obtain a closed system of equations consisting of Eq. (3.8) and the following equations:

$$\omega \Gamma^{\alpha\alpha}_{\alpha i}(\omega) = \sum_{j} T_{ij} \Gamma^{\alpha\alpha}_{\alpha j}(\omega) + V_{i\alpha} \Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega), \tag{3.8a}$$

$$\begin{aligned}\omega \Gamma^{\alpha\alpha}_{i\alpha}(\omega) = \bigg(\frac{\langle n^{-\sigma}_{\alpha i}\rangle}{2\pi} &+ \sum_{ij} T_{ij} \Gamma^{\alpha\alpha}_{j\alpha}(\omega) + V_{i\alpha}\Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) \\ &- \tilde{\mathcal{V}}^{-\sigma}_{\alpha i} \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)\bigg),\end{aligned} \tag{3.8b}$$

$$\begin{aligned}\omega \Gamma^{i\alpha}_{\alpha\alpha}(\omega) = \bigg(\frac{\langle n^{-\sigma}_{i\alpha}\rangle}{2\pi} &+ (2E_{\alpha} + U)\Gamma^{i\alpha}_{\alpha\alpha}(\omega) - \sum_{j} T_{ij} \Gamma^{j\alpha}_{\alpha\alpha}(\omega) \\ &- V_{i\alpha}\Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) + \tilde{\mathcal{V}}^{-\sigma}_{\alpha i} \mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)\bigg).\end{aligned} \tag{3.8c}$$

In the above, $\Sigma_0(\omega)$ is the self-energy as defined in Eq. (3.5) and we have introduced an additional effective transfer matrix element via

$$\tilde{\mathcal{V}}^{-\sigma}_{i\alpha} = \sum_{ij} \langle n^{-\sigma}_{ij}\rangle V_{j\alpha}.$$

This effective transfer matrix element reflects the role played by the charge shared between two substrate atoms (the substrate bond charge). A transfer of charge from site i to α may be brought about via the jth atom by making use of the shared charge $\langle n^{-\sigma}_{ij}\rangle$ to go from i to j and then on to α via the transfer matrix element $V_{j\alpha}$.

Solving Eqs. (3.6) and (3.8a)–(3.8c) for $\Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega)$ and substituting into Eq. (3.4) gives $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$. We find that the solution for $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$ may be written in the following form which allows for a ready interpretation of its physical content:

$$\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega) = \frac{1 - f^{-\sigma}_{\alpha}(\omega)}{\omega - E_{\alpha} - \Sigma_I(\omega)} + \frac{f^{-\sigma}_{\alpha}(\omega)}{\omega - E_{\alpha} - U - \Sigma_A(\omega)}. \tag{3.9}$$

In the above we have introduced three functions $f^{-\sigma}_{\alpha}(\omega)$, $\Sigma_I(\omega)$, and $\Sigma_A(\omega)$, all of which are given in terms of the physical parameters of the system. As we shall see, $f^{-\sigma}_{\alpha}(\omega)$ is the effective probability that the $-\sigma$ orbital of the adsorbate is occupied (at a given frequency ω). $\Sigma_I(\omega)$ is the self-energy for an electron is the adsorbate ionization level interacting with the substrate and $\Sigma_A(\omega)$ is the self-energy for an electron in the adsorbate affinity level. The two terms in Eq. (3.9), we note, have a simple physical interpretation.

The first term corresponds to propagation of a σ-spin electron in the ionization level. This propagator is weighted by the "probability," $1 - f^{-\sigma}_{\alpha}(\omega)$, that the $-\sigma$ spin electron is not there. The second term corresponds to propagation in the affinity level, weighted by the "probability" that the $-\sigma$ spin state is occupied.

We will now discuss the Σ and f functions that appear in Eq. (3.9).

A. $\Sigma_A(\omega)$

The affinity level self-energy, $\Sigma_A(\omega)$, is found to be

$$\Sigma_A(\omega) = 2\sum_{ij} V_{\alpha i} G_{ij} V_{j\alpha} - \sum_{ij} V_{\alpha i} \tilde{G}_{ij} V_{j\alpha}, \tag{3.10}$$

where

$$[\tilde{G}^{-1}]_{ij} = [\omega - (2E_{\alpha} + U)]\delta_{ij} + T_{ij} \tag{3.11}$$

is the propagator for an intermediate state having two electrons on the adsorbate together with a hole in the substrate.

$\Sigma_A(\omega)$ contains three distinct contributions: (i) self-energy of direct scattering, $\Sigma_0(\omega)$; (ii) self-energy of spin-flip scattering, $\Sigma_0(\omega)$; (iii) self-energy of charge-transfer scattering,

$$\tilde{\Sigma}_0(\omega) = \sum_{ij} V_{\alpha i} \tilde{G}_{ij}(\omega) V_{j\alpha}.$$

It is seen that the first two contributions are identical. Thus in situations where correlation is important, *direct and spin-flip scattering contribute equally to the chemisorption process*. The third term comes from charge-transfer scattering and, as expected, it is $\sim V^2/U$ and vanishes in the infinite U limit.

It is worth noting at this point, that in the small V limit our results reduce to those of Brenig and Schonhammer[23] (see Appendix B) who calculated the effects of correlation to order V^2. In particular we can identify the two contributions to their correlation self-energy, $m(\omega)$: the first term arises because of spin-flip scattering, the second term is $\sim V^2/U$ and arises from charge-transfer scattering.

B. $\Sigma_I(\omega)$

The ionization level self-energy, $\Sigma_I(\omega)$, is found to be

$$\Sigma_I(\omega) = \sum_{ij} V_{\alpha i} \mathcal{G}^{\sigma}_{ij}(\omega) V_{j\alpha}, \tag{3.12a}$$

where

$$\mathcal{G}^{\sigma}_{ij}(\omega) \equiv G^{\sigma}_{ij}(\omega) - \frac{U}{\omega - E_{\alpha} - U - \Sigma_A(\omega)} \times \sum_{k} \langle n^{-\sigma}_{ik} \rangle [\, G^{-\sigma}_{kj}(\omega) + \tilde{G}^{-\sigma}_{kj}(\omega)] \,. \tag{3.12b}$$

If we compare Eq. (3.12a) with Eq. (3.5), we see that the metal state Green's function $G^{\sigma}_{ij}(\omega)$, occurring in the ionization level self-energy, is changed to the new Green's function $\mathcal{G}^{\sigma}_{ij}(\omega)$ as defined in Eq. (3.12b). It is important to note that this "renormalization" only occurs if we include spin-flip and/or charge-transfer contributions in the chemisorption process.

In the large U limit, the contribution of spin-flip terms is of the same order (in $V_{\alpha i}$) as the direct scattering terms. It is to be seen that the renormalization of the σ-spin metal propagator is determined by elements of the bond charge matrix and propagators for the $-\sigma$ *spin* electron. Thus the presence of a fluctuating moment on the adsorbate has produced an effective spin-spin interaction in the metal. What has happened is basically this: in the absence of spin-flip scattering, the up- and down-spin states of the Anderson Hamiltonian are independent and degenerate. By including the spin-flip scattering we split the degeneracy and introduce an additional contribution to the self-energy.

As a final remark, we point out that for large negative frequencies (i.e., outside the metal band), the real part of $\mathcal{G}^{\sigma}_{ij}(\omega)$ is negative. For the first term this is obvious; for the second term, both $G^{-\sigma}_{ki}(\omega)$ and $[\,\omega - E_{\alpha} - U - \Sigma_A(\omega)]$ are negative, this, combined with the minus sign, gives rise to an overall negative contribution. This will be of importance in Sec. IV.

C. $f^{-\sigma}_{\alpha}(\omega)$

The effective occupation "probability" $f^{-\sigma}_{\alpha}(\omega)$ can be written

$$f^{-\sigma}_{\alpha}(\omega) = \left(1 + \frac{\Sigma_A(\omega) - \Sigma_I(\omega)}{U}\right)^{-1} \times \left(\langle n_{\alpha-\sigma} \rangle + \sum_{ij} \langle n^{-\sigma}_{\alpha i} \rangle G_{ij} V_{j\alpha} - V_{\alpha i} \tilde{G}_{ij} \langle n^{-\sigma}_{j\alpha} \rangle \right) . \tag{3.13}$$

The numerator reflects the modification to the occupation "probability" produced by bonding, the two additional terms being proportional to the bond charge matrix. Thus the numerator contains the modifications produced by *charge sharing*.

The denominator would be equal to one if U were very large. For finite U the occupation probability is modified by charge transferring back and forth. Thus the denominator contains the modifications produced by *charge fluctuations*.

The expression (3.9) is our general expression for the single-particle propagator $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$. It is easily seen that it satisfies the property of being exact in the limits $V \neq 0$, $U = 0$ and $V = 0$, $U \neq 0$ and interpolates smoothly between these limits. In the former case it gives rise to either a single level or two levels corresponding to weak- ($V \ll$ bandwidth) or strong- ($V \gtrsim$ bandwidth) coupling regimes, respectively. The two levels in the strong-coupling regime correspond to the bonding and antibonding levels. In the latter case ($V = 0$, $U \neq 0$) it gives rise to two poles corresponding to the ionization and electron affinity levels of the nonbonded adsorbate. For both $V \neq 0$ and $U \neq 0$ it has at least two poles and under certain situations, four poles. These four poles correspond to the bonding and antibonding levels arising from the ionization and electron affinity levels each.

It is to be noted that, while the pole structure of $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$ discussed above may give rise to four poles, it does not necessarily imply that the spectral weight function will also always show four peaks. The four energy levels corresponding to the four poles have a finite width, of course, and if the energy separation of these poles becomes small compared to their widths in some region of the parameters V, U, and the clean substrate density of states, then the spectral function would not show the corresponding poles separately, but would manifest the closeness of the poles involved as a single peak at an appropiate intermediate energy. This is an important point to bear in mind in comparing theoretical analyses with spectroscopic data (e.g., photoemission) which reflect the behavior of the density of states, a quantity directly related to the spectral weight function of $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$. Anticipating the rather important conclusions which will be reached in Sec. IV via a comparison of our result (3.9) with the result of the Anderson model and spectroscopic data, we pause here briefly to comment upon the role of Coulomb correlations introduced by U. This also allows us to shed light on the conventional molecular-orbital and valence-bond pictures of quantum chemistry as applied to the phenomenon of chemisorption.

The physical content of Eq. (3.9) can be appreciated from the following considerations. In the absence of $V_{\alpha i}$, $\mathcal{G}^{\sigma}_{\alpha\alpha}(\omega)$ 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.[26] 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 of the form $U\langle n_\alpha^{-\sigma}\rangle$ to the shift in the peak of the E_α derived level). 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 Hartree-Fock (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 (3.9) *always* gives two poles (in contrast to the single pole Hartree-Fock 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 (3.9) for $\mathcal{G}^\sigma_{\alpha\alpha}(\omega)$ 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.

IV. COMPARISON WITH ANDERSON MODEL AND EXPERIMENT

A phenomenological model extensively used to discuss chemisorption is the Anderson model, given originally in the context of local moment formation on paramagnetic inpurities in a bulk nonmagnetic metallic host. In its usual form and as adapted to chemisorption by Grimley, Newns, and others, it consists only of the interaction terms $V^0_{\alpha i}$ and the single Coulomb interaction, $Un_{\alpha\sigma}n_{\alpha-\sigma}$. Thus setting $V^0_{ij}=W=I=0$ in expression (2.3) we regain from (2.2) the standard Anderson model;

$$\mathcal{H}=\sum_{ij}T^0_{ij}C^\dagger_{i\sigma}C_{j\sigma}+\sum_\sigma E^0_\alpha n_{\alpha\sigma}+\tfrac{1}{2}U\sum_\sigma n_{\alpha\sigma}n_{\alpha-\sigma}+\sum_{i\sigma}(V^0_{\alpha i}C^\dagger_{\alpha\sigma}C_{i\sigma}+\text{H.c.}). \tag{4.1}$$

In Eq. (4.1), E^0_α is the valence level for the free absorbate and has been in the past set equal to the ionization potential of the free adsorbate (e.g., -13.6 eV for hydrogen). Since T^0_{ij} is the transfer integral for the clean substrate, the propagator $G^\sigma_{ij}(\omega)$ in Eq. (3.3a) now corresponds to the clean substrate. Consequently, the ionization level self-energy of Eq. (3.12) now becomes

$$\Sigma^{(0)}_I(\omega)=\sum_{ij}V^0_{\alpha i}\mathcal{G}^0_{ij}(\omega)V^0_{j\alpha}. \tag{4.2}$$

We introduce the real and imaginary parts of $\Sigma^{(0)}_I(\omega)$ by writing,

$$\Sigma^{(0)}_I(\omega)=\Lambda^{(0)}_I(\omega)-i\Delta^{(0)}_I(\omega). \tag{4.3}$$

Similar changes occur in the electron-affinity-level self-energy and the occupation function $f(\omega)$. We denote these by $\Sigma^{(0)}_A$ and $f^{(0)}(\omega)$ and correspondingly the adsorbate propagator for the Anderson model by $\mathcal{G}^{(0)\sigma}_{\alpha\alpha}(\omega)$ which follows from Eq. (3.9);

$$\mathcal{G}^{(0)\sigma}_{\alpha\alpha}(\omega)=\frac{1-f^{(0)-\sigma}_\alpha(\omega)}{\omega-E^0_\alpha-\Sigma^{(0)}_I(\omega)}+\frac{f^{(0)-\sigma}_\alpha(\omega)}{\omega-E^0_\alpha-U-\Sigma^{(0)}_A(\omega)}\,. \tag{4.4}$$

From (4.4) it follows that the poles arising from the adsorbate ionization level occur at energies, ω, that are solutions of

$$\omega_\alpha=E^0_\alpha+\Lambda^{(0)}_I(\omega_\alpha). \tag{4.5}$$

Now, we observe that $\Lambda^{(0)}_I(\omega)$ is related to the Hilbert transform of the clean surface density of states of the substrate. Most transition-metal density of states (d and s bands) are centered at $\omega_c\sim 5-7$ eV below the vacuum level.[14] For energies less than ω_c, it is generally true that $\Lambda^{(0)}_I(\omega)$ will be negative (going as $-1/|\omega|$ as $\omega\to-\infty$). Thus if the pole occurs below ω_c, it must occur at an energy *below* E^0_α given by $\omega_\alpha=E^0_\alpha-|\Lambda^{(0)}_I(\omega_\alpha)|$. [At these energies $|\Lambda^{(0)}_I(\omega_\alpha)|\sim 2$ eV.] In the absence of the adsorbate-substrate Coulomb interaction W, E^0_α corresponds to the free ionization level E_I. Thus if $E_I<\omega_c$, the self-consistent position of the pole of $\mathcal{G}^{(0)\sigma}_{\alpha\alpha}$ associated with E_I is *below* E_I by ~ 2 eV. (This is nothing more than a reflection of the fact that an attractive one-body interaction $V^0_{\alpha i}$ always lowers the energy of the bonding level.) Thus the approximate Anderson model has led to the inevitable conclusion that for adsorbates having large ionization potentials, E_I (~ 7 eV), the observed bonding level should be below E_I. By contrast photoemission results for hydrogen ($E_I\sim 13.6$ eV) and oxygen ($E_I\sim 13.6$ eV) adsorbed on transition metals show a peak associated with adsorbate at $\sim 10-11$ eV below the vacuum level.[24,25] This is ~ 3 eV *above* the free ionization level. Thus there is a discrepancy of $\sim 5-6$ eV in the position of the level predicted by the approximate Hamiltonian (4.1) and that observed in photoemission.

A number of possible explanations for this discrepancy come to mind:

(i) 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 been observed and so we discount this explanation.

(ii) The bonding level is indeed below E_I, but the photoemission experiment gives an apparent energy above E_I due to the contribution of final-state relaxation effects.[26] For most systems the required final-state relaxation *shift* would be $\gtrsim 5$ eV, which seems entirely too large and unexpected for valence orbitals. Although a certain upwards final-state relaxation shift is inherently contained in the bonding level as measured by photoemission, a quantitative independent estimate of this shift is at best difficult and has, to the best of our knowledge, never been made. However, the general body of experimental information and comparison between core and valence level spectroscopy suggests to us that for valence orbitals of most covalently bonded adsorbates, this shift is probably ~2–3 eV. Thus we discount this as the *sole* explanation for the observed position.

(iii) 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.

(iv) From the above we are led to the inevitable conclusion that the observed level is indeed associated with the adsorbate ionization level. If this is the case, the approximate Hamiltonian (4.1) in which $E_\alpha^0=E_I$ is clearly inadequate to describe the absorption of atoms having a large ionization potential. The E_α needed is at least that contained in our Eq. (2.3), reflecting the importance of electron-electron interactions between adsorbate and substrate electrons. This gives rise to an upward shift (the same as image at large separations) of the free ionization level. However, the observed level is still in the region where $\Lambda_I^0(\omega)$ is negative, hence, *this upward shift must be large enough* ($\gtrsim 3eV$) *to overcompensate for the downward shift due to the bonding interaction*, $V_{\alpha i}$, giving a level at the observed position.

Thus from points (ii) and (iv) above we come to the realization that the total needed upward shift of the adsorbate ionization level (which we have estimated to be $\gtrsim 5$ eV) arises from two main contributions. One such contribution is the screening and polarization effects that exist in the chemisorbed system even in the absence of any interaction with an external probe. This, we discussed in point (iv) above and will refer to this contribution as a "ground-state" effect. By contrast, the second kind of contribution is a consequence of disturbing the chemisorbed system by an external probe (e.g., photons in photoemission) and arises due to the response of the metallic charge density to the hole left behind by the photoemitted electron. We therefore will refer to this shift, inherent in the nature of the photoemission experiment, as a "final-state relaxation" effect. As mentioned earlier, there is no way of determining this quantatively without ambiguity at the present time. Nevertheless, it may be safely concluded that both the above-discussed effects are contained in the total upward shift of $\gtrsim 5$ eV, possibly contributing almost equally for valence levels of adsorbates like hydrogen, oxygen, etc.

This of course implies that ground-state screening and polarization effects play an important role in chemisorption.[27] The total electron-electron interaction between adsorbate and substrate electrons produces a shift upwards in the adsorbate level given (in Hartree-Fock[28]) by

$$\Delta E_\alpha \sim \sum_{i\sigma} W\langle n_{i\sigma}\rangle .$$

Since this contains a sum over neighboring sites, the value of W itself need not be very large (especially for sites of high coordination). For example, in the centered position (i.e., with four neighbors) we have: $\Delta E_\alpha\sim 4W\sim 2$–$4$ eV implying that $W\approx\frac{1}{2}$–1 eV. However, the presence of the above-mentioned Coulomb interaction, together with the intrasubstrate transfer terms V_{ij}, will cause significant modification of the metal states, altering the response of the metal to the adsorbate. In Sec. V we show that these effects are local in nature, being restricted to a small number of substrate atoms and depend upon the *local* geometry and electronic structure.

V. SUBSTRATE GROUP AND SURFACE CLUSTER

As mentioned in Sec. I the rather local nature of the chemisorption process has led to the notion of a "surface molecular cluster" consisting of the adsorbate and a few neighboring substrate atoms. That such a notion is conceptually meaningful and under certain conditions may also lead to simplicity in actual calculations follows immediately from the preceeding analysis.

From Eq. (3.5) (defining the self-energy of the adsorbate propagator in the absence of U), we observe that the sum over the substrate sites is restricted to a small number of substrate atoms which we will call the "substrate group." The sum is limited by the short-ranged nature of the effective single-body coupling strength V, The presence of a contact interaction, U, does not change the range but enters only through its effect on the bond-matrix elements that are implicit in V [see Eq. (2.3)]. Thus it is clearly seen that the chemical bonding of the adsorbate to the substrate involves only a few substrate atoms. However, the appropriate state of these atoms is the renormalized metal states discussed in Sec. II. The propagation of electrons between these states must be described in a self-consistent manner. This requirement has been overlooked in previous introductions of such a concept.[16,17] They are self-consistently included in our considerations through the presence of G_{ij} in Eq. (3.5).

The meaning of this equation becomes clear if we define a mean strength of interaction via,

$$\overline{V}^2 = \sum_i |V_{\alpha i}|^2 \tag{5.1}$$

and introduce the notation of a "substrate-group" Green's function via,

$$G_c(\omega) = \sum_{ij} \frac{V_{\alpha i}}{\overline{V}} G_{ij}(\omega) \frac{V_{j\alpha}}{\overline{V}} . \tag{5.2}$$

Thus,

$$\Sigma_I(\omega) = \overline{V}^2 G_c(\omega). \tag{5.3}$$

From Eq. (5.2) it is seen that the natural definition of the "group" Green's function is given by a linear combination of the renormalized substrate propagators, G_{ij}, the relative weights being determined by the relative strengths of the interaction $V_{\alpha i}$. We emphasize that defining $G_c(\omega)$ via Eq. (5.2) takes into account the propagation within the entire substrate to all orders in T_{ij}. At no stage has the cluster been considered to be detached from the rest of the substrate.

At this stage one may introduce the notion of a substrate-group "orbital" with energy $E_c(\omega)$ defined via the relation

$$G_c(\omega) = [\omega - E_c(\omega)]^{-1} . \tag{5.4}$$

In the absence of U, Eq. (3.3) describes the problem of the interaction of the single valence orbital of the adsorbate with a *single* substrate group orbital whose energy $E_c(\omega)$ is frequency dependent. The "energy," $E_c(\omega)$, contains the complete response of the substrate and is a well-defined function of substrate parameters (e.g., surface geometry, surface density of states, etc.). The substrate-group orbital, ψ_c, is defined to be a linear combination of substrate sites orbitals, φ_i with the appropriate symmetry. The coefficients in this linear combination are the relative weights of the self-consistently determined coupling strengths, $V_{\alpha i}$. Thus

$$\psi_c = \sum_i \frac{V_{\alpha i}}{\overline{V}} \varphi_i . \tag{5.5}$$

This definition of ψ_c is valid for any position of the adatom not just the symmetric positions considered previously. The introduction of the effective substrate-group orbital may be a useful device for incorporating the electronic and structural properties of the substrate into a description of the chemisorption phenomenon.

VI. EFFECTS OF NONORTHOGONALITY

Our analysis of the chemisorption phenomenon in Secs. II–V proceeded by neglecting the direct overlap between the adsorbate and substrate wave functions. However, in general these wave functions are not orthogonal to each other and their overlap must be taken into account. In this section we therefore provide the mathematical considerations involved in generalizing the preceeding theory to nonzero overlap (i.e., $\langle i|\alpha\rangle \neq 0$). As mentioned in Sec. I, the inclusion of the overlap merely involves a redefinition of the parameters discussed in Secs. II–V. The basic structure of the theory remains the same. This was first shown by Grimley.[8] However, for the sake of completeness as well as to expose the physical and chemical content and implications of nonzero overlap, we provide here a modified version of his proof. In particular we draw attention to the relation between physical observables and single-particle Green's function calculated in a nonorthogonal basis set.

We assume that the system can be described in terms of a set of localized functions. One of these, $|\alpha\rangle$, describes the adsorbate orbital and the subset $\{|i\rangle\}$ describes the site functions. We define the overlap matrix $\vec{\underline{S}}$, via $S_{i} \equiv \langle i|j\rangle$, $S_{\alpha i} \equiv \langle\alpha|i\rangle$. We also define its inverse, $\vec{\underline{D}} \equiv \vec{\underline{S}}^{-1}$.

The set $\{|\alpha\rangle ; |i\rangle\} \equiv \vec{\underline{X}}$ is assumed to be a complete description of chemisorption. (Note that the orbitals $\{|i\rangle\}$ include *only* the s and d orbitals of the substrate, thus the issue of overcompleteness does not arise.)

This being the case, we can expand the field operator, Ψ, in terms of this (nonorthogonal) basis set:

$$\Psi = \sum_i |i\rangle c_i + |\alpha\rangle c_\alpha \equiv \underline{X} \cdot \underline{c} . \tag{6.1}$$

Alternatively, we could have chosen to describe the same system in terms of some *orthogonal* set of states, $\underline{\varphi}$. There exists a transformation that takes us from $\underline{X} \to \underline{\varphi}$ and back again viz.

$$\varphi = \mathrm{X} \cdot \underline{\mathrm{A}} \quad \text{and} \quad \underline{\mathrm{X}} = \underline{\varphi \mathrm{B}}. \tag{6.2}$$

Because the set X is nonorthogonal the transformation described by Eq. (6.2) is nonunitary. As shown by Grimley[8] the operators $\underline{\mathrm{A}}$ and $\underline{\mathrm{B}}$ have the properties:

$$\underline{\mathrm{A}}^\dagger \underline{\mathrm{B}} = \underline{\mathrm{B}}^\dagger \underline{\mathrm{A}} = \underline{1}, \quad \underline{\mathrm{B}}^\dagger \underline{\mathrm{B}} = \underline{\mathrm{S}}, \tag{6.3}$$

where $\underline{1}$, is the unit matrix.

Let us expand the field operator ψ in terms of the orthonormal set, $\underline{\varphi}$.

$$\hat{\psi} = \sum_l \varphi_l a_l = \underline{\varphi} \cdot \underline{\mathrm{a}} \tag{6.4}$$

Now, independently of the representation used, we know that $[\hat{\psi}, \hat{\psi}^\dagger] = \delta(x - x')$, which implies $[a_m, a^\dagger_{m'}] = \delta_{mm'}$. Using Eqs. (6.4) and (6.2) we can write

$$\hat{\psi} = \underline{\varphi} \cdot \underline{\mathrm{a}} = \underline{\mathrm{X}} \cdot \underline{\mathrm{A}} \cdot \underline{\mathrm{a}}\ ;$$

comparing with Eq. (6.1) this implies that

$$\underline{\mathrm{A}} \cdot \underline{\mathrm{a}} = \underline{\mathrm{c}}, \quad \underline{\mathrm{a}}^\dagger \cdot \underline{\mathrm{A}}^\dagger = \underline{\mathrm{c}}^\dagger. \tag{6.5}$$

Thus we have related Fermion operators of the nonorthogonal set to those of the orthogonal set. Using this we can derive the commutation rules for the nonorthogonal basis

$$[\underline{\mathrm{c}}, \underline{\mathrm{c}}^\dagger]_{ij} = (\underline{\mathrm{A}} \cdot [\underline{\mathrm{a}}, \underline{\mathrm{a}}^\dagger] \underline{\mathrm{A}}^\dagger)_{ij} = \sum_{kl} A_{ik} [a_k, a_l^\dagger] A^\dagger_{lj}$$

$$= \sum_k A_{ik} A^\dagger_{kj} = (\underline{\mathrm{AA}}^\dagger)_{ij} \cdot$$

Hence, from Eq. (6.3),

$$[c_i, c_j^\dagger] = D_{ij} = (\mathrm{S}^{-1})_{ij}. \tag{6.6}$$

An immediate consequence of Eq. (6.6) is that

$$n^2_{i\sigma} = D_{ii} n_{i\sigma} \neq n_{i\sigma}. \tag{6.7}$$

This is important when solving the equation of motion for the Γ functions of Sec. III.

Having derived the commutation relations for the nonorthogonal set we now show how to calculate the observables of the system: We can define two different single-particle Green's functions:

$$\begin{aligned} \mathcal{G}_{ij} &= \langle\langle c_i; c_j^\dagger \rangle\rangle_\omega, \quad \text{nonorthogonal;} \\ \tilde{\mathcal{G}}_{ij} &= \langle\langle a_i; a_j^\dagger \rangle\rangle_\omega, \quad \text{orthogonal.} \end{aligned} \tag{6.8}$$

From standard many-body theory we know how to calculate observables for the orthogonal basis. For example, the density of states is related to the trace of the Green's function. Thus,

$$\mathrm{Tr}\, \tilde{\mathcal{G}} = \sum_i \langle\!\langle a_i; a_i^\dagger \rangle\!\rangle_\omega \,.$$

However, $\underline{\mathrm{a}} = \underline{\mathrm{B}} \cdot \underline{\mathrm{c}}$ [see Eqs. (6.3) and (6.5)]. We can therefore write

$$\begin{aligned} \mathrm{Tr}\, \tilde{\mathcal{G}} &= \sum_{jk} B^\dagger_{ij} \langle\!\langle c_j; c_k^\dagger \rangle\!\rangle_w B_{ki} \\ &= \sum_{jk} \left(\sum_i B_{ki} B^\dagger_{ij} \right) \langle\!\langle c_j; c_k^\dagger \rangle\!\rangle_\omega \\ &= \sum_{jk} (\underline{\mathrm{B}}\underline{\mathrm{B}}^\dagger)_{kj}\, \mathcal{G}_{jk} = \sum_k (\underline{\mathrm{S}} \cdot \underline{\mathcal{G}})_{kk} \,. \end{aligned}$$

Hence

$$\mathrm{Tr}\, \underline{\tilde{\mathcal{G}}} = \mathrm{Tr}\, \underline{\mathrm{S}} \cdot \underline{\mathcal{G}}\,. \tag{6.9}$$

Thus the quantity $\underline{\mathrm{S}} \cdot \underline{\mathcal{G}}$ is the important quantity in terms of the observables of the system. (It is worth noting at this point that $\underline{\mathrm{S}} \cdot \underline{\mathcal{G}}$ is exactly the "pseudo"-Green's function used by Bagchi and Cohen in their analysis of chemisorption with an overcomplete basis set.[22]) In Secs. III and IV, the density of states was the object of major interest. Equation (6.9) shows that, in the presence of nonzero overlap, we have only to calculate $\underline{\mathrm{S}} \cdot \underline{\mathcal{G}}$ to compare with the observed spectroscopic data. This becomes a trivial task once we have solved the equations of motion for the Green's function.

To calculate the equations of motion we use the commutation relations (6.6) and Eq. (3.1). For clarity of expression we will just consider a one-body Hamiltonian, $\langle i | \mathcal{H} | j \rangle \equiv H_{ij}$; Hamiltonians having electron-electron interactions can be dealt with in the same way. The equation of motion for $\mathcal{G}_{ij}$ is

$$\omega \mathcal{G}_{ij}(\omega) = D_{ij} + \sum_{kl} D_{ik} H_{kl}\, \mathcal{G}_{lj} \,. \tag{6.10}$$

Let us form $\tilde{\mathcal{G}}_{\alpha\beta} \equiv \sum_\gamma S_{\alpha\gamma} \mathcal{G}_{\gamma\beta}$ and use the fact that $\underline{\mathrm{D}} \cdot \underline{\mathrm{S}} = \underline{1}$ to obtain,

$$\omega \tilde{\mathcal{G}}_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \sum_l H_{\alpha l} \mathcal{G}_{l\beta} \,. \tag{6.11}$$

For the systems we are discussing, we assume that the metal orbitals are orthogonal to one another. This being so, we can write the overlap matrix $\tilde{\mathrm{S}}$ as

$$S_{\alpha\beta} = \delta_{\alpha\beta} + \tilde{S}_{\alpha\beta}$$

with $\tilde{S}_{\alpha\beta} = 0$, if α and β are *both* metal or adsorbate orbitals. Thus we have

$$\tilde{\mathcal{G}}_{\alpha\beta} = \sum_l S_{\alpha l} \mathcal{G}_{l\beta} = \mathcal{G}_{\alpha\beta} + \sum_l \tilde{S}_{\alpha l} \mathcal{G}_{l\beta} \,.$$

Substituting into Eq. (6.11), we have

$$\omega \mathcal{G}_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \sum_l (H_{\alpha l} - \omega \tilde{S}_{\alpha l})\, \mathcal{G}_{l\beta} \,. \tag{6.12}$$

If we compare this with Eq. (3.2), we can see that for a single-particle Hamiltonian the effect of overlap is only to modify the off-diagonal hopping matrix elements.

Next, we discuss the changes introduced by nonzero overlap in the equations of motion of the two-particle Green's functions (the Γ's) and consequently in the equations of motion of the single-particle Green's functions. The changes in the two-particle Green's functions also arise due to the modified commutation relations of the electron creation and annihilation operators occurring in the electron-electron interaction terms. The only modification in these two-particle terms [in addition to the replacement of $V_{\alpha i}$ by $(V_{\alpha i} - \omega\tilde{S}_{\alpha i})$] arises due to the relations of the type expressed in Eq. (6.7). For example, for the model Hamiltonian (2.2), the intra-adsorbate Coulomb interaction term leads to contributions involving $Un^2_{\alpha -\sigma} = D_{\alpha\alpha} U n_{\alpha -\sigma}$. Recalling that $\underline{D} = \underline{S}^{-1}$, the additional factor $D_{\alpha\alpha}$ reflects the correction introduced in the occupation probability due to the normalization of nonorthogonal wave functions of the basis set.

Thus the results derived in Sec. III carry over to the nonzero overlap case by merely changing $V_{\alpha i}$ to $(V_{\alpha i} - \omega\tilde{S}_{\alpha i})$ and U to $D_{\alpha\alpha} U$. The conclusions reached in Sec. IV and the concept of surface molecular cluster discussed in Sec. V also remain unaffected by including the nonorthogonality of the adsorbate-substrate wave functions.

VII. SUMMARY

In this paper we have shown how Coulomb correlations on the adsorbate affect the chemisorption process. It can be seen that such correlations can cause radical departures from the results obtained by standard Hartree-Fock decoupling schemes. The major differences are: (i) The adsorbate Green's function now has two poles; one derived from the ionization level (at $\omega = E_\alpha$) and the other derived from the affinity level (at $\omega = E_\alpha + U$). In contrast, Hartree-Fock decouplings produce a single peak at some intermediate energy $\omega \sim E_\alpha + \frac{1}{2}U$. (ii) The chemisorption self-energy is different for the two levels. (iii) Spin-flipped and ionic configurations contribute to the self-energy of the affinity level. In fact, the former gives as much contribution as the direct scattering term—the only one included in a Hartree-Fock decoupling scheme.

The results with Coulomb correlations have been compared with photoemission data for typical adsorbates on transition metals. This leads us to the conclusion that screening and polarization effects must play an important role in chemisorption. The electron-electron interaction between adsorbate and substrate electrons, together with the intrasubstrate transfer terms V_{ij} produce this screening and polarization, giving rise to substantial modification of the metal states.

In addition to the effects of Coulomb correlations, chemisorption is strongly dependent on the local electronic and lattice structure of the substrate. The formalism presented here uses a site representation to describe chemisorption; thus local effects appear in a natural way and the relative importance of individual properties of the substrate can be distinguished. The introduction of the nonorthogonality of the substrate-adsorbate wave function is a straightforward matter as shown in Sec. VI.

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APPENDIX A: NATURE OF ZUBAREV DECOUPLING

In Sec. III we calculated the equation of motion for the two-particle Green's functions (GF). The approximation used there was to decouple those two-particle GF that contain two metal operators, the assertion being that this retained all terms correct to $O(V^2)$. In this appendix we will now prove that assertion.

The important quantity as far as the single-particle GF is concerned is the two-particle GF $\Gamma^{\alpha\alpha}_{\alpha\alpha}$ [see Eq. (3.2)]. This contains no metal operators. It is connected, by $V_{\alpha i}$, to those two-particle GF that have a single metal operator [Eq. (3.6)]. These are, in turn, connected by $V_{\alpha i}$, to those two-particle GF that have two metal operators. Thus the latter are already of $O(V^2)$ removed from $\Gamma^{\alpha\alpha}_{\alpha\alpha}$.

Thus if we neglect the coupling $V_{\alpha i}$ in *their* equations of motion the result will be exact to $O(V^2)$. This result should not be surprising: neglecting the coupling $V_{\alpha i}$ is tantamount to allowing the electrons to move independently—exactly what is assumed by the decoupling procedure. The purpose of this appendix is to show this explicitly. Their equations of motion can be written (these are written in $\vec{k}$ space for simplicity, the final result can always be Fourier transformed back to the site representation) as

$$\omega\Gamma^{k\alpha}_{p\alpha}(\omega) = \frac{\langle n^{-\sigma}_{kp}\rangle}{2\pi} + E_\alpha \Gamma^{k\alpha}_{p\alpha}(\omega) + (\epsilon_p - \epsilon_k)\Gamma^{k\alpha}_{p\alpha}(\omega) + U\langle\langle c^\dagger_{k-\sigma} c_{p-\sigma} n_{\alpha-\sigma} c_{\alpha\sigma}; c^\dagger_{\alpha\sigma}\rangle\rangle_\omega + O(V) \tag{A1}$$

and,

$$\omega \langle\langle c^\dagger_{k-\sigma} c_{p-\sigma} n_{\alpha-\sigma} c_{\alpha\sigma}; c^\dagger_{\alpha\sigma} \rangle\rangle_w = \frac{\langle n^{-\sigma}_{kp} n_{\alpha-\sigma}\rangle}{2\pi} + (E_\alpha + U + \epsilon_p - \epsilon_k)\, \langle\langle c^\dagger_{k-\sigma} c_{p-\sigma} n_{\alpha-\sigma} c_{\alpha\sigma}; c^\dagger_{\alpha\sigma} \rangle\rangle_\omega + O(V) . \quad \text{(A2)}$$

Since

$$\langle n^{-\sigma}_{kp} n_{\alpha-\sigma}\rangle = \langle n^{-\sigma}_k \rangle \langle n_{\alpha-\sigma}\rangle \delta_{kp} + O(V) ,$$

from Eqs. (A1) and (A2) we see that, to $O(V)$,

$$\langle\langle c^\dagger_{k-\sigma} c_{p-\sigma} n_{\alpha-\sigma} c_{\alpha\sigma}; c^\dagger_{\alpha\sigma} \rangle\rangle_\omega = \delta_{kp} n^{-\sigma}_k \, \Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) .$$

Hence Eq. (A1) becomes

$$\omega \Gamma^{k\alpha}_{p\alpha}(\omega) = \langle n^{-\sigma}_k \rangle \delta_{kp} + (E_\alpha + \delta_{kp} U \langle n^{-\sigma}_k \rangle)\, \Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) + O(V) .$$

Comparing this with Eq. (3.2) we see that

$$\Gamma^{k\alpha}_{p\alpha}(\omega) = \delta_{kp} n^{-\sigma}_k \mathcal{G}_{\alpha\alpha}(\omega) + O(V) . \quad \text{(A3)}$$

This is exactly the Zubarev decoupling result that we have used in Sec. III. By a similar process we can show that two-particle GF's of the form $\Gamma^{\alpha\alpha}_{pk}$ are of $O(V^2)$. Thus the decoupling scheme used in Sec. III is exact to $O(V^2)$, as asserted.

APPENDIX B: COMPARISON WITH BRENIG AND SCHÖNHAMMER

A completely different approach to the problem of correlation in chemisorption has been taken by Brenig and Schönhammer.[23] Instead of dealing with single-particle Green's functions, they calculate directly a certain class of two-particle Green's functions, which in their notation are 2×2 matrices $\mathcal{G}_{\alpha\beta}(z)$. They write down a Dyson (matrix) equation for this Green's function reducing the problem to the evaluation of a self-energy matrix $M_{\alpha\beta}(z)$. The evaluation of this matrix is done to $O(V^2)$. As stated earlier, our method of approach is exact to $O(V^2)$ and so to that order, we should have identical results. The purpose of this appendix is to show that this is indeed the case.

To do so, we will have to establish a correspondence between their notation and ours. Following the definitions given in their paper we define new functions $F_\alpha(\omega)$ by $F_\alpha(\omega) \equiv \sum_\beta \mathcal{G}_{\alpha\beta}(\omega)$. It is easy to see, from their definition of $\mathcal{G}_{\alpha\beta}(\omega)$ that $F_+(\omega) = \Gamma^{\alpha\alpha}_{\alpha\alpha}$ and $F_+(\omega) + F_-(\omega) = \mathcal{G}_{\alpha\alpha}(\omega)$. Their Dyson equation (2–15 of their paper) can then be written in terms of the functions $F_\alpha(\omega)$

$$F_\alpha(\omega) = \mathcal{G}^0_{\alpha\alpha}(z)\left(1 + \sum_\delta M_{\alpha\delta} F_\delta(\omega)\right) . \quad \text{(B1)}$$

Thus their equation for $F_+(\omega)$ takes the form:

$$F_+(\omega) = \mathcal{G}^0_{++}(\omega)\,[1 + M_{++}(\omega) F_+(\omega) + M_{+-}(\omega) F_-(\omega)] . \quad \text{(B2)}$$

We now need explicit expressions for their self-energy matrix $M_{\alpha\beta}$. Using their Eq. (3.8):

$$\underline{A} M(\omega) \underline{A} = A \Sigma_0(\omega) + B m(\omega) , \quad \text{(B3)}$$

where

$$\underline{A} = \begin{pmatrix} \langle n_{\alpha-\sigma}\rangle & 0 \\ 0 & 1 - \langle n_{\alpha-\sigma}\rangle \end{pmatrix}, \quad \underline{B} = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

and Σ_0 is the chemisorption function defined in Eq. (3.5). The function $m(\omega)$ is their "correlation self-energy." Using Eq. (B3) it is straightforward to show that

$$M_{++}(\omega) = \langle n_{\alpha-\sigma}\rangle^{-2} [\Sigma_0(\omega) \langle n_{\alpha-\sigma}\rangle + m(\omega)] ,$$
$$M_{+-}(\omega) = -\langle n_{\alpha-\sigma}\rangle^{-1} (1 - \langle n_{\alpha-\sigma}\rangle)^{-1} m(\omega) . \quad \text{(B4)}$$

Inserting these expressions into Eq. (B2) and using

$$\mathcal{G}^0_{++}(\omega) = \langle n_{\alpha-\sigma}\rangle (\omega - E_\alpha - U)^{-1}$$

we get

$$(\omega - E_\alpha - U) F_+(\omega) = \left(\langle n_{\alpha-\sigma}\rangle + \Sigma_0(\omega) F_+(\omega) + \frac{m(\omega)}{\langle n_{\alpha-\sigma}\rangle} F_+(\omega) - \frac{m(\omega)}{1 - \langle n_{\alpha-\sigma}\rangle} F_-(\omega) \right) . \quad \text{(B5)}$$

Equation (B5) is the Brenig and Schönhammer equation of motion for the two-particle Green's function $\Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega) = F_+(\omega)$. In order to complete our comparison with their work, it is necessary to show that our expression for $\Gamma^{\alpha\alpha}_{\alpha\alpha}$ can be written in the form (B5) and that, to order V^2, our definitions for $m(\omega)$ are identical.

Going back to Sec. III we found that the equation of motion for $\Gamma^{\alpha\alpha}_{\alpha\alpha}(\omega)$ can be written

$$\begin{aligned}(\omega - E_\alpha - U) F_+(\omega) = {} & \langle n_{\alpha-\sigma}\rangle + \Sigma_0(\omega) F_+(\omega) \\ & + [\Sigma_0(\omega) - \tilde{\Sigma}_0(\omega)] F_+(\omega) \\ & - (R + S)[F_+(\omega) + F_-(\omega)] + L - K , \end{aligned} \quad \text{(B6)}$$

where (adopting the notation of Oguchi,[29] who has also considered this problem in yet a third way)

$$
\begin{aligned}
L(\omega) &= \sum_k \frac{V_{\alpha k}\langle n_{k\alpha}\rangle}{\omega-\epsilon_k}\,,\\
K(\omega) &= \sum_k \frac{V_{\alpha k}\langle n_{k\alpha}\rangle}{\omega-2E_\alpha-U+\epsilon_k}\,,\\
R(\omega) &= \sum_k \frac{|V_{\alpha k}|^2\langle n_{k-\sigma}\rangle}{\omega-\epsilon_k}+O(V^4)\,,\\
S(\omega) &= \sum_k \frac{|V_{\alpha k}|^2\langle n_{k-\sigma}\rangle}{\omega-2E_\alpha-U+\epsilon_k}+O(V^4)\,.
\end{aligned}
\qquad \text{(B7)}
$$

Now consider:

$$
\begin{aligned}
L-RF_-(\omega) = i\int \frac{dz}{2\pi}\,\frac{f(z)}{\omega-z}\,[\Sigma_0(z)-\Sigma_0(\omega)]\\
\times\{\mathcal{G}_{\alpha\alpha}(z)-F_-(\omega)\}\,,
\end{aligned}
\qquad \text{(B8)}
$$

where we have used the notation

$$\{\mathcal{G}(\omega)\}_- = \mathcal{G}(\omega+i\eta)-\mathcal{G}(\omega-i\eta),\quad \eta\to 0^+\,.$$

Now using $\mathcal{G}_{\alpha\alpha}(z)=F_+(z)+F_-(z)$, Eq. (B8) can be written

$$
\begin{aligned}
L(\omega)-R(\omega)F_-(\omega) = i\int \frac{dz}{2\pi}\,f(z)\,\frac{\Sigma_0(z)-\Sigma_0(\omega)}{\omega-z}\\
\times\{F_-(\omega)-F_-(z)\}_-\\
+i\int \frac{dz}{2\pi}\,f(z)\,\frac{\Sigma_0(z)-\Sigma_0(\omega)}{\omega-z}\\
\times\{F_+(z)\}_-\,.
\end{aligned}
$$

If $E_\alpha+U>\epsilon_F$, then the second term is of order V^4 since $F_+(z)$ at $V=0$ has no poles below E_F. Also it is easy to see that

$$F_-(z)-F_-(\omega)=(\omega-z)F_-(\omega)F_-(z)(1-\langle n_{\alpha-\sigma}\rangle)^{-1}+O(V^2)\,.$$

Hence retaining terms to $O(V^2)$ only we arrive at

$$
\begin{aligned}
L(\omega)-R(\omega)F_-(\omega) &= F_-(\omega)(1-\langle n_{\alpha-\sigma}\rangle)^{-1}\\
&\quad\times i\int\frac{dz}{2\pi}F_-(z)[\Sigma_0(z)-\Sigma_0(\omega)]\,,\\
L(\omega)-R(\omega)F_-(\omega) &= F_-(\omega)(1-\langle n_{\alpha-\sigma}\rangle)^{-1}\\
&\quad\times\Big(\sum_k V_{\alpha k}\langle n_{k\alpha}\rangle\\
&\qquad-\Sigma_0(\omega)(1-\langle n_{\alpha-\sigma}\rangle)\Big)\,.
\end{aligned}
\qquad \text{(B9)}
$$

Similarly, it can be shown that

$$
\begin{aligned}
K(\omega)+S(\omega)F_+(\omega) &= F_+(\omega)\langle n_{\alpha-\sigma}\rangle^{-1}\\
&\quad\times[V_{\alpha k}\langle n_{k\alpha}\rangle+\tilde{\Sigma}_0(\omega)\langle n_{\alpha-\sigma}\rangle]\,.
\end{aligned}
\qquad \text{(B10)}
$$

Thus

$$
\begin{aligned}
&[\Sigma_0(\omega)-\tilde{\Sigma}_0(\omega)]F_+(\omega)+[L(\omega)-R(\omega)F_-(\omega)]-[K(\omega)+S(\omega)F_+(\omega)]\\
&\qquad=\Sigma_0(\omega)F_+(\omega)-\Sigma_0(\omega)F_-(\omega)+2\sum_k V_{\alpha k}\langle n_{k\alpha}\rangle[F_-(\omega)-F_+(\omega)]\,,
\end{aligned}
$$

which is correct to $O(V^2)$. Inserting this into Eq. (B6) we arrive at

$$
\begin{aligned}
(\omega-E_\alpha-U)F_+(\omega)
&=\langle n_{\alpha-\sigma}\rangle+\Sigma_0(\omega)F_+(\omega)\\
&\quad+\Big(\Sigma_0(\omega)-2\sum_k V_{\alpha k}\langle n_{k\alpha}\rangle\Big)F_+(\omega)\\
&\quad-\Big(\Sigma_0(\omega)-2\sum_k V_{\alpha k}\langle n_{k\alpha}\rangle\Big)F_-(\omega)\,.
\end{aligned}
\qquad \text{(B11)}
$$

Comparing with Eq. (B5), the solution using the method of Brenig and Schönhammer, we see that our results are equivalent if

$$m(\omega)=\tfrac{1}{2}\Big(\Sigma_0(\omega)-2\sum_k V_{\alpha k}\langle n_{k\alpha}\rangle\Big)\,.$$

This is exactly their expression (4.8) for the self-energy in the "weak-coupling" approximation.

Thus we have shown that, in spite of the different methods of approach the two techniques are completely equivalent in the results (to the order of accuracy at which they have been calculated).

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[1] D. O. Hayward and B. M. W. Trapnell, *Chemisorption* (Butterworth, London, 1964); A. Clark, *The Theory of Adsorption and Catalysis* (Academic, New York, 1970).

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

[3] K. H. Johnson and R. P. Messmer, J. Vac. Sci. Tech. 11, 236 (1974).

[4] N. D. Lang, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1973), Vol. 28, p. 1520.

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

[6] A. Madhukar, Phys. Rev. B 8, 4458 (1973).

[7] S. K. Lyo and R. Gomer, Phys. Rev. B 10, 4161 (1974).

[8] T. B. Grimley, Proceedings of the International School of Physics, "Enrico Fermi" course LVII (Academic, New York, to be published).

[9] A. Madhukar, IBM Research Report No. RC5413 (unpublished).

[10] J. E. Demuth, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. 32, 1182 (1974); 32, 595 (1974).

[11] A. Madhukar, Solid State Commun. 14, 461 (1975).

[12] D. N. Zubarev, Sov. Phys.-Usp. 3, 320 (1960).

[13] The relevant bands of the substrate are of s and d character. The sum over orbital sites, i, is then to be interpreted as a sum over sites and bands.

[14] R. Haydock and M. J. Kelly, Surf. Sci. 38, 139 (1973); J. Davenport (unpublished).

[15] For simplicity we have retained only the term $Wn_{\alpha\sigma}n_{i\sigma'}$. Additional terms, such as $W'n_{\alpha\sigma}c^{\dagger}_{i\sigma'}c_{j\sigma'}$, can be treated in a similar manner (see Ref. 9).

[16] B. J. Thorpe, Surf. Sci. 33, 306 (1972).

[17] M. J. Kelly, Surf. Sci. 43, 587 (1974).

[18] T. B. Grimley and C. Pisani, J. Phys. C 7, 2831 (1974).

[19] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[20] We will use script letters to signify Green's functions in the presence of V_{ai} and standard letters for "unperturbed" Green's functions.

[21] A. C. Hewson, Phys. Rev. 144, 420 (1966).

[22] A. Bagchi and M. H. Cohen (unpublished).

[23] W. Brenig and K. Schönhammer, Z. Phys. 267, 201 (1974).

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

[25] D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. 27, 1530 (1974).

[26] J. E. Demuth and D. E. Eastman, Phys. Rev. Lett. 32, 1123 (1974).

[27] A. Madhukar and B. Bell, Phys. Rev. Lett. 34, 1631 (1975).

[28] A Hartree-Fock treatment of U was inadequate because U is a diagonal two-body interaction. Because W is off diagonal in nature (adsorbate-substrate interaction) a Hartree-Fock treatment is probably adequate. Correlations will be important in the affinity level since two electrons on the adsorbate imply a hole in the substrate. Their correlated motion will serve to modify the effect of W in the affinity level.

[29] A. Oguchi, Prog. Theor. Phys. 43, 257 (1970).