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Futuristic structures such as **40**,[61] an "inverted sandwich", and trication **41**, a logical extension of the pyramidal series,[43c] could also be the result of continuing research in the field of pyramidal carbonium ions.

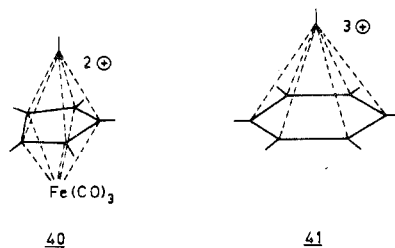laboratory by exploiting procedures which to some extent have already been developed.[33,60] These dications could well reveal a number of interesting details about the bonding in this type of carbonium ions and could open further synthetic perspectives.

40 41

(60) G. Capozzi and H. Hogeveen, *J. Am. Chem. Soc.*, 97, 1479 (1975); R. F. Heldeweg and H. Hogeveen, *Tetrahedron Lett.*, 1517 (1975); H. Hogeveen and E. M. G. A. van Kruchten, research in progress; H. Hogeveen, J. Jorritsma, P. A. Wade, F. van Rantwijk, J. B. Koster, J. J. Prooi, A. Sinnema, and H. van Bekkum, *Tetrahedron Lett.*, 3915 (1974).

(61) For a related organometallic species see: V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, 96, 3090 (1974); L. G. Sneddon, D. C. Beer, and R. N. Grimes, *ibid.*, 95, 6623 (1973).

Some Approaches to the Theory of Chemisorption

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Chemisorption may be defined as adsorption involving significant electron sharing or transfer. Thus it is not only more specific than physisorption, but generally much stronger, with energies of 1–5 eV.

Chemisorption seems to be strongest on transition metals probably because of the presence of available, rather localized, highly directional d orbitals. Almost all elements can be adsorbed. Saturated molecules are strongly adsorbed only upon dissociation into atoms or fragments. Chemisorption invariably involves some charge transfer. For adsorbates with low ionization potential I (i.e., alkalis or alkaline earths) considerable electron deficiency, i.e., polar or even ionic adsorption, is the rule. For substances of high I electron transfer is usually *to* the adsorbate and ≤ 0.1 electron charge. Within a given system there are qualitative differences from crystal plane to crystal plane, and it is also known that distinct binding states occur on a given plane. The greatest variety of modes occurs on body-centered cubic (bccub) rather than face-centered cubic (fccub) substrates; the former are atomically less closely packed, and this suggests that the existence of different modes is connected with adsorbate–substrate geometry. The latter have not been elucidated for more than a handful of states.

In the last few years the experimental study of chemisorption has been revolutionized by a number of new techniques culminating in various electron spectroscopies which promise to reveal the electronic structure of the adsorption complex. These developments seem to have stimulated theoretical efforts, and the theory of chemisorption on metals is now progressing rapidly. Much of the theory is also applicable, with some modifications, to semiconductors.

Cluster Models

The bonding of an adsorbate atom or molecule to a metal surface is not very different in principle from other chemical bonding except that a very large number of substrate atoms and electrons are involved. This necessarily introduces some modifications, for instance the possibility that discrete bonding and antibonding orbitals are replaced by more or less broad resonances. In addition the close spacing in energy of metal electrons gives much greater weight to screening (for instance image effects) than in small molecules. One approach is to make essentially "chemical" calculations on clusters consisting of a small number (5–10) of substrate atoms plus an adsorbate[1] and to hope that the results will simulate the actual system closely enough to allow significant conclusions to be drawn. This approach can take account of image effects and the contribution to bonding of continuum states only by putting in "by hand" such terms at the end of the calculation, if at all. More important, it must ignore the flow of electrons into and out of clusters (imagined as part of the metal adsorbate system). Finally it cannot utilize what is known about the clean metal and its surface. Despite these

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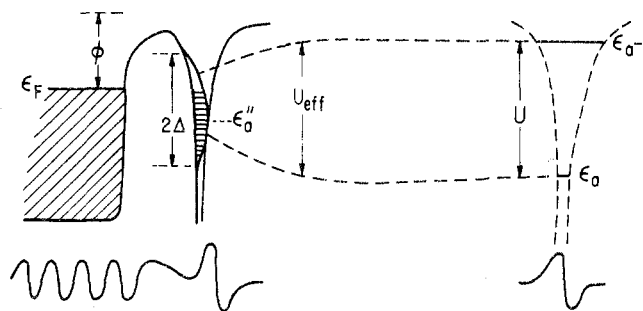(1) K. H. Johnson and R. P. Messmer, *J. Vac. Sci. Technol.*, 11, 236 (1974).

Figure 1. Schematic potential-energy diagram of chemisorption on a metal. ϵ_a and ϵ_a^- are energies of highest filled levels of neutral adsorbate A and ion A⁻, respectively, separated by the intra-atomic Coulomb repulsion U. ϵ_F, Fermi energy; ϕ, work function of metal. ϵ_a'' is the adsorbate level shifted upward by image interaction and intra-adsorbate Coulomb repulsion, but shifted downward by interaction with the metal. Formally, $\epsilon_a'' = \epsilon_a' + \Lambda$ with ϵ_a' defined by eq 13 and Λ defined by eq 16. The broadening of ϵ_a'' is given by 2Δ, defined by eq 15. The amplitude of the Lorentzian "hump" marked by the thick line is the local density of states, ρ_a (eq 8), and is a measure of the amplitude of wave functions at the adsorbate for this energy. A typical wave function is indicated below the potential energy diagram.

limitations, such calculations can be very useful. We shall not discuss them further, but will concentrate instead on methods which accept the challenge of the $\sim 10^{21}$ atom (or electron) system from the outset.

Dielectric Response Method

The least "chemical" approach is that of Kohn and his collaborators,[2] in which the metal is replaced by "jellium," consisting of a fixed, uniform block of positive charge and a mobile electron gas of appropriate density. The calculation proceeds schematically as follows. An adsorbate A is ionized far from the surface and the resultant electron added to the metal. The ion core A⁺ is brought to the surface and the electron gas allowed to rearrange itself self-consistently in response to this external potential. The energy of the resultant charge distribution is calculated and compared with that of the original distribution, yielding the adsorption energy relative to M⁻ + A⁺ where M⁻ stands for the metal with an extra electron. The binding energies so calculated are not very good, but reasonable charge distributions and hence dipole moments, as well as reasonable distributions in energy of the electrons around A⁺, result. We shall not discuss this method in greater detail. In summary, it gives up most of the details of the geometric and orbital structure of the metal surface, and will probably be difficult to extend beyond atomic adsorbates. On the other hand it can take account of screening effects, and of the dielectric response of metal surfaces, more easily than any other method.

Qualitative Description of Metal Adsorbate System

We come then to more chemical methods. Here the natural directions are extensions of LCAO–MO and valence-bond approaches. It will be useful to start with a very pictorial model.

Figure 1 indicates what may happen as an atom A with an initially sharp valence level, characterized by

(2) J. R. Smith, S. C. Ying, and W. Kohn, *Phys. Rev. Lett.*, **30**, 610 (1973); N. Lang, *Solid State Phys.*, **28**, 225 (1973); N. Lang and A. R. Williams, *Phys. Rev. Lett.*, **34**, 531 (1975).

energy ϵ_a $(=-I$, the ionization potential) and state vector $|a\rangle$ approaches a metal surface. As the atom comes close to the surface the level at ϵ_a may broaden by interaction with the metal since tunneling gives it a finite lifetime τ and half-width Δ:

$$\Delta \simeq \hbar/2\tau \qquad (1)$$

This situation is to be expected if ϵ_a lies near the Fermi level ϵ_F $(=-\phi$, the work function) so that the tunneling barrier is relatively transparent. In this situation wave functions for electrons with energy within $\pm\Delta$ of the adsorbate level (shifted by various interactions to be discussed shortly) will be oscillatory in the metal, exponentially decaying in the region between metal and adsorbate, and once again oscillatory at the adsorbate (Figure 1). Thus bonding electrons are nonlocalized. Outside this energy range wave functions will more or less correspond to unperturbed metal functions; that is, they will decay monotonically outside the metal. If the interaction is very strong, we should expect a different result, namely the splitting off of a relatively sharp bonding state below the bottom of the conduction band and an antibonding state above it. (When interaction with a broad s band or with metal continuum states is taken into account the antibonding level will become very broad, and even the bonding level will broaden somewhat). Since the bonding level is now in an energy-forbidden region (for metal electrons) the wave functions of bonding electrons will not be oscillatory in the metal but will decay toward the interior of the metal within a few interatomic spacings, i.e., be localized on the adsorbate and its neighboring substrate atoms. It is also possible to envisage intermediate situations in which there is some localized amplitude at the adsorbate below the conduction band and some amplitude corresponding to nonlocalized electrons within the band. In all cases bonding results if there is a net lowering in energy of the "center of gravity" of the occupied states of the entire system.

As in all bonding, an essential feature is that two electrons may simultaneously be on the adsorbate and interact repulsively. The proper treatment of this intraatomic Coulomb repulsion, U, represents one of the principal difficulties of any calculation. If either bonding is very strong, relative to U, or if electrons hop off and on the adsorbate very rapidly, correlation will not be important and the self-consistent-field or Hartree–Fock approximation which considers the interaction of up-spin (σ) with the average population of down-spin (σ^-) electrons will be adequate. An approximate criterion[3] for the validity of the Hartree–Fock approximation is that $\pi\Delta > U$ or, in the case of a discrete bonding level segregated below the conduction band, that $\pi\epsilon_l > U$, where ϵ_l is the energy of the bonding orbital measured from the Fermi level. Since the average population of electrons of given spin is simply a number, Hartree–Fock is a one-electron theory and very conveniently carried out in a generalization of LCAO–MO schemes. On the other hand, when correlation is important and the Hartree–Fock approximation breaks down, one is dealing with a many-electron problem, which is less

(3) J. R. Schrieffer and D. C. Mattis, *Phys. Rev.*, **140**, 1412 (1965).

easily handled although considerable progress has recently been made.[4,5]

Two additional points need to be made. The first is that ϵ_a is always pushed up in energy as A approaches the surface by what would classically be an image interaction

$$V_{im} = e^2/4x \qquad (2)$$

or $3.6/x$ in eV-ångström units where x is the adsorbate–surface distance. This comes about as follows. The valence electron on A induces its own image in the metal, leading to an attractive interaction $-V_{im}$, but also interacts repulsively with the image of the ion core; since the latter amounts to a charge already in position this interaction is $e^2/2x$ and consequently the net interaction is an increase by V_{im}. (This does not mean of course that the net shift is upward, since the level is also "pulled down" by bonding). Second, the intraatomic Coulomb repulsion U is the difference between the ionization and affinity levels. The former is pushed up by V_{im}, but the affinity level is pulled down by V_{im} since it corresponds to the interaction of an ion with the metal. Consequently the effective U, U_{eff}, is given by

$$U_{eff} = U - 2V_{im} \qquad (3)$$

This effect is nontrivial. In the case of hydrogen, for instance, $U = 12.9$ eV for the free atom, and image interaction probably reduces this to $\sim$6 eV near the equilibrium separation.

Valence Bond Approach

It is well known that the LCAO–MO method exaggerates ionic contributions to the wave function, while the valence-bond approach leaves these out entirely, and thus exaggerates correlation. One approach to chemisorption is therefore to formulate it in generalized valence-bond terms.[6] The formation of strong bonds requires unpaired electrons. However, the metal at ordinary temperatures has no unpaired spins, since electrons occupying the metal states are spin paired. Consequently, formation of a valence bond requires promotion of an electron into the empty states above ϵ_F in order to allow bonding. The promotion costs energy, of course, which is repaid with interest through bond formation. The calculation just outlined is extremely difficult to carry out quantitively and abandons the concept of one-electron levels, so that it is difficult to formulate and analyze spectroscopic measurements. It is also difficult to extend it to polar adsorption, i.e , appreciable charge transfer, although this is possible in principle. Finally it now seems possible to extend LCAO–MO calculations beyond the Hartree–Fock limit. For all these reasons generalizations of the LCAO–MO approach seem to hold the most promise, and the rest of this article is devoted to them. It should be emphasized, of course, that this is a personal viewpoint.

Generalized MO Approach

The system we wish to study consists of a metal

(4) B. Bell and A. Madhukar, to be published; A. Madhukar, to be published; A. Madhukar and B. Bell, to be published.
(5) W. Brenig and K. Schönhammer, *Z. Phys.*, **267**, 201 (1974).
(6) J. R. Schrieffer and R. Gomer, *Surf. Sci.*, **25**, 315 (1971); R. H. Paulson and J. R. Schrieffer, *ibid.*, **48**, 329 (1975).

and an adsorbate. The metal states of interest consist of the partially filled conduction band, $\sim$10 eV wide, and also the metal continuum states which exist for energies >0 relative to the vacuum level. The number of metal states involved is extremely large, of the order of one per metal atom or $\sim 10^{21}$ in all, and concomitantly energy levels in the metal are quasi-continuous. A very convenient way of handling such situations and certainly the one in which much chemisorption work is couched involves Green's functions. For present purposes it suffices to define G by

$$G(\epsilon - \mathcal{H} - i\alpha) = 1 \qquad (4)$$

where $\mathcal{H}$ is the Hamiltonian and α a small positive quantity which will be allowed to approach 0 where convenient. Then for eigenstates of $\mathcal{H}$, $\mathcal{H}|m\rangle = \epsilon|m\rangle$.

$$G_{mm} = \frac{1}{\epsilon - \epsilon_m - i\alpha} = \frac{(\epsilon - \epsilon_m)^2}{(\epsilon - \epsilon_m)^2 + \alpha^2} + i\frac{\alpha}{(\epsilon - \epsilon_m)^2 + \alpha^2} \qquad (5)$$

The imaginary part of G_{mm} thus has all the properties of a delta function and in fact

$$(1/\pi)\,\mathrm{Im}\,G_{mm} = \delta(\epsilon - \epsilon_m) \qquad (6)$$

It follows that the density of states of the system is ρ_m.

$$\rho_m = (1/\pi) \sum_m \delta(\epsilon - \epsilon_m) = (1/\pi)\,\mathrm{Im} \sum_m G_{mm} \qquad (7)$$

It will be very convenient to define also a local density of states, ρ_a, as follows:

$$\rho_a(\epsilon) = \sum_m |\langle a|m\rangle|^2 \,\delta(\epsilon - \epsilon_m) \qquad (8)$$

$\rho_a(\epsilon)$ is the square of the projection of the adsorbate wave function, φ_a, on a system wave function, φ_m, integrated over space, and then summed over all system states. The delta function ensures that only states of energy $\epsilon_m = \epsilon$ contribute. ρ_a represents, so to speak, the weight with which the adsorbate state is represented in all system states of given energy. For instance, for the case depicted in Figure 1 ρ_a would be the Lorentzian shown by the heavy line. For the case of sharp bonding and antibonding orbitals it would be two delta functions at the corresponding energies, and so on. It turns out that ρ_a is very conveniently expressed in terms of G. Using eq 6 for $\delta(\epsilon - \epsilon_m)$ we have

$$\rho_a = (1/\pi)\,\mathrm{Im} \sum_m \langle a|m\rangle\langle m|G|m\rangle\langle m|a\rangle = (1/\pi)\,\mathrm{Im}\,G_{aa} \qquad (9)$$

since by definition the states $|m\rangle$ are orthogonal, so that the single sum in eq 9 can be replaced by sums over m, m'. Since $\sum_m |m\rangle\langle m|$ and $\sum_m |m'\rangle\langle m'|$ are unit operators which can be inserted or extracted between $|a\rangle$ and G the result follows. It should be emphasized that eq 9 is of quite general validity and has nothing to do with the particular choice of basis. All that is required is that G refer to the entire system under study, i.e., that $\mathcal{H}$ be the Hamiltonian of the total system, metal plus adsorbate.

We are interested in ρ_a for the following reasons. First, it provides a simple pictorial description of

what is going on, along the lines indicated in Figure 1, and $\int_{-\infty}^{\epsilon_F} \rho_a d\epsilon$ summed over both spin states gives the valence electron population on A. Second, it turns out that it can be obtained experimentally from field emission energy distributions from adsorbate covered emitters[7] and from photoemission energy distributions.[8] Finally, the chemisorption energy can be expressed in terms of G_{aa} or related quantities.

Newns–Anderson Model

We consider now the simplest chemisorption model along the lines discussed, which is an adaptation by Newns[9] of a model proposed by Anderson[10] to treat magnetic impurities in a solid. Except for the fact that it is couched in Green's functions rather than wave functions it is also identical with a model used earlier by Grimley.[11] The present treatment differs from the original one of Newns by the inclusion of image effects. We take as basis the Bloch states $\{k\}$ of the metal conduction band (in the case of transition metals the d band) and a single adsorbate state $|a\rangle$ and set overlap arbitrarily equal to zero, that is, we assume $\langle k|a\rangle = 0$, and we further assume that this basis is complete. As Hamiltonian we take

$$\mathcal{H} = \mathcal{H}^{(m)} + V^\sigma \qquad (10)$$

where $\mathcal{H}^{(m)}$ is the metal Hamiltonian and V^σ the additional potential introduced by the presence of the adsorbate. The latter consists of the ion core potential $V^{(a)}$, the image shift seen by an electron on A, which has already been discussed, and the mean intraatomic Coulomb repulsion $U_{\text{eff}}\langle n_{\sigma-}\rangle$

$$V^\sigma = V^{(a)} + V_{\text{im}} + U_{\text{eff}}\langle n_{\sigma-}\rangle \qquad (11)$$

The index σ in eq 10 and 11 stands for spin and indicates that a spin σ electron sees only the average field produced by spin σ^- electrons because the exclusion principle precludes simultaneous occupancy of state $|a\rangle$ by two electrons of like spin. All electron–electron interactions not contained in V^σ are ignored.

If all off-diagonal matrix elements of $\mathcal{H}$ except those coupling states $|k\rangle$ to $|a\rangle$ are neglected, G_{aa} can be obtained very straightforwardly, for instance by taking appropriate matrix elements of eq 4, using $\mathcal{H}$ defined by eq 10. The result is

$$G_{aa}^\sigma = \left[\epsilon - \epsilon_a'^\sigma - \sum_k g_k |V_{ak}^{(a)}|^2 \right]^{-1} \qquad (12)$$

where g_k is the unperturbed metal Green's function, $(\epsilon - \epsilon_k - i\alpha)^{-1}$, and

$$\epsilon_a'^\sigma = \mathcal{H}_{aa}^\sigma = \epsilon_a + V_{aa}^{(m)} + V_{\text{im}} + \langle n_{\sigma-}\rangle U_{\text{eff}} \qquad (13)$$

with corresponding expressions for $G_{aa}^{\sigma-}$ and $\epsilon'^{\sigma-}$.

By multiplying numerator and denominator in the sum over k in eq 12 by the complex conjugate of g_k we find

$$G_{aa}^\sigma = (\epsilon - \epsilon_a' - \Lambda - i\Delta)^{-1} \qquad (14)$$

(7) R. Gomer, *Adv. Chem. Phys.*, **27**, 211 (1974); J. W. Gadzuk and E. W. Plummer, *Rev. Mod. Phys.*, **45**, 487 (1973).

(8) E. W. Plummer in "Interactions on Metal Surfaces", R. Gomer, Ed., Springer-Verlag, New York, N.Y., 1975.

(9) D. M. Newns, *Phys. Rev.*, **178**, 1123 (1969).

(10) P. W. Anderson, *Phys. Rev.*, **124**, 41 (1961).

(11) T. B. Grimley, *Proc. Phys. Soc., London*, **90**, 751 (1967), and previous papers.

where

$$\Delta = \pi \sum |V_{ak}^{(a)}|^2 \delta(\epsilon - \epsilon_k) \qquad (15)$$

and

$$\Lambda = P \sum \frac{|V_{ak}^{(a)}|^2}{\epsilon - \epsilon_k} = (1/\pi) P \int_{-\infty}^{\infty} \frac{\Delta(\epsilon')d\epsilon'}{\epsilon - \epsilon'} \qquad (16)$$

where P stands for Cauchy principal part, e.g.,

$$\Lambda = \lim_{\alpha \to 0} \sum_k \frac{|V_{ak}^{(a)}|^2(\epsilon - \epsilon_k)}{(\epsilon - \epsilon_k)^2 + \alpha^2}$$

is the Hilbert transform of Δ as the last equality in eq 16 indicates; this can be verified by substitution of eq 15 in the integral. The important consequence of this relation is that $\Delta(\epsilon)$ determines the shape of $\Lambda(\epsilon)$. The form of G_{aa} is that of a "pure" adsorbate function, $(\epsilon - \epsilon_a')^{-1}$, modified by the inclusion of the all-important chemisorption function, $\Sigma_k |V_{ak}^{(a)}|^2 g_k$, whose real and imaginary parts contain the bonding interaction with the metal. Multiplying numerator and denominator of eq 14 by $(\epsilon - \epsilon_a' - \Lambda + i\Delta)$ we see that

$$\rho_a = (1/\pi) \text{Im } G_{aa} = \frac{\Delta/\pi}{(\epsilon - \epsilon_a' - \Lambda)^2 + \Delta^2} \qquad (17)$$

If Δ and Λ were independent of energy, ρ_a would therefore be a Lorentzian centered on $\epsilon_a' + \Lambda$, of half-width Δ. Further, the tunneling time τ would be related to Δ through

$$1/\tau = 2\Delta/\hbar = (2\pi/\hbar) \sum_k |V_{ak}^{(a)}|^2 \delta(\epsilon - \epsilon_k) \qquad (18)$$

which is just Fermi's golden rule expression.

In most cases the energy dependence of Δ and Λ cannot be neglected, however, and is responsible for the possibility of more complex situations including the separation of discrete localized states above and below the band. We note first from eq 5 and 9 that the infinities, i.e., poles of G_{aa}, correspond to the system eigenstates ϵ_m if we take ϵ to be real. (The form (12) also shows that the zeros of G_{aa} correspond to the metal eigenvalues ϵ_k). G_{aa} can have poles not only within the band (corresponding essentially to shifted metal states) but also outside it where g_k has no poles so that $\Delta = 0$, and the chemisorption function has only a real part Λ if

$$\epsilon - \epsilon_a' - \Lambda = 0 \qquad (19)$$

Equation 19 corresponds to intersection of the line $\epsilon - \epsilon_a'$ vs. ϵ with $\Lambda(\epsilon)$ vs. ϵ. Figure 2 shows some possible situations: zero, one, or two discrete states may occur, and it is clear that this depends not only on the shape of Λ but also on the location of ϵ_a'. Segregation of a single state below the band can be shown to correspond to very weak binding. Absence of localized states generally results when interaction is only moderate, so that $V_{ak}^{(a)}$ and hence Δ are small. In this case ρ_a is a more or less distorted Lorentzian. If, in addition, a substantial portion of ρ_a lies above the Fermi level, i.e., if ϵ_a' lies at or above it, there will be considerable electron deficiency on A. This is the situation encountered with alkali and alkaline earth adsorption. The case of two discrete states, a filled one below the band and an empty one above it, corre-

sponds to strong bonding and because of the fact that these states are in otherwise energy forbidden regions, localized wave functions, in other words the formation of a "surface molecule" with bonding and antibonding levels. We will pursue this point further but first we must look into the as yet undetermined electron populations $\langle n_\sigma \rangle$ and $\langle n_{\sigma-} \rangle$ on A. We see that

$$\langle n_\sigma \rangle = \int_{-\infty}^{\epsilon_F} \rho_a{}^\sigma d\epsilon \quad \langle n_{\sigma-} \rangle = \int_{-\infty}^{\epsilon_F} \rho_a{}^{\sigma-} d\epsilon \quad (20)$$

where the lower limit implies that discrete states must be counted also. Since $\rho_a{}^\sigma$ contains $\langle n_{\sigma-} \rangle$ and vice versa, we have two equations which (in principle at least) can be solved self-consistently for $\langle n_\sigma \rangle$ and $\langle n_{\sigma-} \rangle$. It may happen that there are only solutions $\langle n_\sigma \rangle = \langle n_{\sigma-} \rangle$, the so-called nonmagnetic case. In addition, two symmetric pairs of solutions may occur, $\langle n_\sigma \rangle = a$, $\langle n_{\sigma-} \rangle = b$, with $a \neq b$; and $\langle n_\sigma \rangle = b$, $\langle n_{\sigma-} \rangle = a$. These are the so-called magnetic roots and correspond to lower energy, because they decrease the Coulomb repulsion $U\langle n_{\sigma-} \rangle \langle n_\sigma \rangle$. However, it is generally believed[3,9] that if Coulomb repulsion is so important as to drive the Hartree–Fock solution magnetic, correlation is too important to be treatable in the Hartree–Fock approximation, and consequently the appearance of magnetic solutions is simply a signal that Hartree–Fock is inadequate. Fortunately it turns out that in many cases of interest the reduction of U by the image interaction leads only to nonmagnetic solutions. In any case we will limit our discussion to these.

We are now able to evaluate the chemisorption energy E_{ad} as the difference in energies of the interacting and noninteracting systems. Quite generally,

$$-E_{ad} = \sum_\sigma \left(\int_{-\infty}^{\epsilon_F} \epsilon \rho_m{}^\sigma d\epsilon - \int_{-\infty}^{\epsilon^0_F} \epsilon \rho_k d\epsilon \right) -$$
$$\epsilon_a - V_{im} - U_{eff}\langle n_\sigma \rangle \langle n_{\sigma-} \rangle \quad (21)$$

Here ρ_m and ρ_k are the densities of state of the total system and metal, respectively. The term V_{im} must be substracted because it has been included in ϵ_a'; its substraction allows for the fact that a neutral, noninteracting atom near the surface leads to no net energy change, even though ϵ_a is shifted. Finally the term in U_{eff} must be included since it has been counted twice in the sum over spins. ρ_k is given by $(1/\pi)$ Im g_k. ρ_m can be found by evaluating the matrix elements G_{kk} explicitly. After some manipulation it can be shown that the final result is

$$-E_{ad} = \sum_\sigma \int_{-\infty}^{\epsilon_F} (\epsilon - \epsilon_F) \Delta \rho d\epsilon +$$
$$(\epsilon_F - \epsilon_a) - V_{im} - U_{eff}\langle n_\sigma \rangle \langle n_{\sigma-} \rangle \quad (22)$$

where $\Delta \rho \equiv \rho_m - \rho_k$. For the present model it can be shown[12] that

$$\Delta \rho = (1/\pi) \text{ Im} \frac{\partial}{\partial \epsilon} \ln G_{aa}{}^{-1} \quad (23)$$

It is worth noting that for pure ionic adsorption eq 22

(12) S. Lyo and R. Gomer, *Phys. Rev., B*, **10**, 4161 (1974).

reduces to $E_{ad} = \phi - I + V_{im}$, which corresponds to the energy gain of transferring an electron (at $-I$) from A to the Fermi level, (at $-\phi$) plus the attractive image interaction of A$^+$ with the metal.

We have seen that the quantity

$$\Delta = \pi \sum_k |V_{ak}{}^{(a)}|^2 \delta(\epsilon - \epsilon_k)$$

plays a central role in the theory. It is, however, difficult and not very illuminating to evaluate matrix elements like V_{ak} directly, and we therefore reformulate Δ and similar quantities in terms of localized metal orbitals, for instance atomic d orbitals, or combinations of a small number of such orbitals on metal atoms interacting directly with the adsorbate. We shall call these group orbitals and denote them by $|g\rangle$. For instance, if an adsorbate were sitting directly on top of a metal atom we might use a single d_{z^2} orbital. We can write

$$V_{ak}{}^{(a)} = \sum_{g'} V_{ag'}{}^{(a)} \langle g'|k\rangle \simeq V_{ag}{}^{(a)} \langle g|k\rangle \quad (24)$$

i.e., we assume only one single (group) orbital leads to a nonvanishing matrix element V_{ag}. Then

$$\Delta = \pi |V_{ag}{}^{(a)}|^2 \sum_k |\langle g|k\rangle|^2 \delta(\epsilon - \epsilon_k) = \epsilon |V_{ag}{}^{(a)}|^2 \rho_g \quad (25)$$

where $\rho_g \equiv \Sigma_k |\langle g|k\rangle|^2 \delta(\epsilon - \epsilon_k)$ is a local density of states for the substrate group orbital, and is often called a surface density of states. We have thus couched the theory in terms of very local features which depend on surface and adsorbate–surface geometry. It is now easy to treat the case of "surface molecule" formation. If the localized states are far above and below the band we can write in their vicinity, calling the band center ϵ_c

$$\Lambda(\epsilon) \simeq (\epsilon - \epsilon_c)^{-1} \pi^{-1} \int_{-\infty}^{\infty} \Delta(\epsilon') d\epsilon =$$
$$(\epsilon - \epsilon_c)^{-1} |V_{ag}{}^{(a)}|^2 \int_{-\infty}^{\infty} \sum_k |\langle k|g\rangle|^2 \delta(\epsilon_k - \epsilon') d\epsilon' =$$
$$\frac{|V_{ag}{}^{(a)}|^2}{\epsilon - \epsilon_c} \quad (26)$$

Since we assume the $\{k\}$ to be complete, $\Sigma_k |\langle g|k\rangle|^2 = 1$. Then from eq 19 we have

$$(\epsilon - \epsilon_a')(\epsilon - \epsilon_c) = |V_{ag}{}^{(a)}|^2 \quad (27)$$

or

$$\epsilon = \frac{1}{2}(\epsilon_c + \epsilon_a' \pm \sqrt{(\epsilon_a' - \epsilon_c)^2 + 4|V_{ag}{}^{(a)}|^2}) \quad (28)$$

which are the energies of bonding and antibonding levels of a surface molecule.

Extension to a Complete Basis

The theory presented so far is straightforward and transparent and contains all the qualitative features we should expect to find in more realistic ones, at least in Hartree–Fock approximation. However it neglects overlap between the metal and adsorbate states, and it uses a very incomplete basis, since one would expect the metal continuum states to be quite important for bonding *outside* the metal where the bound states must after all decay rapidly. We can see
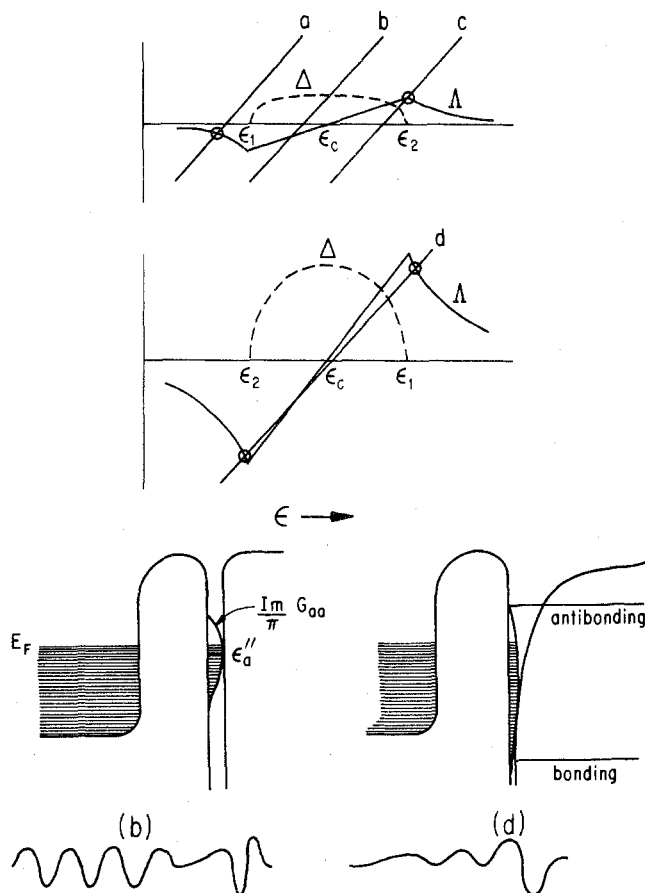
Figure 2. (a) Relations between Δ and Λ for small and large Δ. ϵ_1 and ϵ_2 are the upper and lower limits of the relevant band, ϵ_c is the energy of the band center. Four possible intersections of $\epsilon - \epsilon_a'$ with Λ are shown: (a) a single localized state below the band; (b) no localized states: (c) a localized state above the band; (d) localized states above and below the band. (b) Schematic potential diagrams indicating local densities of state for cases b and d depicted in Figure 2a. Schematic wave functions corresponding to delocalized (b) and localized (d) electrons are also shown.

very simply that the inclusion of continuum states in $\Sigma_k g_k |V_{ak}|^2$ should make a contribution only to its real part, i.e., Λ, since g_k for continuum states has no poles below the vacuum level. This contribution could be 1–2 eV. If we therefore use as basis the totality of metal states (band and continuum) we should improve matters, but we now face a logical difficulty. The set $\{k\}$ so defined *is* complete and therefore contains $|a\rangle$, that is, $\{k\}$ plus $|a\rangle$ is overcomplete. It is clear, however, that we can write G and $\mathcal{H}$ in terms of any complete basis and that the problem is then to introduce $|a\rangle$ somehow. There are a number of ways of accomplishing this,[13-15] all similar although yielding slightly different looking results since all are approximations. The simplest to explain is the following:

$$V_{kk'} = \sum_b \langle k|V|b\rangle \langle b|k'\rangle \approx V_{ka}\langle a|k\rangle \quad (29)$$

where $\{b\}$ is the set of all adsorbate states. We assume that the only important term in $\{b\}$ is $|a\rangle$. Overlap is now automatically included. A slightly different ap-

(13) P. W. Anderson and W. L. McMillan in "Theory of Magnetism in Transition Metals", W. Marshall, Ed., Academic Press, New York, N.Y., 1967, p 50.

(14) K. Terakura and J. Kanamori, *Prog. Theor. Phys.*, **46**, 1007 (1971), and previous papers.

(15) D. Penn, *Phys. Rev. B*, **9**, 844 (1974).

proximation[12] which can be obtained from eq 29 assumes $V_{ak'} = V_{aa}\langle a|k'\rangle$, which with eq 29 gives

$$V_{kk'} = \frac{V_{ka}V_{ak'}}{V_{aa}} \quad (30)$$

Equations 29 and 30 are not wholly equivalent because they are approximate. By using (30) in the Green's function equation one can show that the important part of the denominator of G_{aa} has the form L

$$L = \epsilon - \epsilon_a' - \sum_k g_k |V_{ak'}|^2 \quad (31)$$

where

$$V_{ak'} = V_{ak}^{(a)} + (\epsilon_k - \epsilon)\langle a|k\rangle \quad (32)$$

$V_{ak'}$ is thus rather similar to $V_{ak}^{(a)}$ and reduces to the latter when $\epsilon \simeq \epsilon_k$ (which is most likely when the overlap $\langle a|k\rangle$ is large) or when $\langle a|k\rangle$ is zero. Thus the new form of G_{aa} is similar to the Newns–Anderson version. There are important differences, however. For instance, the set $\{k\}$ is now truly complete so that the sum over k in eq 31 can be expanded using the explicit form of $V_{ak'}$ given by eq 32. The result is

$$L = V_{aa}^{(a)} - \sum_k g_k |V_{ak}^{(a)}|^2 = V_{aa}^{(a)} - \Lambda - i\Delta \quad (33)$$

Although ϵ has vanished altogether L^{-1} still has poles. For present purposes it suffices to make the approximations $V_{aa}^{(a)} = \bar{V}$, $V_{ak}^{(a)} = \bar{V}\langle a|k\rangle$, where $\bar{V}$ is an average strength of the potential. These transform L into

$$L = (1/\bar{V})^2 [(1/\bar{V}) - \Lambda'' - i\Delta''] \quad (34)$$

where

$$\Delta'' = \pi \sum_k |\langle a|k\rangle|^2 \delta(\epsilon - \epsilon_k) \quad (35)$$

and

$$\Lambda'' = (1/\pi)P \int_{-\infty}^{\infty} \frac{\Delta''(\epsilon')d\epsilon'}{\epsilon - \epsilon'} \quad (36)$$

It is evident that the general forms of Δ'' and Λ'' are similar to those of Δ and Λ, respectively (Figure 3), and that a discrete bonding state corresponds to an intersection of $1/\bar{V}$ with Λ'' below the band while a resonance corresponds to an intersection *in* the band. A localized antibonding state can occur only if there is a gap between the band and the continuum and the intersection of $1/\bar{V}$ with Λ'' falls in this region. Otherwise the antibonding state will be a broad resonance.

It should be apparent that the shape of ρ_a depends on that of Λ'' which in turn depends on Δ''. The latter, as we have seen, is largely determined by ρ_g, the surface density of states of the local substrate (group) orbital overlapping with the adsorbate orbital. In particular, peaks and valleys in ρ_g will lead to resonances or antiresonances in the band, even if there is a main localized state below the band.

Finally we can also calculate the chemisorption energy, which turns out to be given by eq 22 and 23 with G_{aa}^{-1} replaced by L.

Lyo and the author[12] have carried out a calculation of H adsorption on tungsten along these lines. They were able to obtain a good value for E_{ad} and could re-
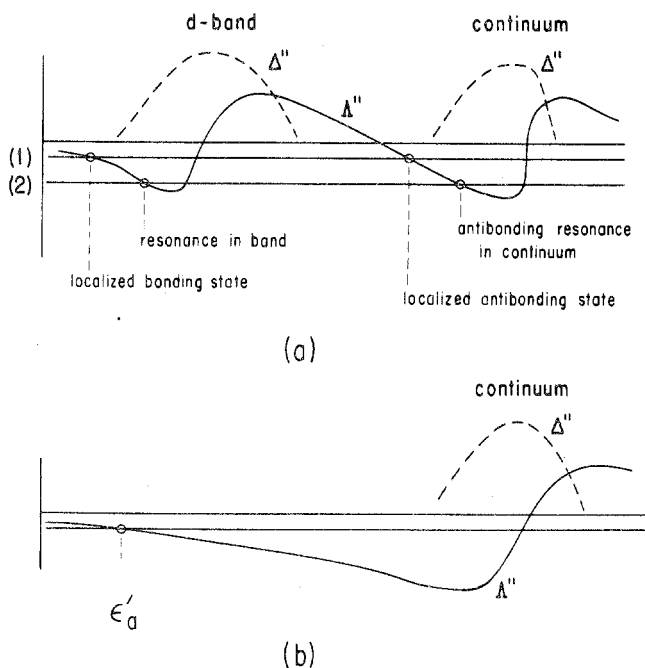
Figure 3. Plots of Δ'' and Λ'' vs. energy. (a) Finite overlap with d-band states assumed. Horizontal lines are $1/\bar{V}$: Line 1 assumes $\bar{V}$ of sufficient strength to cause segregation of localized states above and below the d band; line 2 assumes $\bar{V}$ is too weak for this, so only resonances in the band and in the continuum result. (b) Overlap with the d band is assumed to be zero. In this case the only contribution to Λ'' comes from the continuum; this produces ϵ_a' as indicated.

produce the main peak in ρ_a at 5.5 eV below ϵ_F[8] as well as the subsidiary peak[8] seen at ~1 eV below ϵ_F by a reasonable choice of overlap and a reasonable model for ρ_g. The solutions were nonmagnetic and stayed so when V_{im} was arbitrarily set equal to zero. This, plus the fact that U_{eff} meets the Hartree–Fock criterion, strongly suggests that the Hartree–Fock approximation is adequate in this case.

Although these facts are very encouraging, two caveats are in order. First, chemisorption energy is a very indifferent criterion of success. Equation 22 indicates that it amounts in essence to $\phi - I$ plus an integral over the density of states which tends to wash out details. (In fairness to the theory, however, this also explains the fact that E_{ad} ~3 eV for H adsorption on most transition metals whose work functions ϕ all are 4.5–5 eV.) Second, structure in ρ_a can arise from other causes than structure in ρ_g, for instance the inclusion of higher adsorbate states and from correlation effects which are neglected in Hartree–Fock theory. Thus the detailed confirmation of the validity of Hartree–Fock theory will have to await more detailed calculations of ρ_g, which are now under way in a number of laboratories.[16,17]

Reformulation in Site Representation

We have seen that local surface properties enter importantly into chemisorption. Although it was simplest to start with a momentum representation, i.e., metal k states, we made a switch to local states eventually. It has recently been shown by Grimley[18] and also by Bell and Madhukar,[4] that it is possible to

start in a localized representation ab initio, using Wannier-like functions for appropriately defined group orbitals. The theory is most naturally couched again in Green's function language, and one arrives at a cluster Green's function which refers to the adsorbate and the substrate atoms it interacts with directly. Unlike the cluster calculations referred to at the beginning of this article the cluster Green's function discussed here takes full account of the coupling of the cluster to the rest of the metal. In addition, the scattering from states $|k\rangle$ to $|k'\rangle$, which was neglected (since we largely neglected matrix elements of the form $V_{kk'}$) in the previous theories, can be included straightforwardly here as a term corresponding to hopping of an electron from site i to site j under the influence of the adsorbate potential V. It is also possible to include overlap in this formulation. On the other hand the localized basis employed here is the Fourier transform of the momentum states in a single band, and it is not simple to include continuum states directly. However, we have seen that the latter contribute only a real term to G_{aa}^{-1} in the region of chief interest, i.e., $\epsilon < 0$. Thus it should be possible to put in the continuum contribution "by hand". The site representation should therefore give good results also for ρ_a except for $\epsilon > 0$.

Beyond Hartree–Fock

Although we have given arguments why the Hartree–Fock approximation should be adequate for many chemisorption calculations, it is clearly of considerable interest to go beyond it if possible. Bell and Madhukar[4] have recently succeeded in doing this in the site representation which amounts to a molecular orbital calculation; to date the treatment neglects overlap. Their result for the cluster Green's function G_{aa} has the form

$$G_{aa}^{\sigma} = \frac{1 - \langle n_{\sigma^-}\rangle_{eff}}{\epsilon - \epsilon_a' - \Sigma_1(\epsilon)} + \frac{\langle n_{\sigma^-}\rangle_{eff}}{\epsilon - \epsilon_a' - U_{eff} - \Sigma_2(\epsilon)} \quad (37)$$

where $\langle n_{\sigma^-}\rangle_{eff}$ is an effective, energy-dependent occupation number and Σ_1 and Σ_2 are self-energies (i.e., generalizations of the chemisorption function $\Sigma_k g_k |V_{ak}|^2$). It is evident that eq 37 has a most suggestive form. Its first part corresponds to the Green's function of a single electron on A, and U is not explicitly present. The second part corresponds to double occupancy; the full U_{eff}, not $\langle n\rangle U_{eff}$, appears in the denominator. The two parts are weighted according to the (effective) occupations of A by one and two electrons, respectively.[19]

A detailed discussion of the self-energies is quite beyond the scope of this article, but it is worthwhile stating that the self-energy corresponding to two electrons on A contains three components: a direct scattering term, corresponding to an electron on A

(16) R. Haydock and M. J. Kelly, *Surf. Sci.*, **38**, 139 (1973).
(17) D. Kalkstein and P. Soven, *Surf. Sci.*, **26**, 85 (1971); R. Davenport, J. R. Schrieffer, and R. L. Einstein, to be published.
(18) T. B. Grimley and C. Pisani, *J. Phys. C*, **7**, 283 (1974).

(19) This statement requires some explication. The peak arising from "single occupancy" is clearly lower in energy than the "double occupancy" peak and corresponds, crudely, to a filled bonding orbital. "Single occupancy" must not be taken to mean a single bonding electron, but rather a valence bond structure with one bonding electron more or less on A and the other(s) more or less on appropriate metal atoms. The "double occupancy" peak corresponds to the ionic part of the LCAO–MO wave function. These two peaks are merged into a single one in Hartree–Fock, which corresponds reasonably well to the "single occupancy" peak of the more exact theory. This suggests that there may be some fortuitous cancelations in Hartree–Fock, but also that the main contribution to bonding comes from "single occupancy," for large U.

with spin σ scattering to M and vice versa and spin-flip terms, corresponding to an electron on A with spin σ scattering to the metal and an electron of spin σ^- scattering from metal to A. These terms correspond to single occupancy of A but appear in Σ_2 as contributions from intermediate states. It turns out that these two terms are identical. Finally, the third piece of Σ_2 corresponds to scattering of an electron of spin σ into A when an electron of spin σ^- is already on A and vice versa, i.e., corresponds to double occupancy. Σ_1 is the "chemisorption function" in site representation. $\langle n_{\sigma^-} \rangle$ contains the direct and spin-flip terms already mentioned, as well as terms corresponding to double occupancy which arise from intermediate states. Spin-flip processes also occur in the valence-bond method because of overlap only since double occupancy of A is excluded a priori. In the Bell–Madhukar treatment spin flip (or better spin fluctuations) arises from Coulomb scattering on the adsorbate. The inclusion of overlap in this theory will undoubtedly also produce terms like those occurring in the valence bond method. The Bell–Madhukar equations go over into those derived by Brenig and Schönhammer[5] in the weak V limit and into the Hartree–Fock equations in the weak U limit. In the infinite U limit only the first term in eq 37 is present and corresponds to single occupancy of A.

The form of eq 37 shows that there can be nonmagnetic solutions, i.e., $G_{aa}{}^{\sigma} = G_{aa}{}^{\sigma^-}$, $\langle n_\sigma \rangle = \langle n_{\sigma^-} \rangle$, with two distinct peaks in ρ_a arising from singly occupied and doubly occupied A, respectively. In the Hartree–Fock limit these peaks would merge into a single peak. Further it *may* happen that magnetic solutions occur and in that case there would be four rather than two peaks in the *observed* ρ_a, which is an average over at least a few adsorbate atoms and would thus give $\rho_a{}^{\sigma}$ and $\rho_a{}^{\sigma^-}$ approximately equal weight.

One of the defects of the methods we have been discussing so far is that effects like the image shift of ϵ_a and the reduction in U to U_{eff} have been put in ad hoc, and Coulomb repulsion *except* on A has been neglected. Very recently Madhukar and Bell[4] have extended the calculations just discussed to include s bands and continuum states. It then turns out that these (screening) effects enter quite naturally. Thus we see that the two main contributions to chemisorption on transition metals, localized bonding via directional d-like orbitals, and screening effects via nonlocalized s electrons (and interaction of normally unoccupied continuum states), are beginning to emerge from a single approach.

Adsorbate–Adsorbate Interactions

So far we have implicitly assumed an isolated adsorbate atom on an infinite surface. At appreciable coverages there will be interaction between the adsorbate particles. The most obvious contribution, discussed by Boudart[20] (many years ago) and by the author,[21] amounts to dipole–dipole repulsion of the ad-

sorbates when there is charge transfer. This can amount to several electron volts in the case of alkali adsorption.[22] There is, however, a more subtle effect, even for adsorbates with small or zero dipole moment, namely an indirect interaction mediated by the substrate. This has been considered by Grimley[23] and by Einstein and Schrieffer,[24] among others. This interaction is generally small, 1–2% of the binding energy, but can be repulsive or attractive depending on the adsorbate–adsorbate distance. Thus it can, despite its small magnitude, lead to ordering of adsorbate arrays. Such effects have been seen by low-energy electron diffraction.[25]

Conclusion

The foregoing has attempted to outline the present status of chemisorption at the equilibrium configuration. It should be apparent that we have a reasonable qualitative understanding of what is going on, that there is even some hope of introducing real structure, and that calculations may move from the model Hamiltonian stage in the foreseeable future. What then remains to be done? The first point to note is that "image effects" and screening in general have been treated in a very ad hoc manner. The first improvement would consist of a more realistic calculation of such effects for transition metals. As pointed out in the last section, a start in this direction is being made. The second point is that multilevel adsorbates or the contributions from higher adsorbate states have so far been largely ignored. Extension of the theories outlined here to include this does not, in my opinion, constitute a very major step, except computationally, but one which certainly must soon be taken. Next, nothing at all has been said about adsorbate–surface repulsion, so that we are not as yet able to calculate equilibrium separation, but must assume a value for it. Finally, no one has as yet spent much thought or effort on the calculation of properties at surface–adsorbate distances larger than the equilibrium separation. At large distances one can almost certainly use perturbative methods without undue difficulty. At intermediate separations where the Hartree–Fock criterion *must* break down because of weak coupling *and* weak image interaction, approaches like those outlined in the preceding section will undoubtedly come into their own. This region is important, of course, if we wish to understand kinetic phenomena associated with chemisorption. Thus chemisorption research, experimental and theoretical, appears to have an assured future for some time to come.

(20) M. Boudart, *J. Am. Chem. Soc.*, 74, 3556 (1952).
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(24) T. L. Einstein and J. R. Schrieffer, *Phys. Rev. B*, 7, 3629 (1973).
(25) P. J. Estrup and J. Anderson, *J. Chem. Phys.*, 45, 2254 (1966).