small. We have, using Eq. (1),

$$\tfrac{1}{2}\langle W_{\mathbf{k}}{}^{2s}|W_{\mathbf{k}'}{}^{2s*}W_{\mathbf{k}'}{}^{2s}|W_{\mathbf{k}}{}^{2s}\rangle_{\text{av kk}',\text{other ion exch}}$$

$$=\tfrac{1}{2}Z^2\sum_\nu\Big\langle(A_{2s}(k)A_{2s}(k'))^2(1-\sum_t|A_t(k)|^2)^{-1}$$

$$\times(1-\sum_t|A_t(k')|^2)^{-1}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\nu}\int\int d^3r_2d^3r_1$$

$$\times\tilde{\psi}_{2s}{}^2(\mathbf{r}_1-\mathbf{R}_\nu)\tilde{\psi}_{2s}{}^2(\mathbf{r}_2)|\mathbf{r}_1-\mathbf{r}_2|^{-1}\Big\rangle_{\text{av kk}'},\quad\text{(A21)}$$

where we have already performed one of the two sums over lattice sites. The integral above is identical to that for the Coulomb potential between two spherical charge densities and is just $1/R_\nu$. The angular $\mathbf{kk}'$ average of $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\nu}$ is $j_0(kR_\nu)j_0(k'R_\nu)$. Since we are not interested in great accuracy here, we may separately average the renormalization factors and $j_0(kR_\nu)j_0(k'R_\nu)$ over k and k' to obtain

$$\tfrac{1}{2}\langle W_{\mathbf{k}}{}^{2s}|W_{\mathbf{k}'}{}^{2s*}W_{\mathbf{k}'}{}^{2s}|W_{\mathbf{k}}{}^{2s}\rangle_{\text{av kk}',\text{other ion exch}}$$

$$=\tfrac{9}{2}Z^2k_F\langle A_{2s}(k)(1-\sum_t|A_t(k)|^2)^{-1}\rangle_{\text{av }k}{}^2$$

$$\times\sum_\nu\left(\frac{\sin k_FR_\nu}{k_FR_\nu}-\cos k_FR_\nu\right)^2(k_FR_\nu)^{-5}.\quad\text{(A22)}$$

We summed Eq. (A22) over 922 neighboring sites and obtained a contribution of 0.000263 Ry/ion to the binding energy. The terms involving $1s$ and $2p$ wiggles will be much smaller than this, while $\langle W|SS|W\rangle$ and $\langle W|SW|W\rangle$ terms should be of the same order of magnitude and of varying sign. We therefore estimate the uncertainty in our calculation due to the neglect of interion wiggle exchange to be 0.001 Ry/ion.

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Self-Consistent Model of Hydrogen Chemisorption*

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The chemisorption of a hydrogen atom on a transition-metal surface is treated theoretically on the basis of the Anderson Hamiltonian in Hartree-Fock approximation, which includes the interelectronic interaction within the $1s$ orbital. One-electron theory is shown to be inadequate for this problem. The localized states which may occur are discussed. A simple expression for the chemisorption energy ΔE is obtained, and a variational method is given for obtaining its self-consistent value. The metal eigenfunctions enter ΔE only through a function $\Delta(\epsilon)$, and the foregoing results are exemplified and applied when this function is semi-elliptical. When the band is half-filled, a single analytic formula for the one-electron part of ΔE is obtained, in accord with the Kohn-Majumdar theorem. With some further assumptions, ΔE and the charge on the atom are calculated for adsorption on Ti, Cr, Ni, and Cu. The values of the hopping integral between the $1s$ orbital and a neighboring metal d orbital required to fit the experimental ΔE are found to be similar and are reasonable. The correct prediction that $|\Delta E|_{\text{Ni}}>|\Delta E|_{\text{Cu}}$ is believed to be significant. A suggestive correlation is found between observations of catalytic ortho-para hydrogen interconversion on Pd-Au alloys and a rigid-band calculation of ΔE.

I. INTRODUCTION

CHEMISORPTION, the adsorption of an atomic or molecular species with an energy change of the order of electron volts, is an important physical property of transition metals, which are generally the most active metals in this respect.[1,2] We shall be concerned with atomic adsorbates in particular, which are frequently formed on chemisorption of molecular gases.[1,2] A coverage of the order of one adatom per surface atom is usually the maximum attainable. A preliminary classification on the basis of the dipole layer associated with a given surface coverage of adsorbate, and in certain cases additional evidence, may be made.[1,2] Alkali atoms are usually found to exist on transition-metal surfaces substantially in a cationic state, H and N in an approximately neutral state, with O possibly forming anions.[1,2] Theoretically, the same type of treatment may be inappropriate to all three types; for example, image force stabilization plays a central role in alkali chemisorption.[1,3] The atomic characteristics favorable to cationic, anionic, and "neutral" chemisorption are evidently small ionization

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potential I, large electron affinity A, and the concurrence of large I with small A, respectively.[1]

The present work is restricted to the simplest "neutral" adsorbate, hydrogen, and is concerned with the calculation of charge distribution and chemisorption energy ΔE for transition-metal substrates. ΔE is defined as the energy change on the adsorption of an isolated H atom. The binding of a neutral adsorbate is dependent on quantum-mechanical coupling between the adsorbate and metal wave functions, and, from the band theory or molecular orbital standpoint of this work, may be attributed to one-electron hopping processes. Early band-theory treatments of chemisorption aimed at the calculation of localized states associated with the adsorbate.[4–8] A formula for ΔE in one-electron approximation has been given by Grimley.[6] Recently[9] the latter author has calculated the interaction energy between adsorbed atoms by a model essentially equivalent to that developed here, and a similar model has been employed by Bennett and Falicov[10] to calculate the charge distribution in alkali adsorption. A number of other treatments have also been given.[11–13] A preliminary account of the present work has already been published.[14]

A limited basis consisting of the hydrogen $1s$ orbital denoted by $|a\rangle$, and the self-consistent eigenstates $|k\rangle$ of the unperturbed semi-infinite metal will be adopted. The states $|k\rangle$ will be assumed to be orthogonal to $|a\rangle$. The condensed notation $|k\rangle$ is employed to include the wave vector parallel to the surface, a quantum number for the out-of-surface direction, and a band index.

Let the eigenvalues belonging to the states $|a\rangle$ and $|k\rangle$ with the adatom at infinite distance from the surface be ϵ_a and ϵ_k. It will be assumed that $\langle a|H|a\rangle=\epsilon_a$ and $\langle k|H|k\rangle=\epsilon_k$ after chemisorption. The only nonzero matrix elements of the perturbation resulting in adsorption will be assumed to be V_{ak}, given by

$$V_{ak}=\int \varphi_{1s}^*(\mathbf{x})H_{\mathrm{HF}}(\mathbf{x})\varphi_k(\mathbf{x})d^3x, \tag{1}$$

in which H_{HF} is the Hartree-Fock self-consistent Hamiltonian after chemisorption.

For hydrogen $I=13.6$ eV, $A=0.7$ eV, and the work functions of transition metals are close to $\varphi\simeq 4.5$ eV. Hence from a hydrogen atom far from the surface, an energy ~ 3.8 eV is required to create an H^- ion, and ~ 9.1 eV to form a bare proton, which should be compared with the observed $\Delta E\simeq -3.5$ eV.[1,2] It would evidently be wrong to use the simple one-electron approximation, with $\epsilon_a=-13.6$ eV relative to the vacuum, since this would give $\Delta E\lesssim -9.1$ eV, including both the ionic contribution and the energy lowering due to the V_{ak}. The energy of the $1s$ orbital is in fact uncertain within the range -9.1 to $+3.8$ eV relative to the Fermi level, and on the scale of ΔE in no way resembles a one-electron level.[6] The large difference $I-A$ for hydrogen arises from the repulsive Coulomb integral U_0 between two electrons in the $1s$ orbital, defined by

$$U_0=\int\int \varphi_{1s}^*(\mathbf{x})\varphi_{1s}^*(\mathbf{y})\frac{e^2}{|\mathbf{x}-\mathbf{y}|}\varphi_{1s}(\mathbf{x})\varphi_{1s}(\mathbf{y})d^3xd^3y. \tag{2}$$

The Coulomb integral must be included explicitly in a calculation of ΔE. In fact, $U_0=17.0$ eV, which exceeds $I-A$ due to neglect of correlation, and this will here be allowed for by redefining an effective Coulomb integral U as

$$U=I-A=12.9 \text{ eV}. \tag{3}$$

The resulting model is equivalent to Anderson's description of magnetic impurities in alloys. The Hamiltonian may be written in second-quantized form:

$$H=\sum_\sigma \epsilon_a n_{a\sigma}+\sum_{k,\sigma}\epsilon_k n_{k\sigma}+\sum_{k,\sigma}(V_{ak}c_{a\sigma}^\dagger c_{k\sigma}+\text{H.c.}) + Un_{a\sigma}n_{a-\sigma}, \tag{4}$$

in which σ denotes spin. The first and second terms describe the set of unperturbed eigenstates $|a\rangle$ and $|k\rangle$. The third expression introduces the hopping terms $V_{ak}c_{a\sigma}^\dagger c_{k\sigma}$ coupling these eigenstates, and the last term describes the Coulomb interaction between electrons of opposite spin in the $1s$ orbital.

The smaller energy spread of the d-type $|k\rangle$ states, lying near the Fermi level in transition metals, relative to those in the sp band, is a factor tending to increase the relative contribution of these states to ΔE. Experimentally, the importance of the d contribution is suggested by the inability of most nontransition metals to dissociatively chemisorb H_2 (which requires $|\Delta E|>2.24$ eV),[1,2] though some may adsorb atomic hydrogen.[1,2] For these reasons the contribution of the sp band will ultimately be neglected as a first approximation, an assumption which leads to some success in the interpretation of certain catalyctic measurements (see Sec. VI). The ensuing formal development is, however, independent of any assumption about the $|k\rangle$ states.

II. HARTREE-FOCK SOLUTION

We shall here follow Anderson in employing the Hartree-Fock approximation to the solution of (4). Subsequent to Anderson's initial paper,[15] the HF

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approximation has been shown to lead to probably spurious results for the localized magnetic moment,[16–19] but it is not believed to be a cause of such serious error in the present calculation of ΔE. The reasons for this are: (a) Treatment of the simple two-electron diatomic system, in which the set of $|k\rangle$ are replaced by a single atomic orbital $|b\rangle$, shows that even when $U\rightarrow\infty$ the error in replacing ΔE by ΔE_{HF} lies between 50 and 29% of ΔE. The fact that the error is bounded when $U\rightarrow\infty$ is probably of more general validity. (b) Calculation of ground-state energy does not depend sensitively on the wave function because of the variational principle. This also applies to ΔE, since the HF solution is exact when the V_{ak} are identically zero.[18] (c) The HF approximation includes the perturbation U only to first order, and should be valid for sufficiently small U. In the present problem U is not small, but nevertheless the HF calculations described below (see Sec. V) suggest that electron correlation is not playing a predominant role. In particular, the solutions are nonmagnetic.

The Fock Hamiltonian H^σ, which in unrestricted HF approximation may depend on the spin σ, is obtained[15] by replacing the two-particle interaction $Un_{a-\sigma}n_{a\sigma}$ by $U\langle n_{a-\sigma}\rangle n_{a\sigma}$ and may be written

$$H^\sigma=\epsilon_\sigma n_{a\sigma}+\sum_k \epsilon_k n_{k\sigma}+\sum_k (V_{ak}c_{a\sigma}{}^\dagger c_{k\sigma}+\mathrm{H.c.}), \quad (5a)$$

where

$$\epsilon_\sigma=\epsilon_a+U\langle n_{a-\sigma}\rangle. \quad (5b)$$

ϵ_σ here defines an effective adatom level of spin σ. It is convenient to introduce the one-electron Green's operator corresponding to the H^σ:

$$G^\sigma(\epsilon)=[(\epsilon+is)I-H^\sigma]^{-1}, \quad s=0^+, \quad (6)$$

where I is the unit operator. Thus the matrix equation for G is

$$(I\epsilon-H^\sigma)G^\sigma(\epsilon)=I. \quad (7)$$

This equation may be easily solved in the unperturbed representation to give the Green's function $G_{aa}{}^\sigma$[15]:

$$G_{aa}{}^\sigma(\epsilon)=\left[\epsilon-\epsilon_\sigma-\sum_k \frac{|V_{ak}|^2}{\epsilon-\epsilon_k+is}\right]^{-1}, \quad (8)$$

$$=[\epsilon-\epsilon_\sigma-\Lambda(\epsilon)+i\Delta(\epsilon)]^{-1}, \quad (9)$$

where

$$\Delta(\epsilon)=-\mathrm{Im}\sum_k[|V_{ak}|^2/(\epsilon-\epsilon_k+is)]$$

$$=\pi\sum_k |V_{ak}|^2\delta(\epsilon-\epsilon_k), \quad (10a)$$

$$\Lambda(\epsilon)=\frac{P}{\pi}\int_{-\infty}^{\infty}\frac{\Delta(\epsilon')d\epsilon'}{\epsilon-\epsilon'}, \quad (10b)$$

where P denotes the Cauchy principal value.

$\Delta(\epsilon)$ is seen to be a weighted density-of-states function, with $\Lambda(\epsilon)$ as its Hilbert transform. We may define a projected density of states for the adatom orbital in terms of the Fock eigenfunctions $|m\sigma\rangle$ by

$$\rho_{aa}{}^\sigma(\epsilon)=\sum_m |\langle m\sigma|a\rangle|^2\delta(\epsilon-\epsilon_{m\sigma}). \quad (11)$$

Now from (6), G^σ may be expressed in the perturbed representation as

$$G_{mm'}{}^\sigma(\epsilon)=\delta_{mm'}/(\epsilon-\epsilon_{m\sigma}+is), \quad (12)$$

whence, on transforming to the unperturbed representation

$$G_{aa}{}^\sigma(\epsilon)=\sum_m \frac{|\langle m\sigma|a\rangle|^2}{\epsilon-\epsilon_{m\sigma}+is}, \quad (13)$$

from which

$$\rho_{aa}{}^\sigma(\epsilon)=-\pi^{-1}\,\mathrm{Im}G_{aa}{}^\sigma(\epsilon)$$

$$=\frac{\pi^{-1}\Delta(\epsilon)}{[\epsilon-\epsilon_\sigma-\Lambda(\epsilon)]^2+\Delta^2(\epsilon)}. \quad (14)$$

The only new feature introduced into these results of Anderson is allowance for the energy dependence of Δ and Λ, which is unavoidable because the bandwidth in the present problem is not especially large. As a consequence, there arises the possibility of localized states.

From comparison of the expressions (8) and (13) for $G_{aa}{}^\sigma$ it is seen that the Fock eigenvalues $\epsilon_{m\sigma}$ are roots of

$$\epsilon-\epsilon_\sigma-\sum_k \frac{|V_{ak}|^2}{\epsilon-\epsilon_k}=0. \quad (15)$$

This equation has the interpolative property that each root $\epsilon_{m\sigma}$ is always trapped between a pair of unperturbed eigenvalues ϵ_k, except for one root each at the upper and lower band edges, which may detach themselves from the band. Referring to (9) we see that poles of $G_{aa}{}^\sigma$ may occur outside the band, when $\Delta=0$, given by the solutions of

$$\epsilon-\epsilon_\sigma-\Lambda(\epsilon)=0. \quad (16)$$

The residue of $G_{aa}{}^\sigma$ at a root $\epsilon_{l\sigma}$ is seen from (13) to give the occupation number $\langle n_{a\sigma}\rangle_l=|\langle a|l\sigma\rangle|^2$ of the corresponding eigenstate $|l\sigma\rangle$ on the adatom orbital. This is then

$$\langle n_{a\sigma}\rangle_l=[1-\Lambda'(\epsilon_{l\sigma})]^{-1}, \quad (17)$$

where the prime denotes differentiation. From the definition (10b) of Λ, Λ' is evidently negative at all points outside the band, so that $\langle n_{a\sigma}\rangle_l$ is a positive number between 0 and 1. Therefore $\epsilon_{l\sigma}$ refers to a state *localized* in the region of the adatom.

The formation of the roots of (16) is shown in Fig. 1. From the monotonic variation of Λ outside the band it is

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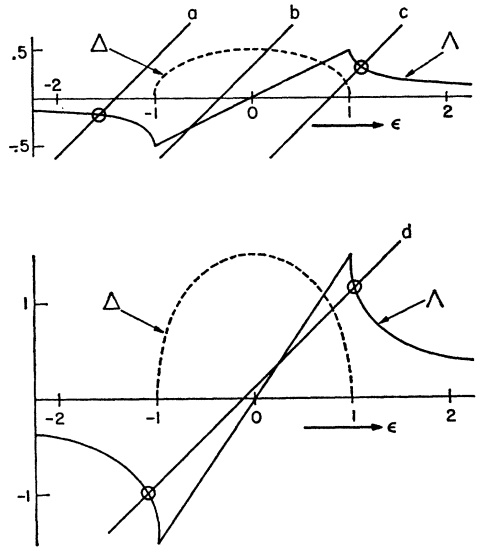

FIG. 1. Semielliptical $\Delta(\epsilon)$ with Hilbert transform $\Lambda(\epsilon)$. In the notation of IV, units are -2β, with $\beta'=0.5$ (upper figure) and $\beta'=\frac{3}{2}$ (lower figure). Intersections of $\epsilon-\epsilon_\sigma$ (lines a, b, c, d) with Λ define localized states. The various cases, i.e., zero (b), one (a and c), and two (d), localized states are shown.

clear that at most one localized state can be found in each of the regions bounding the band.

Defining the upper and lower band edges at ϵ_1 and ϵ_0, respectively, the conditions for localized states are

$$\epsilon_{l\sigma}>\epsilon_1, \quad \epsilon_1-\epsilon_\sigma<\Lambda(\epsilon_1), \tag{18a}$$

$$\epsilon_{l\sigma}<\epsilon_0, \quad \epsilon_0-\epsilon_\sigma>\Lambda(\epsilon_0). \tag{18b}$$

We may obtain some intuitive understanding of the problem by considering two limiting cases. If the separation of ϵ_σ from any part of the band always greatly exceeds $\Delta(\epsilon)$, then $\Lambda(\epsilon_\sigma)$ and $\Lambda'(\epsilon_\sigma)$ will be small. Then $\epsilon_{l\sigma}\simeq\epsilon_\sigma$ (see Fig. 1) and $\langle n_{a\sigma}\rangle_l\simeq 1$. In this case when the coupling between the effective level ϵ_σ and the band is weak there is only one localized state, which differs little from the adatom orbital itself.

The second case is the limit of strong adatom-metal coupling. If $\Delta(\epsilon)$ over most of the band greatly exceeds both its width and the separation of ϵ_σ from its center, then $\Lambda(\epsilon)$ will be very large near the band and both (18a) and (18b) satisfied. There must result two localized states widely straddling the band, so that (16) may be approximated by

$$\epsilon-\epsilon_\sigma-(\epsilon-\epsilon_c)^{-1}\pi^{-1}\int_{\epsilon_0}^{\epsilon_1}\Delta(\epsilon')d\epsilon'=0, \tag{19}$$

or

$$(\epsilon-\epsilon_\sigma)(\epsilon-\epsilon_c)-\sum_k|V_{ak}|^2=0, \tag{20}$$

where ϵ_c is the band center.

The $|k\rangle$ may be expressed in terms of localized orbitals $|j\rangle$ on each metal atomic site. The $|j\rangle$ will be assumed to be orthonormal. For the present purposes it is more appropriate to identify the $|j\rangle$ with atomic orbitals than the less well localized Löwdin orbitals.[20] We then have

$$V_{ak}=\sum_j\beta_j'\langle j|k\rangle, \tag{21}$$

where

$$\beta_j'=\langle a|V|j\rangle. \tag{22}$$

Then (20) becomes

$$(\epsilon-\epsilon_\sigma)(\epsilon-\epsilon_c)-\sum_j|\beta_j'|^2=0, \tag{23}$$

$$\epsilon_{l\sigma}=2^{-1}(\epsilon_c+\epsilon_\sigma)\pm 2^{-1}[(\epsilon_\sigma-\epsilon_c)^2+4\sum_j|\beta_j'|^2]^{1/2}. \tag{24}$$

These eigenvalues are just the bonding and antibonding levels of the "molecule" consisting of the orbital $|a\rangle$ and the metal orbitals $|j\rangle$ isolated from the metal. It is also easily shown that $\langle n_{a\sigma}\rangle_l\simeq\frac{1}{2}$ in this case.

To summarize, under weak coupling conditions a localized state exists approximating the adatom orbital $|a\rangle$, whereas in the strong coupling case two localized states exist approximating the bonding and antibonding states of the molecule consisting only of $|a\rangle$ and the metal atomic orbitals to which it is directly coupled.

Poles may also occur in $G_{aa}^\sigma(\epsilon)$ within the band at complex energies given by the roots of

$$[\epsilon-\epsilon_\sigma-\Lambda(\epsilon)]^2+\Delta^2(\epsilon)=0. \tag{25}$$

These roots may be termed virtual states. They have the significance that their energy, translated into complex frequency, governs the time evolution of the state $|a\rangle$, as may be seen on taking the time Fourier transform of $G_{aa}^\sigma(\epsilon)$.

Let us define the function $N(n_{-\sigma})$ (we shall frequently abbreviate $\langle n_{a\sigma}\rangle$ to n_σ) as the occupation number $\langle n_{a\sigma}\rangle$ due to the occupied Fock eigenfunctions of spin σ when the effective level ϵ_σ is set at $\epsilon_\sigma=\epsilon_a+Un_{-\sigma}$. Then

$$N(n_{-\sigma})=\int_{\epsilon_0}^{0}\rho_{aa}^\sigma(\epsilon,\epsilon_\sigma)+\langle n_{a\sigma}\rangle_l, \tag{26}$$

where the second term, given by (17), is to be included only when a localized state exists below the band, and we take the Fermi level as energy zero. Both terms on the right of (26) depend on ϵ_σ, which gives rise to the dependence on $n_{-\sigma}$. Since increasing ϵ_σ should decrease $\langle n_{a\sigma}\rangle$, and $U>0$, $N(n_{-\sigma})$ should be a decreasing function of $n_{-\sigma}$. The equations for the self-consistent $n_{\pm\sigma}$ are[15]

$$n_\sigma=N(n_{-\sigma}), \tag{27a}$$

$$n_{-\sigma}=N(n_\sigma), \tag{27b}$$

or

$$N[N(n_\sigma)]-n_\sigma=0. \tag{28}$$

These equations always have a "nonmagnetic" root for which $n_\sigma=n_{-\sigma}$. An additional symmetrical pair of solutions of "magnetic" type for which $n_\sigma\neq n_{-\sigma}$ may

[20] P. O. Lowdin, J. Chem. Phys. 18, 365 (1950).

also exist, and when they do exist the magnetic solutions have the lower energy.[15] The condition for the existence of magnetic solutions is[15]

$$[dN(n_\sigma)/dn_\sigma]_{n_\sigma=N(n_\sigma)}<-1. \tag{29}$$

An example of the solution of Eqs. (27) for a magnetic case is shown in Fig. 5.

III. CHEMISORPTION ENERGY

The energy change consequent upon switching on the V_{ak}, when the unperturbed system contains one particle in the orbital $|a\rangle$, so that $\epsilon_a+U>0$, $\epsilon_a<0$, is

$$\Delta E=[\sum_{\substack{m,\sigma\\ \text{occ}}}\epsilon_{m\sigma}-U\langle n_{a\sigma}\rangle\langle n_{a-\sigma}\rangle]-[2\sum_{\substack{k\\ \text{occ}}}\epsilon_k+\epsilon_a]. \tag{30}$$

The first and second terms are the energy of the perturbed and unperturbed systems, respectively; in the former the expectation value of the interaction energy appears negatively because it has already been counted twice over in the sum of Fock eigenvalues. The summations are over occupied orbitals only. It is convenient to define a one-electron energy change $\Delta E^{1\sigma}$ by

$$\Delta E^{1\sigma}=\sum_{\substack{m\\ \text{occ}}}\epsilon_{m\sigma}-\sum_{\substack{k\\ \text{occ}}}\epsilon_k, \tag{31}$$

so that

$$\Delta E=\sum_\sigma \Delta E^{1\sigma}-U\langle n_{a\sigma}\rangle\langle n_{a-\sigma}\rangle-\epsilon_a. \tag{32}$$

Since $\langle n_{a\sigma}\rangle$ is calculable from the expression (26), it remains to calculate $\Delta E^{1\sigma}$. We use the theorem[21] that, if $f(z)$ is a function analytic within the contour C and $\varphi(z)$ is analytic within C except at a finite number of poles, then

$$\frac{1}{2\pi i}\int_c f(z)\frac{\varphi'(z)}{\varphi(z)}dz=\sum_i r_i f(a_i)-\sum_i s_i f(b_i), \tag{33}$$

where the a_i are the zeros and the b_i the poles of φ within C, having the multiplicities r_i and s_i, respectively.

$\Delta E^{1\sigma}$ may thus be expressed in terms of a contour integral in the ϵ plane by taking $f(\epsilon)=\epsilon$, when

$$\Delta E^{1\sigma}=\frac{1}{2\pi i}\int_c \epsilon\frac{d}{d\epsilon}\ln\left[\epsilon-\epsilon_\sigma-\sum_k\frac{|V_{ak}|^2}{\epsilon-\epsilon_k}\right]d\epsilon. \tag{34}$$

We have here used the fact that the argument of the logarithm has poles at the ϵ_k and, from (15), zeros at the $\epsilon_{m\sigma}$. C is to enclose all the occupied eigenvalues. Expanding (34) by parts,

$$\Delta E^{1\sigma}=\frac{1}{2\pi i}\left|\epsilon\ln\left[\epsilon-\epsilon_\sigma-\sum_k\frac{|V_{ak}|^2}{\epsilon-\epsilon_k}\right]\right|_c - \frac{1}{2\pi i}\int_c\ln\left[\epsilon-\epsilon_\sigma-\sum_k\frac{|V_{ak}|^2}{\epsilon-\epsilon_k}\right]d\epsilon. \tag{35}$$

[21] E. T. Whittaker and G. N. Watson, *Course of Modern Analysis* (Cambridge University Press, London, 1965), Sec. 6.3.

If we adopt the Fermi level as energy zero, the integrated part is zero. Employing the rectangular contour defined by the points $\epsilon_0\pm is$, $\pm is$, we may neglect the end portions as $s\to 0$, so that

$$\Delta E^{1\sigma}=-\frac{1}{2\pi i}\int_0^{\epsilon_0}\ln\left[\epsilon-\epsilon_\sigma-\sum_k\frac{|V_{ak}|^2}{\epsilon-\epsilon_k+is}\right]d\epsilon - \frac{1}{2\pi i}\int_{\epsilon_0}^{0}\ln\left[\epsilon-\epsilon_\sigma-\sum_k\frac{|V_{ak}|^2}{\epsilon-\epsilon_k-is}\right]d\epsilon, \tag{36}$$

$$=\frac{1}{\pi}\int_{\epsilon_0}^{0}\tan^{-1}\left[\frac{\Delta(\epsilon)}{\epsilon-\epsilon_\sigma-\Lambda(\epsilon)}\right]d\epsilon, \tag{37}$$

where we have used (10). The $\tan^{-1}$ is here to be taken in the range $0\to-\pi$. When an occupied localized state exists the contour C should include both the occupied band eigenvalues and the isolated pole at $\epsilon_{l\sigma}$ below the band. It is convenient to split C into two parts C_1 and C_2, where C_1 encloses $\epsilon_{l\sigma}$ and the lowest unperturbed band eigenvalue at ϵ_0, and C_2 the remaining occupied band eigenvalues $\epsilon_{m\sigma}$ and ϵ_k, all of which lie above ϵ_0 by the interpolative property. The contribution from C_1 is just $\epsilon_{l\sigma}-\epsilon_0$. The removal of one perturbed and one unperturbed eigenvalue from the bottom of the band leaves the C_2 contribution unaffected, whence in this case

$$\Delta E^{1\sigma}=\epsilon_{l\sigma}-\epsilon_0+\frac{1}{\pi}\int_{\epsilon_0}^{0}\tan^{-1}\left[\frac{\Delta(\epsilon)}{\epsilon-\epsilon_\sigma-\Lambda(\epsilon)}\right]d\epsilon. \tag{38}$$

Combining these results with (32), we have

$$\Delta E=\sum_\sigma\left\{\epsilon_{l\sigma}+\frac{1}{\pi}\int_{\epsilon_0}^{0}\tan^{-1}\left[\frac{\Delta(\epsilon)}{\epsilon-\epsilon_\sigma-\Lambda(\epsilon)}\right]d\epsilon\right\} - \epsilon_a-U\langle n_{a\sigma}\rangle\langle n_{a-\sigma}\rangle, \tag{39}$$

where $0<\tan^{-1}<\pi$ when an occupied localized state of energy $\epsilon_{l\sigma}$ exists, but if not then $-\pi<\tan^{-1}<0$ and $\epsilon_{l\sigma}=0$.

Both $\Delta E^{1\sigma}$ and $\langle n_{a\sigma}\rangle$, and hence ΔE, depend explicitly on the metal eigenstates $|k\rangle$ only through the functions Δ and Λ, the latter being itself determined by Δ. This result is not in fact dependent on the HF approximation, as may be proven by expressing ΔE in terms of the diagrammatic methods of Schrieffer *et al.*[16,17]

It may be shown from Eq. (39) that $\Delta E\to 0$ when $\Delta\to 0$. When the V_{ak} are finite the system is always at liberty to adopt its unperturbed ground state, for which the expectation value of the off-diagonal perturbation is zero, and therefore $\Delta E=0$. Hence ΔE is always less than or equal to zero. It is satisfactory that this physically correct result is obtained within the present approximation.

It is relevant to state here without proof (which is a straightforward application of perturbation theory) a

result applicable when $\epsilon_a \to -\infty$, but ϵ_a+U finite; i.e., when the ionization potential of the adatom is very large. It is then found that a self-consistent solution is

$$\langle n_{a\sigma}\rangle \to 1, \quad \epsilon_{-\sigma} \to \epsilon_a+U, \quad \epsilon_\sigma \to -\infty, \tag{40a}$$

$$\Delta E \to \Delta E^{1-\sigma}. \tag{40b}$$

In other words ΔE is here half what would be calculated on replacing the adatom by a single one-electron level defined by its electron affinity, because only electrons of spin $-\sigma$ interact with the adatom. This was assumed initially in the work of Bennett and Falicov.[10]

It will now be convenient to employ the following theorem. Let a Hamiltonian H be a function $H(g)$ of some scalar variable g, and let $|n\rangle_g$ be an eigenstate of $H(g)$. Then

$$\frac{\partial}{\partial g}{}_g\langle n|H|n\rangle_g = {}_g\langle n|\frac{\partial H(g)}{\partial g}|n\rangle_g. \tag{41}$$

This relation is trivial to prove when $|n\rangle_g$ is an exact eigenstate of $H(g)$. However, it may also be shown to remain valid for an approximate ground state $|0\rangle_g$, provided that the values of any variable parameters in $|0\rangle_g$ are chosen so as to minimize the energy at each value of g.[22] This theorem is therefore applicable to the HF ground state, which is derivable from the Variational Principle.

Let us first apply the theorem to the Fock Hamiltonian H^σ (5), at fixed $\langle n_{a-\sigma}\rangle$, obtaining

$$\frac{\partial}{\partial g}\langle m\sigma|H^\sigma|m\sigma\rangle = \frac{\partial \epsilon_{m\sigma}}{\partial g} = \langle m\sigma|\frac{\partial H^\sigma}{\partial g}|m\sigma\rangle, \tag{42}$$

where $|m\sigma\rangle$ is an exact eigenstate of H^σ. If $g=\epsilon_\sigma$, then

$$\partial\epsilon_{m\sigma}/\partial\epsilon_\sigma = \langle m\sigma|n_{a\sigma}|m\sigma\rangle. \tag{43}$$

If $m=l$ this provides an alternative formula to (17) for $\langle n_{a\sigma}\rangle_l$. Now summing (43) over all occupied eigenvalues and using (31), since the ϵ_k do not depend on ϵ_σ, we obtain

$$\partial\Delta E^{1\sigma}/\partial\epsilon_\sigma = N(n_{-\sigma}), \tag{44}$$

where we have used (26). This provides a useful relation between (26) and (37).

Let us consider the variational properties of ΔE with respect to the two variables $\langle n_{a\pm\sigma}\rangle = n_{\pm\sigma}$, allowing these to be independent. ΔE is given by (39),

$$\Delta E = -\epsilon_a + \sum_\sigma \Delta E^{1\sigma}(\epsilon_a+Un_{-\sigma}) - Un_\sigma n_{-\sigma}, \tag{45}$$

where we have explicitly shown the dependence of ΔE on $n_{-\sigma}$ through ϵ_σ. Then

$$\begin{aligned}\frac{\partial \Delta E}{\partial n_\sigma} &= \frac{\partial}{\partial n_\sigma}\Delta E^{1-\sigma}(\epsilon_a+Un_\sigma) - Un_{-\sigma} \\ &= U\frac{\partial}{\partial \epsilon_{-\sigma}}\Delta E^{1-\sigma}(\epsilon_{-\sigma}) - Un_{-\sigma} \\ &= U[N(n_\sigma)-n_{-\sigma}],\end{aligned} \tag{46}$$

where we have made use of (44). Thus the self-consistency condition (28) is equivalent to requiring that ΔE be stationary with respect to n_σ and $n_{-\sigma}$.

From (46) we also have

$$\frac{\partial^2 \Delta E}{\partial n_\sigma{}^2} = U\frac{\partial N(n_\sigma)}{\partial n_\sigma} > 0. \tag{47}$$

The last step follows since, as noted above, $N(n_\sigma)$ is expected to be a monotonically decreasing function of n_σ, and $U>0$. At $n_{-\sigma}=$ const, ΔE is therefore concave towards the n_σ axis, with a maximum when $N(n_\sigma)=n_{-\sigma}$.

We shall now consider $\Delta E(n_\sigma, n_{-\sigma})$ as a function of n_σ when $n_{-\sigma}=N(n_\sigma)$; i.e., along the full curve in Fig. 5. Substituting this relation for $n_{-\sigma}$ into (45) and differentiating, we obtain

$$U^{-1}\frac{d}{dn_\sigma}\Delta E = N'(n_\sigma)[N(N(n_\sigma))-n_\sigma], \tag{48}$$

$$\begin{aligned}U^{-1}\frac{d^2}{dn_\sigma{}^2}\Delta E &= N''(n_\sigma)[N(N(n_\sigma))-n_\sigma] \\ &\quad + N'(n_\sigma)[N'(N(n_\sigma))N'(n_\sigma)-1].\end{aligned} \tag{49}$$

By means of the self-consistency condition (28), these equations may be simplified at a self-consistent point to

$$U^{-1}(d\Delta E/dn_\sigma) = 0, \tag{50}$$

$$U^{-1}(d^2\Delta E/dn_\sigma{}^2) = N'(n_\sigma)[N'(n_{-\sigma})N'(n_\sigma)-1]. \tag{51}$$

At the permanent nonmagnetic root of (28), at which $n_\sigma=n_{-\sigma}$, the condition for ΔE to have a *maximum* is seen from the second derivative to be that $|N'(n_\sigma)|>1$. This is identical with the Anderson condition (29) for the existence of magnetic solutions. Hence ΔE has a minimum at the nonmagnetic root when other roots do not exist. Now since the function N must be bounded between 0 and 1, it is evident from (48) that at extreme values of n_σ ΔE always increases monotonically with $|n_\sigma|$. Hence when magnetic roots do exist, so that ΔE has a maximum at the nonmagnetic root, ΔE must have a minimum at the magnetic roots, giving them always a lower energy than the nonmagnetic root.[15] Thus, considering in this way ΔE as a function of n_σ with $n_{-\sigma}=N(n_\sigma)$, ΔE monotonically decreases as n_σ is increased from large negative values, goes through either a single minimum or double minima separated by a maximum at the self-consistent values of n_σ, and then increases

[22] A. C. Hurley, Proc. Roy. Soc. (London) **A266**, 179 (1954).

monotonically as n_σ becomes large positive. From what has been said it is evident that ΔE has a saddle point at the true (lowest energy) self-consistent points.

To summarize, ΔE has a maximum as a function of n_σ with $n_{-\sigma}$ fixed, and the lowest of all such maxima as $n_{-\sigma}$ is allowed to vary gives the self-consistent point.

IV. SEMIELLIPTICAL $\Delta(\epsilon)$

We now need to adopt a specific form for $\Delta(\epsilon)$. In the Introduction reasons were given for neglecting, as a first approximation, the contribution to ΔE from states $|k\rangle$ other than those lying in the d band. In fact, the transition-metal d band may often be well approximated by a tight-binding model,[23] although with the full fivefold degeneracy this remains a rather complex system. Unfortunately even for the simpler two- and three-dimensional lattices having only one tight-binding band $\Delta(\epsilon)$ may not be obtained in analytic form, but analytic solution is possible for a one-dimensional system. We shall consider below a chain of atomic orbitals connected only by nearest-neighbor hopping integrals, to which the atom a may be attached terminally, and show that in this case $\Delta(\epsilon)$ takes a semielliptical form. Now experimentally ΔE is found to be comparable with the d-band width, and the same turns out to be true for Δ, so it is unlikely that the detailed structure of Δ will have an important effect on the results. Hence we shall suppose that a semielliptical $\Delta(\epsilon)$ may be taken as a convenient approximation, without restricting the results to the one-dimensional model.

Consider a chain of atoms labelled by $i=0, 1, \cdots, N$, each with a single atomic orbital $|i\rangle$ such that in the AO representation

$$\langle i|j\rangle=\delta_{ij}, \tag{52}$$

$$H_{ii}=0, \quad i=0, 1, \cdots, N \tag{53}$$

$$H_{ii\pm1}=\beta, \quad i=1, 2, \cdots, N-1 \tag{54}$$

(53) redefines our energy zero as that of the self-energy of the AO's and this zero will be retained below unless otherwise stated. Assuming the atoms are separated by unit distance, the eigenvalues ϵ_θ and normalized eigenfunctions $|\theta\rangle$ are[5]

$$\epsilon_\theta=2\beta\cos\theta, \tag{55}$$

$$|\theta\rangle=2^{1/2}(N+1)^{-1/2}\textstyle\sum_i \sin(i+1)\theta\,|i\rangle, \tag{56}$$

where

$$\theta=n\pi/(N+1), \quad n=1, 2, \cdots, N. \tag{57}$$

We shall henceforth suppose that β is negative and measure energy in -2β units so that

$$\epsilon_\theta=-\cos\theta. \tag{58}$$

Now let the adatom be attached to the end of the chain near atom 0, and assume that in the notation of (21) above $\beta_j'=\beta'\delta_{0j}$ so that only the matrix element connecting orbital $|a\rangle$ with ortibal $|0\rangle$ is nonzero. Then from (21) and (56)

$$V_{ak}=\beta'\langle 0|\theta\rangle =\beta' 2^{1/2}(N+1)^{-1/2}\sin\theta. \tag{59}$$

Inserting this expression into (10a), we obtain

$$\begin{aligned}\Delta(\epsilon)&=2\pi\beta'^2(N+1)^{-1}\sum_\theta \sin^2\theta\,\delta(\epsilon+\cos\theta)\\ &=2\beta'^2\int_0^\pi d\theta\,\sin^2\theta\,\delta(\epsilon+\cos\theta)\\ &=2\beta'^2(1-\epsilon^2)^{1/2}.\end{aligned} \tag{60}$$

This gives the semielliptical form for Δ. Using (60), Λ is now given by

$$\begin{aligned}\Lambda(\epsilon)&=2\beta'^2\frac{P}{\pi}\int_{-1}^{1}\frac{(1-\epsilon'^2)^{1/2}}{\epsilon-\epsilon'}d\epsilon'\\ &=\frac{\beta'^2}{\pi}P\int_0^{2\pi}\frac{\sin^2\theta d\theta}{\epsilon+\cos\theta},\end{aligned} \tag{61}$$

from which we obtain

$$\Lambda(\epsilon)=2\beta'^2\epsilon, \quad |\epsilon|<1 \tag{62a}$$

$$=2\beta'^2[\epsilon+(\epsilon^2-1)^{1/2}], \quad \epsilon<-1 \tag{62b}$$

$$=2\beta'^2[\epsilon-(\epsilon^2-1)^{1/2}], \quad \epsilon>1. \tag{62c}$$

These results for Δ and Λ are shown in Fig. 1.

From (60), (62a), and (14) we obtain the density of states in the adatom orbital:

$$\rho_{aa}{}^\sigma=2\pi^{-1}\beta'^2(1-\epsilon^2)^{1/2}[\epsilon^2(1-4\beta'^2) -2\epsilon\epsilon_\sigma(1-2\beta'^2)+(4\beta'^4+\epsilon_\sigma{}^2)]^{-1}. \tag{63}$$

The roots of the denominator are

$$\epsilon=(1-4\beta'^2)^{-1}[(1-2\beta'^2)\epsilon_\sigma\pm 2i\beta'^2(1-4\beta'^2-\epsilon_\sigma{}^2)^{1/2}], \tag{64}$$

so that the condition for complex roots (virtual states) is

$$\epsilon_\sigma{}^2+4\beta'^2<1. \tag{65}$$

A sharp peak in $\rho_{aa}{}^\sigma$ occurs when there is a virtual state near the real axis and may also occur near the band edge at which a localized state is about to separate. A localized state, unless close to the band, generally reduces $\rho_{aa}{}^\sigma$ to a low value.

The conditions (18) for localized states become[5]

$$\epsilon_{l\sigma}>1, \quad \epsilon_\sigma>1-2\beta'^2, \tag{66a}$$

$$\epsilon_{l\sigma}<-1, \quad \epsilon_\sigma<2\beta'^2-1. \tag{66b}$$

The localized state energies are given by the *real* roots (64) of the denominator of $\rho_{aa}{}^\sigma$:

$$\epsilon_{l\sigma}=(1-4\beta'^2)^{-1}[(1-2\beta'^2)\epsilon_\sigma\pm 2\beta'^2(4\beta'^2+\epsilon_\sigma{}^2-1)^{1/2}] \tag{67}$$

$$\underset{\beta'=\frac{1}{2}}{=}(1+4\epsilon_\sigma{}^2)/4\epsilon_\sigma. \tag{68}$$

[23] F. M. Mueller, Phys. Rev. 153, 659 (1967).

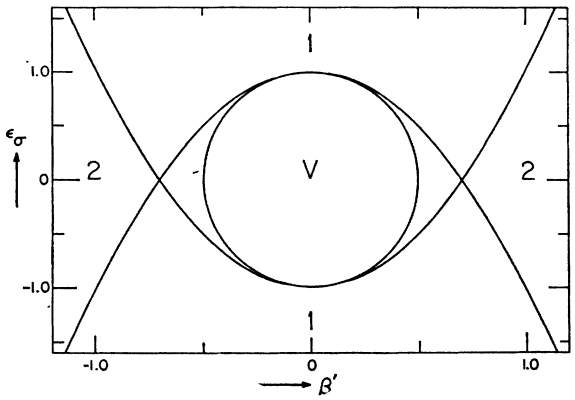

FIG. 2. Number of localized states for various β' and ϵ_σ, employing -2β units. V signifies the existence of a virtual state.

The quantity $\langle n_{a\sigma}\rangle_l$ may be easily obtained from (67) and (43)

$$\langle n_{a\sigma}\rangle_l = (1-4\beta'^2)^{-1}[(1-2\beta'^2) \mp 2\beta'^2\epsilon_\sigma(4\beta'^2+\epsilon_\sigma^2-1)^{-1/2}] \quad (69)$$

$$\underset{\beta'=\frac{1}{2}}{=} (4\epsilon_\sigma^2-1)/4\epsilon_\sigma^2. \quad (70)$$

In (67) and (69) + refers to $\epsilon_{l\sigma}<-1$ and − to $\epsilon_{l\sigma}>1$. The regions of existence of localized and virtual states are shown in Fig. 2; this may be compared with the general conclusions of II. From (67), $\epsilon_{l\sigma}$ appear to be defined outside the regions (66), but in fact these anomalous eigenvalues correspond to negative and unphysical $\langle n_{a\sigma}\rangle_l$. As a consequence, in this region of Fig. 2 neither localized nor virtual states exist.

Some examples of the function $\rho_{aa}{}^\sigma$ when the level ϵ_σ lies in the band are shown in Fig. 3. β' increases in going from curve 1 to curve 4. Curve 1 shows a sharp

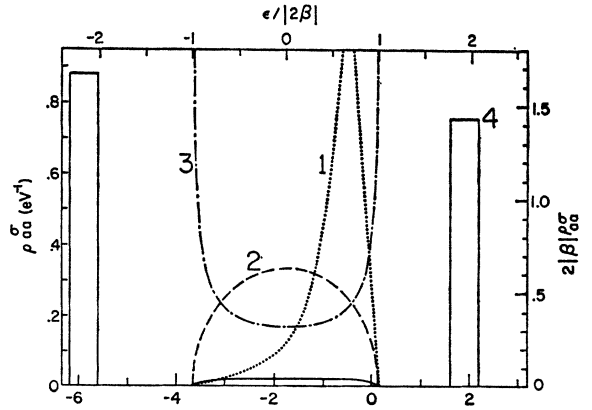

FIG. 3. Density of states $\rho_{aa}{}^\sigma$ for various parameters. The values of $\beta'/2\beta$ are $\frac{1}{2}$, $\frac{1}{2}$, $2^{-1/2}$, and 1.975, and those of $\epsilon_\sigma/|2\beta|$ are $\frac{1}{2}$, 0, 0, and −0.258 in curves 1, 2, 3, and 4, respectively. Energies are relative to band center. The scales marked in eV are based on the Ni d band. The parameters in curve 4 are appropriate to the observed chemisorption energy of H or Ni (see Table I). Portions of the curves lying outside the band represent δ functions (localized states) of equal area.

peak near ϵ_σ which indicates a virtual state, whereas at somewhat larger β' this structure tends to be smeared out as in 2 (which is actually a special case). At still larger β' a double-humped structure may develop, due to nascent localized states, of which curve 3 is a pathological case. Finally in curve 4 the extreme molecular case is reached in which almost the entire density of states lies in the bonding and antibonding states of a weakly perturbed $a-0$ molecule. Considerable diversity is evidently shown over quite a narrow range of parameters.

In the present case the expression (37) for $\Delta E^{1\sigma}$ becomes, when (66b) does not hold (no localized state below band),

$$\Delta E^{1\sigma} = \pi^{-1}\int_{-1}^{\epsilon_F} \tan^{-1}\left[\frac{-2\beta'^2(1-\epsilon^2)^{1/2}}{(2\beta'^2-1)\epsilon+\epsilon_\sigma}\right]d\epsilon, \quad (71)$$

taking $-\pi<\tan^{-1}<0$. If an occupied localized state exists we add the term $(\epsilon_{l\sigma}-\epsilon_F)$, where $\epsilon_{l\sigma}$ is given by (67) with positive sign, and in addition take $0<\tan^{-1}<\pi$.

The analytical solution of this integral may be given when the band is half-filled ($\epsilon_F=0$), and is most easily obtained by returning to the expression (36). The result is

$$\Delta E^{1\sigma} = \pi^{-1}(4\beta'^2-1)^{-1}\{\epsilon_\sigma(1-2\beta'^2)\tan^{-1}(\epsilon_\sigma/2\beta'^2) + 2\beta'^2(1-4\beta'^2-\epsilon_\sigma^2)^{1/2} \times\ln[(1-2\beta'^2+(1-4\beta'^2-\epsilon_\sigma^2)^{1/2}) \times(4\beta'^4+\epsilon_\sigma^2)^{-1/2}]\}+\tfrac{1}{2}\epsilon_\sigma, \quad (72)$$

which may be rewritten in the absence of virtual states:

$$\Delta E^{1\sigma} = \pi^{-1}(4\beta'^2-1)^{-1}\{\epsilon_\sigma(1-2\beta'^2)\tan^{-1}(\epsilon_\sigma/2\beta'^2) + 2\beta'^2(4\beta'^2+\epsilon_\sigma^2-1)^{1/2}\tan^{-1}[(4\beta'^2+\epsilon_\sigma^2-1)^{1/2} \times(2\beta'^2-1)^{-1}]\}+\tfrac{1}{2}\epsilon_\sigma, \quad (73)$$

$$\Delta E^{1\sigma}\underset{\beta'=0.5}{=} -\frac{1}{2\pi}\left\{1+\left(2\epsilon_\sigma+\frac{1}{2\epsilon_\sigma}\right)\tan^{-1}2\epsilon_\sigma\right\}+\tfrac{1}{2}\epsilon_\sigma, \quad (74)$$

where the $\tan^{-1}$ takes its principal value except in the last term in braces of (73), in which $-\pi<\tan^{-1}<0$. A result equivalent to that for $\beta'=0.5$ has been obtained by Grimley[6] in one-electron approximation.

It is noteworthy that $\Delta E^{1\sigma}$ may thus be given by a single analytic formula (72) for all values of the parameters ϵ_σ and β' despite the appearance of localized states. This is in fact an example of the Kohn-Majumdar theorem,[24] since, being defined at constant $\langle n_{a-\sigma}\rangle$, $\Delta E^{1\sigma}$ is just a one-electron energy change.

These results may be applied to the calculation of ΔE when $U=0$. Then, from (32),

$$\Delta E = 2\Delta E^{1\sigma}(\epsilon_a)-\epsilon_a+\epsilon_F. \quad (75)$$

[24] W. Kohn and C. Majumdar, Phys. Rev. 138, A1617 (1965).

Calculating $\Delta E^{1\sigma}$ from (71) and (67), and using this expression, the results plotted in Fig. 4 for the cases $\epsilon_F=0$ and $\epsilon_F=0.9$ are obtained. It may be deduced from (71) that the one-electron ΔE has the symmetry

$$\Delta E(\epsilon_a,\epsilon_F)=\Delta E(-\epsilon_a,-\epsilon_F), \tag{76}$$

so that (with the exception of the points of appearance of virtual and localized states) the $\epsilon_F=0.9$ curves also apply to $\epsilon_F=-0.9$ on reflection in the vertical axis. Figure 4 illustrates the fact that, contrary to experiment (see Sec. I), $|\Delta E|>|\epsilon_a-\epsilon_F|$ when $U=0$. From (4), (30), and (41) we have

$$\partial\Delta E/\partial\epsilon_a=2\langle n_{a\sigma}\rangle-1, \tag{77}$$

which shows first of all that the maxima of the curves in Fig. 3 correspond to charge neutrality of the adatom. Using this relation, it will also be evident from Fig. 3 that the adatom will deviate markedly from neutrality when $|\epsilon_a-\epsilon_F|>1$, i.e., outside the region of Fig. 4. According to the interpretation of V, the present energy unit of -2β is half the d-band width (see Table I), thus for hydrogen on Ni, $|\epsilon_a-\epsilon_F|\sim 4.5$. These results show the unsuitability of the one-electron approximation in the present problem in some detail.

V. HYDROGEN CHEMISORPTION

Having selected a semielliptical form for $\Delta(\epsilon)$, it remains to determine the height and width parameters of this function. Consistent with our assumption that the d band plays the predominant role in the interaction leading to chemisorption, we shall further assume that the width of $\Delta(\epsilon)$ may be identified with the d-band width in the substrate metal. The height parameter of $\Delta(\epsilon)$ will be left as an empirical quantity to be determined by experiment. In order to give some physical significance to this parameter, we express $\Delta(\epsilon)$ in the localized orbital representation so that from (10a) and (21)

$$\Delta(\epsilon)=\pi\sum_{i,j,k,n}\beta_i'\beta_j'\langle i|k_n\rangle\langle k_n|j\rangle\delta[\epsilon-\epsilon(k_n)]. \tag{78}$$

In this expression $|k_n\rangle$ is the state of quantum number k in the nth band; it may be supposed for simplicity that the eigenstates of the semi-infinite metal may all be mapped in a semi-infinite *real* wave-number space. Surface states and the classification of the $|k\rangle$ are discussed by Heine.[25] If the localized orbitals $|i\rangle$ are orthonormal, then from the completeness of the set $|k_n\rangle$

$$\int_{-\infty}^{\infty}\Delta(\epsilon)d\epsilon=\pi\sum_i|\beta_i'|^2. \tag{79}$$

In the case of the foregoing semi-infinite chain model, the area of $\Delta(\epsilon)$ is $\pi\beta'^2$. Hence if the correspondence between the model and actual functions Δ at a given

[25] V. Heine, Proc. Phys. Soc. (London) 81, 300 (1963).

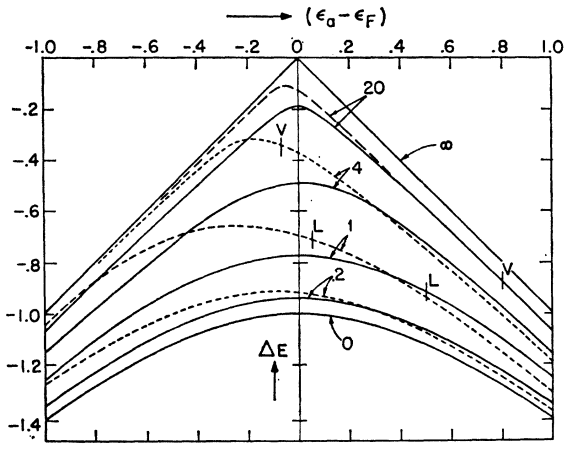

FIG. 4. ΔE when $U=0$, for $\epsilon_F=0$ (full curves) and $\epsilon_F=0.9$ (broken curves). Curves are numbered according to the band width. All units are $-2\beta'$. L signifies the appearance of an occupied localized state, and V that of a virtual state (the virtual state at $\epsilon_a-\epsilon_F=0.8$ refers to $\epsilon_F=0.9$).

bandwidth is made by assuming equal areas,

$$\beta'=(\sum_i|\beta_i'|^2)^{1/2}. \tag{80}$$

If we identify the states $|i\rangle$ with strongly localized atomic d orbitals, and restrict ourselves to cases where a is surrounded by a certain number M of nearest-neighbor metal atoms each occupying an equivalent site with respect to the adatom, then assuming β_i' is nonzero only when $|i\rangle$ is a nearest neighbor we have

$$\beta'=M^{1/2}\langle a|H_{\rm HF}|d_{3z^2-r^2}\rangle, \tag{81}$$

where $d_{2z^2-r^2}$ is the d orbital belonging to a nearest-neighbor metal atom having zero angular momentum about the axis, taken as along OZ, connecting it with the adatom. The integral $\langle a|H_{\rm HF}|d_{3z^2-r^2}\rangle$ depends on the equilibrium adatom-metal bond length and the self-consistent potential, for which reason we shall not attempt its calculation from first principles.

In the absence of an analytical formula for $\langle n_{a\sigma}\rangle$ at general ϵ_F, the numerical integration of (63) is necessary to obtain $N(n_\sigma)$ [(26)] and thus solve the self-consistent problem in the Anderson form (28). This causes some

TABLE I. Experimental parameters for Ti, Cr, Ni, and Cu, and theoretical values of the excess adatom charge.

	Bandwidth[a] (eV)	Fermi level[b] (eV)	Work function[c] (eV)	Experimental $-\Delta E$ (eV)	$\beta_{\rm expt}'$ (eV)	Theoretical excess adatom charge (electrons)
Ti	8.60	−2.04	3.86	>3.10[d]	>3.72	0.39
Cr	6.10	0.69	4.56	3.22[e]	3.75	0.23
Ni	3.80	1.76	4.50	2.89[f]	3.75	0.16
Cu	2.70	2.90	4.46	2.41[d]	4.17	0.06–0.20

[a] See Ref. 26.
[b] Measured from band center. See Ref. 26.
[c] See Ref. 2, Appendix I.
[d] Reference 27.
[e] Reference 28.
[f] References 29–31.
[g] Reference 32.

difficulty due to the appearance of the sharp peaks in $\rho_{aa}{}^{\sigma}(\epsilon)$ which were noted above, and for this reason the method of looking for the saddle point in $\Delta E(n_\sigma,n_{-\sigma})$ formulated in III was used. For a chosen set of parameters, $\Delta E^{1\sigma}$ is first tabulated by numerical integration of the expression (71), in which the integrand is conveniently bounded (with inclusion of the localized state energy where appropriate), for a set of approximately 10^2 evenly spaced values of ϵ_σ. The chemisorption energy may now be calculated for a grid of approximately 10^4 coordinates in the range $0\leqslant n_{\pm\sigma}\leqslant 1$ by the algebraic relation

$$\Delta E(n_\sigma,n_{-\sigma})=\sum_\sigma \Delta E^{1\sigma}(\epsilon_a+Un_{-\sigma}) - \epsilon_a+\epsilon_F-Un_\sigma n_{-\sigma}. \quad (82)$$

As justified in Sec. III, the saddle point is obtained by selecting the greatest of the ΔE obtained when one coordinate, say n_σ, is held fixed, and then choosing the least of the set of ΔE corresponding to each n_σ. The second part of the calculation may be repeated for a narrow range of ϵ_a and U. An example of the type of $N(n_\sigma)$ function generated is shown in Fig. 5, which also illustrates the Anderson self-consistency condition.

The parameters employed in the calculations were taken as follows. For the hydrogen atom $U=12.9$ eV (see Sec. I) and $\epsilon_a=-13.6$ eV$+\delta$, relative to vacuum level. δ is a small correction rather arbitrarily taken as $\delta=-0.7$ eV, which is intended to allow for partial penetration by the adatom of the metal surface dipole layer, assuming this exists and is negative outwards. However, the dependence of the results on δ is small. Calculations have been limited to the metals Ti, Cr, Ni, and Cu for which the parameters[2,26] are summarized in Table I. A slight modification to the method of calculating ΔE is necessary for Cu when magnetic solutions occur. A localized state *above* the band, of one spin direction only, is then found to be occupied, and its energy must be added into ΔE.

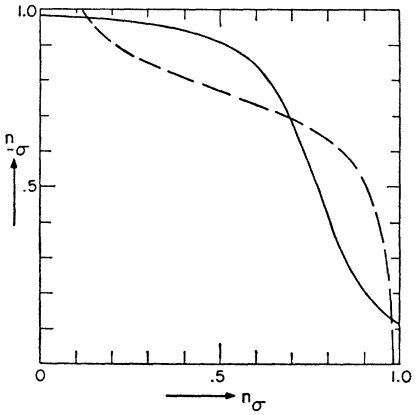

FIG. 5. Equations $n_{-\sigma}=N(n_\sigma)$ (full curve) and $n_\sigma=N(n_{-\sigma})$ (broken curve) for $\epsilon_F=0$, $\epsilon_a=-2.5$, $U=3.25$, $\beta'=0.5$, $\Delta E=-0.176$, in -2β units. The intersections of the curves give the self-consistent $n_{\pm\sigma}$.

[26] L. F. Mattheiss, Bull. Am. Phys. Soc. 8, 222 (1963).

Experimental measurements[27–32] of ΔE, whose results are also given in Table I, refer to adsorption on clean but heterogeneous surfaces in the limit of low coverage. Although this limit is presumed to minimize the effects of interaction between the adsorbed atoms, uncertainties remain as to the statistical weights of the exposed crystal planes and the crystal-plane selectively of adsorption. These uncertainties become especially serious when considering the relatively small variation of ΔE with substrate metal, and are unlikely to be resolved until measurements on single crystal planes become available.

The self-consistent results for ΔE and for the expectation value q of adatom charge are given in Figs. 6 and 7, respectively, as a function of β'. Discontinuaties at the magnetic transition point, especially serious for copper, are noticeable and are discussed briefly in the Appendix. The behavior as $\beta'\to 0$ is evidently physically correct, and this is in contrast with the one-electron approximation. When β' becomes sufficiently large, the effects of U may be neglected, and the adatom together with the neighboring atomic orbital $|0\rangle$ of the chain behave as if belonging to the diatomic molecule $a-0$ (see Sec. II), which is effectively symmetrical. Hence as $\beta'\to\infty$,

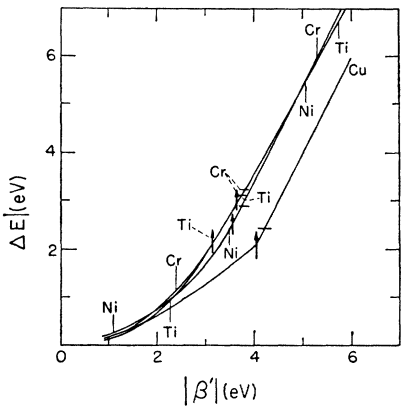

FIG. 6. Self-consistent HF ΔE versus hopping integral β' for four transition metals. Arrows indicate the magnetic transition points, with the magnetic region to their left. Horizontal bars give experimental ΔE, that for Ti being a lower limit.

$q/e\to 1$ in agreement with the trend at large β' in Fig. 7. As regards ΔE, let us write the Hamiltonian (4) for our chain model in the AO representation, with the aid of (21) and the relation $\beta_i'=\beta'\delta_{0i}$, then take the

[27] G. Wedler and H. Strothenk, Z. Phys. Chem. (Frankfurt) 48, 86 (1966).
[28] O. Beeck, Discussions Faraday Soc. 8, 118 (1950).
[29] M. Wahba and C. Kemball, Trans. Faraday Soc. 49, 1351 (1953).
[30] F. Sweett and E. K. Rideal, Proc. Roy. Soc. (London) A257, 291 (1960).
[31] O. Beeck, Advan. Catalysis 2, 151 (1950).
[32] D. D. Eley, in *Chemisorption*, edited by W. E. Garner (Butterworths Scientific Publications Ltd., London, 1957), p. 157.

expectation value with respect to the ground state and differentiate with respect to β', using (41), to obtain the result

$$\partial\Delta E/\partial\beta' = 2\sum_{\sigma}\langle c_{0\sigma}^{\dagger}c_{a\sigma}\rangle. \tag{83}$$

The right-hand side is twice the generalized bond order for the $a-0$ bond, and in the limit of the diatomic molecule takes on the value $\partial\Delta E/\partial\beta'=2$. In fact this is actually obeyed fairly well by the curves of Fig. 6 for $\beta'>4$ eV.

From the experimental ΔE values of β' may be determined, and these in turn used to evaluate the charge q, as summarized in Table I. In all cases the experimental points fall just on the nonmagnetic side

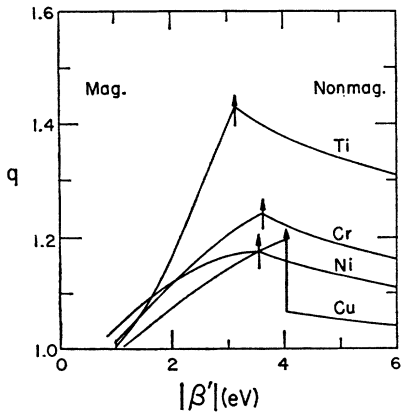

FIG. 7. Adatom charge in units of e versus β'. Arrows indicate magnetic transition points, with magnetic region to their left.

of the transition point, which is satisfactory in view of the rigorous paramagnetism of the present chain model.[16] The absence of magnetism suggest that electron correlation is not too important, and this might also be inferred from the closeness of the bond order (83) to the presumed maximum value of 1; these conclusions are consistent with our use of the HF approximation. Now referring to the expression (81) for β', and making the reasonable supposition that $3\leqslant M\leqslant 4$, it is found from the β' values in Table I that $1.9<|\langle a|H_{\mathrm{HF}}|d_{3z^2-r^2}\rangle|<2.4$ eV. This range seems reasonable for the coupling integral, which is satisfactory.

The prediction of relative chemisorption energies is probably significant only for nickel and copper. For these metals it is evident from Fig. 6 that the correct ordering of ΔE will be obtained provided they are assumed to have similar β', which may be justified by their neighboring locations in the periodic table and identical structure.

The only experimental measurements bearing on the charge q is that of the change in work function $\Delta\varphi$ on chemisorption.[1,2] For the metals in question the precision of measurement of $\Delta\varphi$ is not high at present, but its value apparently lies in the region $0.3\leqslant\Delta\varphi\leqslant 0.5$ V.[2] The sign of $\Delta\varphi$ is in agreement with the prediction

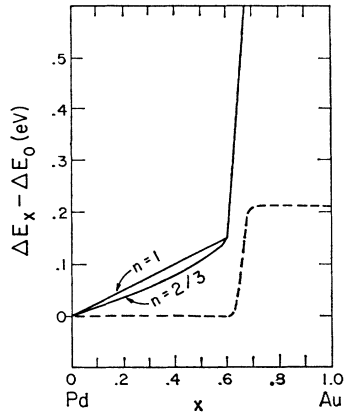

FIG. 8. Calculated hydrogen chemisorption energy ΔE for alloy $Pd_{1-x}Au_x$ (full curve). For significance of n, see Eq. (85) of text. Broken curve shows experimental activation energy E_a of hydrogen interconversion, with adjusted zero.

of the present model that the excess charge is negative. On the rather crude assumption, necessitated by the surface heterogeneity, of a surface adsorbate concentration of 10^{15} cm^{-2}, together with the present calculated excess charge of $q-e\sim 0.3e$, a dipole length of 0.1 Å is deduced. Allowing for an image charge, the adatom-surface distance is given as 0.05 Å. Although at least an order of magnitude below any possible H-metal bond length, that is not impossible if adsorption of the H atom in concave surface sites were assumed.[33]

VI. CATALYSIS OF HYDROGEN INTERCONVERSION REACTIONS

Couper and Eley[34] have measured the activation energy E_a, defined by

$$K=Pe^{-E_a/kT}, \tag{84}$$

where K is the rate constant and P is a slowly varying function of the temperature T, for heterogeneous ortho-para hydrogen equilibration at the surface of the alloy $Pd_{1-x}Au_x$. The dependence of lattice constant on x is negligible for this alloy. The authors attribute the sharp increase in E_a observed for $x\geqslant 0.6$ (see Fig. 8) to the filling up of the d band, which, from the paramagnetic susceptibility,[35] apparently occurs close to $x=0.6$. Qualitatively similar results have been obtained on other alloys of Ni, Pd, and Pt with group-I*b* metals.[36–38] However, in evaluating these experiments

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[34] A. Couper and D. D. Eley, Discussions Faraday Soc. **8**, 172 (1950).
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[36] M. A. Avdeenko, G. K. Boreskov, and M. G. Slin'ko, in *Problems of Kinetics and Catalysis*, edited by S. Z. Roginskii (U.S.S.R. Academy of Science Press, Moscow, 1957), Vol. 9, p. 61.
[37] G. Rienäcker and B. Sarry, Z. anorg. Chem. **257**, 41 (1948).
[38] G. Rienäcker and G. Vormum, Z. anorg. Chem. **283**, 287 (1956).

the poor conditions of surface purity obtainable[2] and present ignorance of the reaction mechanism[2] should be kept in mind. According to one suggested mechanism[39] the reaction proceeds via atomically adsorbed hydrogen as intermediary, and it therefore seems likely that any anomaly in ΔE at $x=0.6$ will be reflected in E_a. A simple calculation of the ΔE variation for this alloy will be made, for which we adopt a rigid-band model with $W=3.80$ eV (appropriate for Ni) and $\varphi=4.50$ eV,[2] both W and φ being assumed independent of x. The concentration x of gold now enters the calculation only via the separation $\epsilon_{Fx}-\epsilon_{F0}$ of the Fermi level from its energy in pure Pd. We shall take $\epsilon_{F1}-\epsilon_{F0.6}=2.4$ eV,[40] and (more approximately) $\epsilon_{F0}-\epsilon_{F0.6}=-0.14$ eV,[26] and then interpolate by means of the expressions

$$\epsilon_{Fx}-\epsilon_{F\,0.6}=(\epsilon_{F1}-\epsilon_{F\,0.6})(x-0.6)/0.4, \qquad 0.6<x<1 \tag{85a}$$

$$=(\epsilon_{F0}-\epsilon_{F\,0.6})[(0.6-x)/0.6]^n, \qquad 0<x<0.6. \tag{85b}$$

The first expression implies a constant sp-band density of states above the d band, and the second either a constant ($n=1$) or parabolic ($n=\frac{2}{3}$) density of states near the upper edge of the d band. ΔE can now be calculated as a function of x following the same method used above, in which the adatom is supposed to interact with the d band alone. The resulting variation of $\Delta E_x-\Delta E_0$ is shown in Fig. 8 with $\beta'=3.5$ eV, there being little dependence of this quantity on β' near $\beta'=4$ eV. The notable decrease in $|\Delta E|$ as the d band drops below the Fermi level is suggestive in relation to the activation energy, but an attempt to relate ΔE and E_a with more precision would not seem justified in view of the present uncertainties both as to the reaction mechanism and the state of the surface.

VII. CONCLUSIONS

For reasons discussed in this paper, the one-electron approximation is not a satisfactory basis for calculating the chemisorption energy either of hydrogen or other neutral adsorbates. The present work has attempted to provide a more realistic model in the case of hydrogen by allowing for the strong interelectronic interaction within the adatom orbital. It has been found that, neglecting the sp band, the experimental ΔE for several $3d$ metals may be fitted by using values of the hopping integral between the $1s$ orbital and neighboring metal d orbitals which appear to be reasonable. This assumes the validity of the tight-binding approximation for the d band. It is correctly predicted that the chemisorption energy on Ni exceeds that on Cu, assuming a similar distribution of active surface planes in the experimental samples of these metals and similar adatom-metal hopping integrals. The observed similarity of ΔE for Ti, Cr, and Ni is plausible within the context of the present results. It should be noted that ΔE on Mn is[41] anomalously low relative to neighboring $3d$ metals in lying between that of Ni and Cu; the complex structure of this element is unfortunately an obstacle to theoretical treatment.

The total charge on the hydrogen atom is predicted to decrease from $q=1.4e$ on Ti to $q=1.2e$ on Ni. These values of q are greater than unity, as is indeed observed, but are too large to be in quantitative agreement with the observed surface potentials unless partial burying of the adsorbate in concave surface sites is assumed. This is in general plausible, though it is questionable whether closely packed planes such as the (110) of the bcc and (111) or the fcc structures can offer such sites. Application of the model to the activation energy of hydrogen interconversion on PdAu alloys is not clear cut due to the present deficiencies both in experimental technique and knowledge of the reaction mechanism. However, a suggestive correlation is found between the fall in ΔE calculated from the present model, together with the rigid-band approximation, and the increase in activation energy observed at the point of filling of the d band. More detailed comparison of the present theory with experiment would require measurements of ΔE and charge distribution for adsorption on single crystal surfaces.

Of the various defects in the present model the disregard of interelectronic interaction other than within the $1s$ orbital is perhaps the most obvious. This interaction results in screening of the charge distribution, with an associated energy change related to the classical image force term. Uncertainty as to the exact location of the adsorbed hydrogen atom and the unperturbed surface charge distribution hinder theoretical treatment of this problem. Exchange between the $|a\rangle$ and $|k\rangle$ orbitals, whose correct treatment requires acknowledgement of their nonorthogonality, may also make a substantial contribution to ΔE of the Heitler-London type. The most obvious correction to the restriction of the basis set would be allowance for change in radius of the $1s$ orbital.[10] The effects of using the HF approximation, which includes the perturbation U only to first order, are not believed to be too serious, but the calculation of higher-order corrections is a matter of some difficulty. In general ΔE may be expressed as follows in terms of the Green's function $G_{aa}{}^{\sigma}$ as defined by Schrieffer and Mattis[16]:

$$\Delta E=\frac{1}{\pi i}\sum_{k,\sigma}\int_0^1\frac{dg}{g}\int_c\frac{|gV_{ak}|^2}{\epsilon-\epsilon_k+i\delta\,\mathrm{sgn}\epsilon}G_{aa}{}^{\sigma}(\epsilon)d\epsilon, \qquad \delta=0^+ \tag{86}$$

in which the Fermi level is energy zero, g is a coupling

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[41] E. Greenhalgh, D. O. Hayward, and B. M. W. Trapnell, J. Phys. Chem. 61, 1254 (1957).

parameter multiplying the V_{ak} and eventually set equal to unity, and C is a contour consisting of the real axis and a semicircle in the upper half-plane. According to the validity criterion of Schrieffer and Mattis,[16] the t-matrix approximation which they used is invalid in the present case. Calculation of the second-order corrections to ΔE should however be possible. It may be noted that when the Fermi level is above the band an exact solution to the problem is obtainable.

Most if not all of these neglected effects are likely to result in a larger $|\Delta E|$ at a given β' than calculated from the present theory. $|\beta'|$ is expected to be overestimated if obtained, as above, by comparison of the theoretical and observed ΔE. Unfortunately reducing β' significantly results in "magnetic" HF solutions, an indicator that the HF approximation is itself breaking down, so that the consequences are uncertain.

In view of the difficulties in calculating the total energy, and also in determining the charge q experimentally, it is worth considering alternative quantities such as the density of states $\rho_{aa}{}^{\sigma}$. The ion neutralization spectroscopy of Hagstrum[42] yields a density of states which under some conditions may be approximately identified with $\rho_{aa}{}^{\sigma}$. Curve 4 of Fig. 3 shows the predictions of the present theory in the case of H on Ni; the effect of H-s-band interaction would be to broaden the δ-function peaks due to localized states. The separation of the peaks from the band is probably overestimated due to the choice of β', but as pointed out above it is difficult to correct for this. It may be significant that peaks below the Fermi level have been observed by Hagstrum[42] for O, S, and Se on Ni.

Generalization of the present model to other neutral adsorbates such as N is possible in principle. In the case of nitrogen, the contribution of both s and p orbitals to ΔE should be included in view of the large observed binding energies,[1,2] with some proliferation of uncertain parameters. The application to models of this general type to alkali adsorption seems more promising.[10]

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[42] H. D. Hagstrum (to be published).

APPENDIX: DISCONTINUITIES AT THE TRANSITION POINT

Let g be a certain parameter in the Hamiltonian which is to be varied about the magnetic transition point g_c. Let the magnetic solutions be in the region $g>g_c$. The nonmagnetic root of the self-consistency equation

$$N[g,N(g,n_\sigma)]-n_\sigma=0, \tag{A1}$$

which will be denoted by n_0, is a solution of the simpler equation

$$N(g,n_0)=n_0, \tag{A2}$$

and will obviously behave in a quite regular manner near g_c. Now, by expanding (A1) up to first order in g and third order in n_σ, a procedure which will here be omitted for reasons of space, and using the regularity of n_0, it may be shown that, to lowest order in $g-g_c$, the magnetic roots near g_c are given by

$$n_{\pm\sigma}-n_c=\pm\lambda(g-g_c)^{1/2}, \tag{A3}$$

where λ is a constant and n_c the value $n_\sigma=n_0$ at g_c. The square-root singularity in n_σ is evidently absent from $\sum_\sigma n_\sigma$ and $n_\sigma n_{-\sigma}$, which vary linearly with $g-g_c$ near g_c, but with a constant of proportionality found to be unconnected with that of the first-order term in the expansion of n_0 about g_c. Hence $(\partial/\partial g)(\sum_\sigma n_\sigma)$ and $(\partial/\partial g)(n_\sigma n_{-\sigma})$ undergo a stepwise discontinuity at g_c. This is in accord with Fig. 6, where $g=\beta'$, except for the case of Cu, where the anomaly is due to the band lying below the Fermi level, and will not be discussed further here.

The behavior of ΔE near g_c might be found by considering the expansion of ΔE near g_c up to first order in g and fourth order in n_σ, $n_{-\sigma}$. We shall merely note that, since from (4) and (41)

$$\partial\Delta E/\partial\epsilon_a=\sum_\sigma n_\sigma, \tag{A4}$$

$$\partial\Delta E/\partial U=n_\sigma n_{-\sigma}, \tag{A5}$$

together with the above results concerning the discontinuities of the right-hand side of these equations, it follows that on taking $g=\epsilon_a$ in (A4) and $g=U$ in (A5) that ΔE should have a discontinuity only in its second derivatives with respect to ϵ_a and U. It is very probable that this conclusion applies also to $g=\beta'$, which would be consistent with Fig. 5, again with the exception of Cu.