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Systematics of the binding energy of oxygen and hydrogen on transition-metal surfaces. I.

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The chemisorption energy of simple gases on transition metals follows some remarkable systematic trends. We construct a simple theory which leads to an understanding of the observed trends and relates the chemisorption energy to the essential parameters characterizing the transition metals, viz., the mean energy of their density of states, the bandwidth, and the number of *d* electrons. The theory is applied to the adsorption of hydrogen and oxygen on 3*d* and 4*d* transition metals. The positions of the atomic levels of hydrogen and oxygen (and nitrogen) with respect to the *d* bands of the transition metals is such that the primary binding comes from transfer of *d* electrons from surface metal atoms to the adatoms and to low-energy bonding resonances induced in the metal atoms. However, there is large enough hybridization of the adatom orbitals with the surface metal-atom orbitals that the local density of states of the metal atoms is significantly altered throughout the band. Correspondingly the metal parameters that determine the binding energy are the average position of the *d* band with respect to the adatom orbital energy and the overall width of the *d* band.

I. INTRODUCTION

One of the simplest properties characterizing the interaction of gases with solid surfaces is the chemisorption energy, ΔH_{ads}, of the adsorbed species. The experimental results for ΔH_{ads} for the simplest gases H_2, N_2, O_2, CO, NO, etc., on transition metals reveal some simple and fairly general trends which have been known for a long time.[1] The purpose of this paper is to derive the physical basis for these trends by simple but well-defined methods and to express ΔH_{ads} in terms of simple parameters of the adsorbed atoms and in terms of a few essential parameters characterizing the transition metals that have clear meaning in the theory of such solids. In an accompanying paper,[2] hereafter referred to as II, a much more detailed picture of the transition metals is used for calculations, and many of the assumptions made in this paper are verified. In this and the next paper, we will be concerned with the adsorption energy of atomic hydrogen and oxygen on the surface of transition metals. H_2 and O_2 can dissociate on most transition metals and the extensive experimental results on their atomic adsorption energy have recently been compiled by Toyashima and Somorjai[3] (TS). TS have also compiled the data for adsorption energy for atomic nitrogen with trends similar to those of oxygen.

II. SUMMARY OF EXPERIMENTAL RESULTS

In Figs. 1 and 2, the experimental results for ΔH_{bond}, the binding energy of H and O on polycrystalline transition-metal surfaces, as deduced from the compilation of TS, are shown. $\Delta H_{\text{bond}}(x)$ for atomic adsorption of x is obtained from ΔH_{ads}, the heat of adsorption by

$$\Delta H_{\text{bond}}(x) = (\Delta H_{\text{ads}} + D_{x2})/2 \quad , \qquad (1)$$

where D_{x2} is the dissociation energy of the free diatomic molecule x_2. TS have also compiled the (somewhat less extensive) data for single-crystal surfaces and find that for a given surface there are several values for ΔH_{bond} corresponding to different binding sites. The highest ΔH_{bond} on single-crystal surfaces do, however, obey the same trends as on polycrystalline surfaces, even though the value of ΔH_{bond} is 20–50% lower on the former than on the latter.

The most significant trend in the data is that ΔH_{bond} for all adsorbed species considered is maximum at the beginning of the transition-metal series and decreases as the group number (or number of *d* electrons) increases; the decrease is faster at the beginning of the series and appears to saturate as we approach the end. Within the scatter of the data

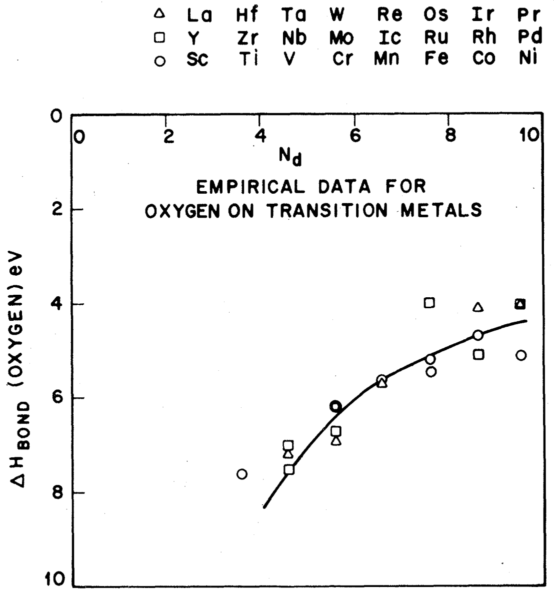


FIG. 1. Experimentally deduced binding energy of atomic oxygen on polycrystalline transition-metal surfaces. These are taken from the compilation of Toyashima and Somarjai, Ref. 1.

there is no discernible systematic variation for the metals within a group. On the single-crystal surfaces the highest ΔH_{bond} for different surfaces of individual metals do not show any conclusive systematic behavior, although a slight decrease as the coordination number of the surface atom increases may be discerned.

The binding energy of hydrogen on transition metals is typically about half to a third that of oxygen, and hydrogen has a much smaller variation across the series. The binding energy of nitrogen is about 20% larger than that of oxygen.[3]

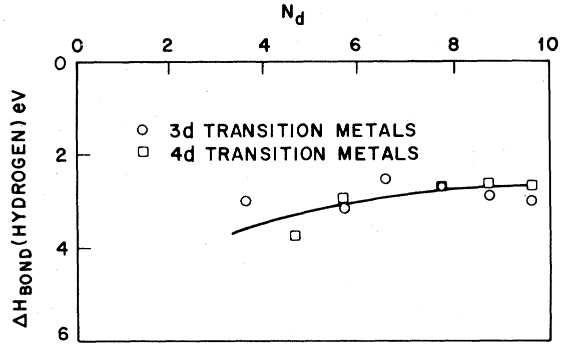


FIG. 2. Experimentally deduced binding energy of atomic hydrogen on polycrystalline transition-metal surfaces. These are taken from the compilation of Toyashima and Somarjai, Ref. 1.

There have been several attempts to correlate trends in ΔH_{ads} with those in other measured properties, the most significant of these perhaps are the correlations[4] between ΔH_{ads} for a given gas and the heat of formation per metal atom of the corresponding transition-metal compound. We try here to understand the trends in ΔH_{ads} on a more fundamental basis in terms of the essential parameters characterizing the transition metals. The methods used here are not new—it is only that we take the semiempirical model approach[5] more seriously than taken hitherto and try to come to grips with and learn from the systematics in the experimental results. A one-electron model calculation on this problem has previously been done by Haydock and Wilson.[6]

III. ESSENTIAL PARAMETERS CHARACTERIZING ELECTRONIC STRUCTURE OF TRANSITION METALS

The systematics summarized above suggest that the general behavior is governed by some general features of transition-metal electronic structure, rather than by the details of features in the density of states.

The valence-electron structure of transition metals consists of the relatively tightly bound *d* bands hybridizing with nearby free-electron *s*-*p* bands. Most of the physical and chemical properties of transition metals are primarily governed by the relatively tightly bound *d* electrons.[7] Thus, for example, bonding properties like the cohesive energy of the transition metals and the heat of formation of transition-metal alloys is explained by *d*-*d* metallic bonds. Although the nearly free *s* and *p* electrons do not contribute in a significant way directly to the bonding, they play an important role in allowing *d*-electron charge transfers to occur in bonding between dissimilar atoms without a prohibitive cost in electron-electron repulsive energy.[8] Being nearly free, they are the most effective in screening charge imbalances. Thus, for example, the energy cost of $2d^ns \rightarrow d^{n+1}s + d^{n-1}s$ is about 10 eV, whereas that for $2d^ns \rightarrow d^{n+1}s^0 + d^{n-1}s^2$ is only about 2 eV.[9]

In our treatment of the bonding of adsorbed atoms (adatoms) at transition-metal surfaces, we will also assume that the adatom bond is primarily with the *d* orbitals and that the free *s*-*p* electrons serve primarily to renormalize parameters so that the adatom—*d*-orbital bond is most effective. Generally the change in the *s*-electron wave functions in order for them to form bonds with the adatoms are quite different from those involved in renormalizing the *d*-electron parameters so that the latter form most effective bonds with the adatom orbitals. Our assumption in this paper is that the overall energetics favor the role of *s* electrons as primarily renormalizing the *d* parameters and screening charge imbalances rather than directly bonding to the adatom orbitals. This assumption is based on the experience with transition-metal alloys[8, 10] and our confidence in it is reinforced by the results of the first-principle calculations of adsorbates on transition metals by Louie[11] and by Feibelman and Hamann.[12]

Now, we turn to the *d* electrons. The minimum essential parameters necessary to characterize the *d* bands of a transition metal are: (1) the mean energy or the first moment of the density of states; (2) the bandwidth or the second moment of the density of states; and (3) the number of *d* electrons or the Fermi energy.

The trends in the cohesive energy of transition metals[7] and the heat of formation of their alloys[10] have been explained in terms of these three basic parameters.

On the surface of a transition metal, the second moment is smaller due to fewer neighbors[13]; the surface charge density is also somewhat different due to surface perturbation.[14] These effects are somewhat reduced by renormalization of the mean energy due to Coulomb interactions.

In Table I, we list the *d*-band parameters used in the calculations. These were obtained by renormalized atom calculations by Hodges, Watson, and Ehrenreich,[15] and subsequent improved calculations by Watson.

Note that the Fermi energy with respect to vacuum does not vary significantly across a given transition-metal series. There is a significant variation in the bandwidth as we go to the right of the series—the *d* orbitals shrink, the lattice parameter increases, and the *d*-bandwidth decreases. The most significant trend, however, is in the position of the mean energy of the band—it decreases rapidly to the right as the (screened) nuclear potential becomes increasingly attractive We note here that the binding-energy trends described in Sec. II do have a trend similar to the variation in the mean energy. The physics of this correlation will be described in our concluding section.

TABLE I. Bottom and top of *d* band, and Fermi level, written down with respect to center of gravity of band, taken from Watson (Ref. 15). Measured work functions from Michaelson (Ref. 19). All numbers are in eV.

	Bottom	Top	E_F	Work function
	of d band			
Sc	−3.34	2.27	−2.28	3.5
Ti	−3.90	2.65	−1.55	4.33
V	−4.46	3.02	−1.24	4.3
Cr	−4.62	3.09	−0.49	4.5
Mn	−3.89	2.53	0.47	4.1
Fe	−3.49	2.24	1.22	4.5
Co	−3.25	2.07	1.42	5.0
Ni	−2.84	1.80	1.50	5.15
Y	−3.69	3.14	−2.09	3.1
Zr	−4.51	3.94	−1.52	4.05
Nb	−5.23	4.61	−0.94	4.3
Mo	−5.42	4.73	0.49	4.6
Tc	−5.26	4.50	0.63	. . .
Ru	−4.91	4.13	2.47	4.71
Rh	−4.18	3.42	2.47	4.98
Pd	−1.76	4.10	3.79	5.12
La	−4.30	4.03	−2.2 to −2.6	3.5
Hf	−3.73	4.87	−2.10	3.9
Ta	−5.78	5.64	−1.52	4.25
W	−6.03	5.92	0.02	4.55
Re	−6.06	5.96	0.53	4.96
Os	−5.75	5.66	2.51	4.83
Ir	−5.07	5.00	2.99	5.27
Pt	−4.04	4.13	3.29	5.65

IV. EXPRESSION FOR ΔH_{bond}

Our starting point for a calculation of ΔH_{bond} is an expression for ΔH_{bond} in terms of the change in the local density of states of the tight-binding orbitals of the adatoms and of the transition-metal atoms, upon adsorption. The local density of states $n_{i\alpha}(\epsilon)$ at energy ϵ for an orbital α on an atom i, before adsorption is defined as

$$n_{i\alpha}(\epsilon)=\sum_{\mu}\delta(\epsilon-\epsilon_{\mu})\left|[\Psi_{\mu}(r),\phi_{i\alpha}(r)]\right|^2 \ , \tag{2}$$

where $\Psi_{\mu}(r)$ is an eigenfunction of the problem, with eigenvalue ϵ_{μ}, and $\phi_{i\alpha}(r)$ is the tight-binding basis function for the orbital α on atom i. We will also need the charge associated with (i,α):

$$N_{i\alpha}=\int_{-\infty}^{\epsilon_f} d\epsilon n_{i\alpha}(\epsilon) \tag{3}$$

and the mean energy of $n_{i\alpha}(\epsilon)$:

$$C_{i\alpha}=\int_{-\infty}^{\infty} d\epsilon\epsilon n_{i\alpha}(\epsilon)\Big/\int_{-\infty}^{\infty} d\epsilon n_{i\alpha}(\epsilon) \ . \tag{4}$$

The corresponding quantities upon adsorption are denoted by a tilde; thus $\tilde{n}_{i\alpha}(\epsilon)$, $\tilde{N}_{i\alpha}$, $\tilde{C}_{i\alpha}$, etc.

In terms of the quantities defined above, ΔH_{bond} in a self-consistent one-electron approximation is given by

$$\Delta H_{\text{bond}}=\sum_{i,\alpha}\left(\int_{-\infty}^{\tilde{\epsilon}_f}\epsilon\tilde{n}_{i,\alpha}(\epsilon)-\int_{-\infty}^{\epsilon_f}\epsilon n_{i,\alpha}(\epsilon)-\Delta H_{\text{d.c.}}\right) \ , \tag{5}$$

where $\Delta H_{\text{d.c.}}$ is the change in the Hartree and the exchange-correlation energy multiply counted in the first part of Eq. (5).

In the Hartree approximation

$$\Delta H_{\text{d.c.}}=\tfrac{1}{2}\Delta\int d\vec{r}\int d\vec{r}\,'\sum_{i\neq j;\alpha,\beta}\frac{\rho_{i\alpha}(\vec{r})\rho_{j\beta}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \ , \tag{6}$$

where $\rho_{i\alpha}(r)$ is the charge density associated with the orbital (i,α) before adsorption. We can write

$$\Delta H_{\text{d.c.}}=\tfrac{1}{2}\sum_{i\neq j;\alpha,\beta}\int d\vec{r}\int d\vec{r}\,'\left(\frac{\Delta\rho_{i\alpha}(r)}{|\vec{r}-\vec{r}\,'|}[\rho_{j\beta}(\vec{r}\,')+\Delta\rho_{j\beta}(\vec{r}\,')]+\frac{\Delta\rho_{j\beta}(r')}{|\vec{r}-\vec{r}\,'|}\rho_{i\alpha}(\vec{r})\right) \ , \tag{7}$$

$$=\tfrac{1}{2}\sum_{j\beta}\int d\vec{r}\,'\delta V_h(r')\tilde{\rho}_{j\beta}(r')+\tfrac{1}{2}\sum_{i,\alpha}\int d\vec{r}\delta V_H(r)\rho_{i\alpha}(r) \ , \tag{8}$$

where $\delta V_h(\vec{r})$ is the change in the Hartree potential at $\vec{r}$. If the variation of δV_H within a cell is ignored

$$\Delta H_{\text{d.c.}}=\tfrac{1}{2}\sum_{i\alpha}\delta V_{h,i\alpha}(\tilde{N}_{i\alpha}+N_{i\alpha}) \ . \tag{9}$$

If exchange-correlation potential V_{xc} is treated in the $\rho^{1/3}(r)$ approximation, Eq. (9) is still true up to $O(\Delta N_{i\alpha}^2)$ with $\delta V_{h,i\alpha}+\delta V_{\text{xc},i\alpha}$ replacing $\delta V_{h,i\alpha}$. Now we define

$$\Delta C_{i\alpha}\equiv\tilde{C}_{i\alpha}-C_{i\alpha}\equiv\delta V_{h,i\alpha}+\delta V_{\text{xc},i\alpha} \ , \tag{10}$$

so that Eq. (5) becomes

$$\Delta H_{\text{bond}}=\sum_{i,\alpha}\left(\int_{-\infty}^{\tilde{E}_f}d\epsilon\epsilon\tilde{n}_{i\alpha}(\epsilon)-\int_{-\infty}^{E_f}d\epsilon\epsilon n_{i\alpha}(\epsilon)-\tfrac{1}{2}\Delta C_{i\alpha}(\tilde{N}_{i\alpha}+N_{i\alpha})\right) \ . \tag{11}$$

A related expression has been derived by Lannoo and Allan.[16]

With $\sum_{i,\alpha}\Delta N_{i,\alpha}=0$, Eq. (11) can be written in, perhaps, a more revealing form

$$\Delta H_{\text{bond}}=\sum_{i,\alpha}\left((\tilde{E}_{i\alpha}-E_{i\alpha})-\tfrac{1}{2}\sum_{j}(D_{i\alpha,j\beta}+\tilde{D}_{i\alpha,j\beta})\Delta N_{j\beta}\right) \tag{12}$$

with

$$E_{i\alpha}=\int_{-\infty}^{\epsilon_f}(E-C_{i\alpha})n_{i\alpha}(\epsilon)d\epsilon \tag{13}$$

and

$$D_{i\alpha,j\beta}=C_{i\alpha}-C_{j\beta} \ , \quad \tilde{D}_{i\alpha,j\beta}=\tilde{C}_{i\alpha}-\tilde{C}_{j\beta} \ . \tag{14}$$

The first term in Eq. (12) is evidently a covalent (or metallic type) bonding term and the second an ionic-type term. The two are of course not independent. The covalency-type term represents the change in the one-electron eigenfunctions,[17] which is reflected in the change in the density of states. This in turn affects the charge transfer. Self-consistency of $\tilde{C}$ with charge transfer again connects the two.

V. SPECIFICATION OF THE DENSITY OF STATES

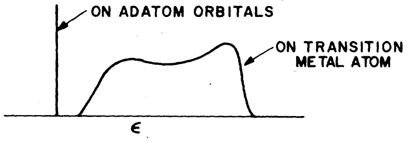
To calculate ΔH_{bond} from Eq. (5), we need to specify the density of states of the adatom and of the transition-metal atoms before and after adsorption.

Our point of view here is that the general trends described in II do not need a detailed description of the density of states. The gross features of the density of states are found by the first few moments evaluated in the tight-binding approximation. The further constraints on the density of states are that the first moments be (self-) consistent with the charge transfer and the associated Coulomb interactions. An additional important constraint is that the system obey charge neutrality locally. We shall take locally here to mean the adatom and its immediate neighboring atoms of the transition metal. This local charge neutrality cannot in general be obeyed in a model with only intra-atomic interactions. In actual systems local charge neutrality (or Friedel sum rule) is enforced through the long-range nature of the Coulomb interaction (the Newns-Anderson model[5] obeys it only for the symmetric case, ϵ_d and $\epsilon_d + U$ disposed symmetrically about ϵ_f). We parametrize these interactions through a near-neighbor interatomic Coulomb interaction.

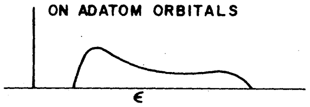
The change in the shape of the local density of states LDS on adsorption is affected by the transfer matrix for electrons between the adatom orbitals and the metal-atom orbitals and the relative position of the LDS of these orbitals. For our cases of interest, the unperturbed levels of the adatom lie near the bottom of the *d* band. Then if the unperturbed shape of the local density of states is as shown in Fig. 3(a), the perturbed local density of states on the adatom orbital and on the metal atoms to which a transfer matrix element exists will be as shown in Figs. 3(b) and 3(c), respectively.

We will now fix the primary features of the perturbed LDS by determining the first three moments. Instead of working in terms of individual metal-atom orbitals, it is more convenient to work in terms of group orbitals, which are linear combinations of the orbitals on metal atoms situated similarly with respect to the adatom and which couple similarly to a given orbital on the adatom.

(a) SCHEMATIC LOCAL DENSITY OF STATES BEFORE ADSORPTION



(b) SCHEMATIC LOCAL DENSITY OF STATES AFTER ADSORPTION



(c) ON TRANSITION-METAL ATOM AT SURFACE

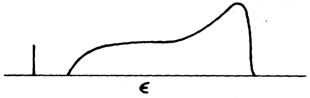


FIG. 3. (a)−(c) Schematic variations of the local density of states of an adatom and the transition-metal atoms with which it directly interacts, upon adsorption.

In this paper, the adatom orbitals are treated as degenerate, orthogonal, and equivalent. For oxygen and nitrogen, we ignore the 2*s* orbitals and consider the six 2*p* orbitals. For hydrogen we consider the two 1*s* orbitals. Although for oxygen and nitrogen, the $2p_x$, $2p_y$, $2p_z$ orbitals belong to a different representation of the point group with the adatom absorbed, say, at a center site on a surface of square symmetry, we ignore the distinction between them and consider that they are coupled to their respective metal group orbitals with the same transfer matrix element V. (This is one of the simplifications removed in II.)

Let ϵ_a specify the (mean energy) of the adatom orbitals before adsorption and ϵ_1 that of the metal group orbitals discussed above. Let $\tilde{\epsilon}_a$ and $\tilde{\epsilon}_1$ be the corresponding quantities after adsorption. This is merely a relabeling of the C_i's of Sec. IV. The second moment about ϵ_1 of the group orbital is taken as $\frac{1}{16}W^2$ for a band of width W. If the mean energy of this group orbital is different from that of the bulk, called C hereafter, the third moment about ϵ_1 of the LDS is $\frac{1}{16}W^2(C-\epsilon_1)$.

The LDS of the perturbed group orbital about $\tilde{\epsilon}_1$ has the second moment $\frac{1}{16}W^2 + V^2$ about $\tilde{\epsilon}_1$ while its third moment is $\frac{1}{16}W^2(C-\tilde{\epsilon}_1) + V^2(\tilde{\epsilon}_a - \tilde{\epsilon}_1)$.

The second moment of the adatom orbital is V^2 about $\tilde{\epsilon}_a$, while its third moment is $V^2(\tilde{\epsilon}_1 - \tilde{\epsilon}_a)$ about $\tilde{\epsilon}_a$.

We also consider orbitals on the atoms that are nearest neighbors to the adatom but whose transfer matrix element to the adatom orbital is nearly zero due to orthogonality. They are important because charge is in general transferred to them. Thus, for example, for chemisorption at a center site on a (001) surface, an adatom is in contact with at least four metal atoms, each of which has ten (*d*) orbitals. Apart from the group orbitals that couple directly to the adatom, there will be many linear combinations that have no hopping integrals to the adatom and at worst only small hopping integrals to the directly coupled group orbitals. When there are six adsorption orbitals and 40 metal orbitals, there must be 34 such weakly coupled group orbitals. We call these the "type-2" orbitals as distinct from the directly coupled "type-1" group orbitals. The type-2 orbitals experience the same Coulombic forces as the others, and we take account of their contribution to the binding by specifying the center of gravity ($\tilde{\epsilon}_2$) and second moment about $\tilde{\epsilon}_2(\frac{1}{16}W^2)$ of their LDS.

Given the LDS for each orbital in the system, the corresponding charges are obtained. We require that the orbital energies be consistent with the derived charges, as discussed earlier. For our purposes we require at least three electrostatic parameters in the algorithm we use for the orbital energies. We write

$$\tilde{\epsilon}_a = \epsilon_a + U_a \sum_{\substack{\text{adatom}\\ \text{orbitals}\\ a' \neq a}} \Delta N_{a'} + U_{am} \sum_{\substack{\text{all}\\ \text{metal}\\ \text{orbitals}}} \Delta N_m \ , \tag{15}$$

$$\tilde{\epsilon}_1 = \epsilon_1 + U_m \sum_{\substack{\text{all metal}\\ \text{orbitals}\\ m' \neq m}} \Delta N_{m'} + U_{am} \sum_{\substack{\text{all}\\ \text{adatom}\\ \text{orbitals}}} \Delta N_a \ , \tag{16}$$

$$\tilde{\epsilon}_2 = \epsilon_2 + U_m \sum_{m'} \Delta N_{m'} + U_{am} \sum_{a} \Delta N_a \ . \tag{17}$$

ϵ_a is given. ϵ_1 and ϵ_2 are given by repeating the whole problem in the absence of the adatom. Then

$$\epsilon_1 = \epsilon_2 = C + U_m \sum_{m'} (N_{m'} - N_{\text{bulk}}) \ , \tag{18}$$

where C is the mean energy of the d orbitals in the bulk.

For the remaining metal atoms, i.e., all those that are not nearest neighbors of the adatom, the second moments of the corresponding local densities of states will be unchanged on chemisorption. Since the perturbation due to the adatom decays rapidly as one progresses into the solid, there is no need to impose self-consistency for these sites, and all the relevant orbital energies are kept equal to C. Similarly, any change in third moment will be zero (except, strictly, for second-nearest-neighbor sites, where it will be very small) and so within the approximations of this model the energetic contribution to the heat of adsorption from these atoms is zero.

We should have, in principle, distinguished the interaction between orbitals with the same z component of spins and those with different z component of spin by introducing an exchange energy. If the adsorption is, as we believe, to a state of zero total spin, this would have merely introduced an additional parameter without adding any essential new insight.

Having specified the first three moments of the LDS on the relevant orbitals, we generate an expression, $n_{i\alpha}(\epsilon)$, with these moments and use it in Eq. (5) together with the self-consistency and the charge neutrality criteria to calculate ΔH_{ads}. As discussed earlier, we believe the precise form of $n_{i\alpha}(\epsilon)$ is unimportant, and that any reasonable shape with the specified moments and which has the qualitative features illustrated in Fig. 3 will do. The form used here is given in the Appendix. In the next paper (II) this simplification is also tested.

[With the form of LDS in the Appendix, one runs into some trouble for transition metal to the extreme right (Ni, Pd, Pt) which have number of d electrons/atom greater than about nine. This is because with this form the LDS after absorption is extremely rapidly varying at the upper edge of the band. Our results for such cases are extrapolations of those for d electrons/atom less than nine.]

We now summarize the procedure of the calculations. First, the LDS and the charge on the surface group orbitals is determined, using Eq. (18) and the specified second moment of the LDS. Second, the first three moments of the LDS on the adatom orbital and the type-I and type-II group orbitals are determined self-consistently using the form for the LDS given in the Appendix, and Eqs. (15)–(17). In this calculation U_{am} is adjusted so that local charge neutrality

$$\sum_i \Delta N_i = 0 \tag{19}$$

is obtained. In Eq. (19) the sum is over the adatom and the type-I and the type-II orbitals. These self-consistent moments are inserted back in (A) to obtain the final LDS on all the concerned orbitals. This is used in Eq. (11) to find ΔH_{bond}.

For atoms with partially filled shells (like hydrogen and oxygen) there is an additional important point to bear in mind. The occupation in the adsorbed state is assumed to be the same for all orbitals. It is most convenient for the calculations to first *prepare* the free atom in a state with all orbitals equally occupied and calculate the bonding energy using Eq. (12) with respect to it. The actual bonding energy is then found by adding the energy difference between the prepared atom and the actual free atom.

VI. CHOICE OF PARAMETERS

The important parameters characterizing the transition metals discussed in Sec. III have been listed in Table I. We must also specify the repulsion energy parameter U_m for d electrons on the same metal atom. As also discussed in Sec. III, the U_m we are interested in is a renormalized quantity, which takes into account the redistribution (screening) of s electrons due to d electron charge variations. This renormalized U_m is believed to have a value of about 3 eV. Such a number has also been deduced from microscopic calculations of transition-metal alloys.[8] Of course, the screening at the surface will in general be different in the bulk with a corresponding variation in U_m. In our calculations we have varied U_m from 2–4 eV and examined its effect on the binding energy. However, U_m is kept constant going across the series, as we do not believe it varies significantly from one transition metal to another.

The ionization level energy I_0 and the affinity level energy A_0 for free atoms of H, N, and O are well known. These quantities are strongly renormalized due to image effects as the (charged) atoms approach a metal. For distance R from a metal much larger than the screening length of the metal

$$I(R) \approx I_0 + e^2/4R \ , \quad A(R) \approx A_0 - e^2/4R \ . \tag{20}$$

This effect is modified as the adatom comes close to the metal and the image energies join to the exchange-correlation energies. The electron-electron repulsion parameter for the adatom is reduced from

$$U_a(R)=I(R)-A(R) \qquad (21)$$

For $R \approx 1$ Å, this gives U_a for oxygen of ~ 5 eV. In our calculations we have varied U_a from 3 to 6 eV and studied its effect on chemisorption. Again we have kept U_a constant going across the transition-metal series.

The effect on the adatom level ϵ_a as the atom approaches the metal is only of a dipolar nature and we ignore it. Generally ϵ_a lies above but not close to the ionization energy. We have taken it to be equal to the ionization energy at the surface. Thus it depends on U_a.

As already discussed, the adatom nearest metal atom(s) Coulomb-energy parameter U_{am} has been determined in the present calculation by requiring local charge neutrality. It is gratifying that U_{am} thus obtained varies very little going across the transition-metal series (see Fig. 4) and has the reasonable value of about 1 eV.

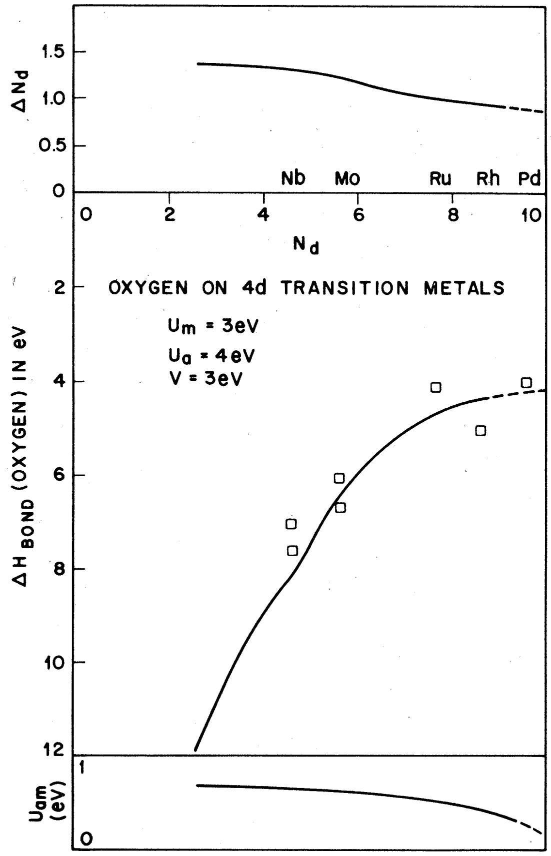


FIG. 4. Calculated and experimentally obtained binding energy for oxygen on $4d$-transition-metal surfaces. Also given is the (d-electron) charge transfer to oxygen and the metal-atom–adatom Coulomb parameter required to obtain local charge neutrality.

The adatom–metal-atom transfer matrix element V has been calculated for oxygen p_z orbital and Ni $(3z^2-r^2)$ orbital at the observed separation by Bullett[18] to be ~ 0.5 eV. In this paper all orbitals have been treated as equivalent. For O on a center site of a 100 surface, one can then obtain V for O to metal group orbital of ~ 2 eV. On polycrystalline surfaces the adsorption is most likely on a site of larger coordination giving thereby a large V. With $U_a=4$ and $U_m=3$ the V needed to obtain agreement with experimental results for O on $4d$ metals is ~ 3 eV.

To calculate V and its variation across the series, one needs to know the equilibrium separation of the adatom from the surface. We have calculated V for cases in which the equilibrium separation is known experimentally by using the Slater-Koster method and atomic wave functions and potentials. The details are given in Paper II. What is chiefly of interest here is that the calculations reveal that within the accuracy with which we calculate ΔH_{bond} here, V can be taken as a constant across the series.

What we shall establish through our results in the next section is that within the range of the U parameters and V used, the trends in the binding are simply related to the gross metallic parameters W and C, with the overall magnitude determined largely by V.

VII. RESULTS AND DISCUSSIONS

In Fig. 4, we present our calculated results for the binding energy of oxygen on $4d$ metals, using the parameters specified in Table I[19] and on the figure. The experimental results are also shown, as is the calculated ΔN_a, the d-electron charge transfer to the oxygen atom and the parameter U_{am} required to achieve local charge neutrality. U_{am} is of order $\frac{1}{2}$ eV and varies smoothly across the series. ΔN_a is of order-1 electron and also varies smoothly. As discussed in Sec. III, we envisage that the s-electron charge on the pure metal surface moves back on to the surface transition-metal atoms to screen the d-electron charge flow and give us renormalized repulsion parameters, U_m, etc.

In Fig. 5, we present the calculated binding energy for oxygen on $3d$ metals together with the experimental results.

In Fig. 6, we compare the results obtained by varying the various parameters for oxygen on $4d$ series. A larger U_m or U_a leads to an overall reduction in the binding energy without affecting the general trend. A larger V leads to an increased binding energy again without affecting the general trend.

In Fig. 7, we present results for hydrogen adsorbed on the $4d$-series metals together with the experimental results.

Our results for nitrogen compare equally well with the experimental results, and give about $\frac{1}{2}$ electron

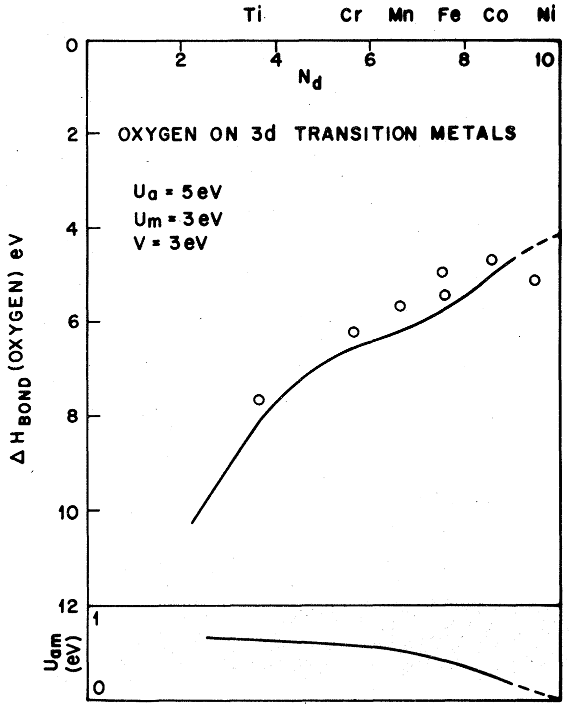


FIG. 5. Calculated and experimentally obtained binding energy for oxygen on 3*d*-transition-metal surfaces. Also given is the (*d*-electron) charge transfer to oxygen and the metal-atom—adatom Coulomb parameter required to obtain local charge neutrality.

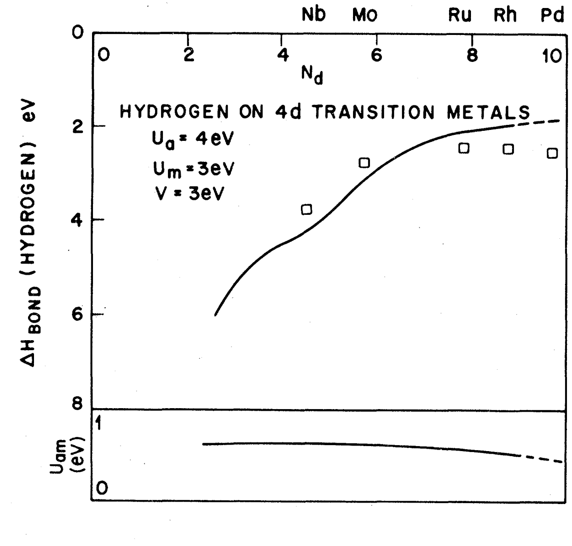


FIG. 6. Calculated and experimentally obtained binding energy for hydrogen on 4*d*-transition-metal surfaces. Also given is the (*d*-electron) charge transfer to hydrogen and the metal-atom—adatom Coulomb parameter required to obtain local charge neutrality.

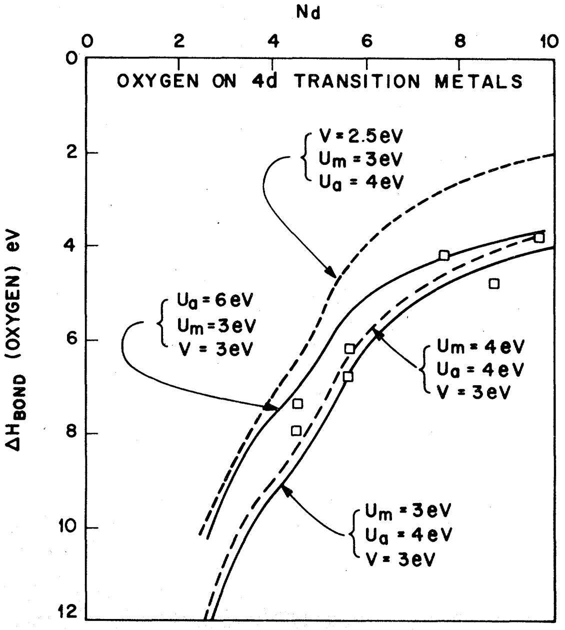


FIG. 7. Calculations for oxygen binding energy on 4*d*-transition-metal surface for various parameters. The experimental points are also shown.

larger charge transfer than oxygen and somewhat larger binding energy.

If we do not insist on local charge neutrality and keep U_{am} constant ≈ 0.5 eV for all the metals in a given series, the binding energy is not significantly different from the results presented, but the charge imbalance can be as much as $\frac{1}{2}$ electron.

We have used the extensively compiled data for chemisorption on polycrystalline surfaces for comparison purposes. These data refer to the initial heats of adsorption and as mentioned in Sec. I is larger than on single-crystal surfaces. The presumption is that the data reflect bonding at maximally coordinated sites, similar for polycrystalline surfaces of different metals, where the bonding would be the strongest.

Having obtained the systematics of the chemisorption energies of simple atoms on transition metals from a relatively simple calculation, we are able now to comment on the physics of the problem. From an examination of Table I and the experimental results, one can make the empirical observation that the transition-metal parameter primarily determining the trend is the mean energy of the *d* band. The reason is the following: the change in the density of states near the top of the *d* band or the bottom is nearly the same as that near the center of the *d* band if

$$\frac{W^2V^2}{2[(\epsilon_a-C)^2+4V^2]^2} << 1 ,$$

as may be verified by second-order perturbation theory. This condition is always met in the problems under consideration. If the variations in LDS are similar in all energy ranges of the *d* bands, the characteristic *d*-band parameter playing the crucial role may be taken to be the mean energy of the *d* band. It is for the same reason that our simple characterization of the *d* band has worked: detailed features of the band are unimportant if there is similar variation everywhere. In any event this assumption is checked in detail in the following paper.

If the important metallic parameter determining the change in LDS is C, two points follow. As C approaches the *partially filled* level ϵ_a the binding energy due to interaction through V and the charge transfer to the lower-energy state *decreases*. This may be verified by diagonalizing the matrix of degenerate levels at ϵ_a connected to the degenerate levels at C through V and calculating the new energy through filling the lowest levels. The difference in energy before and after adsorption will be $[\frac{1}{4}(\epsilon_a - C)^2 + nV^2]^{1/2}$, where n is the degeneracy at C. Also as C approaches ϵ_a the antibinding levels formed of the interaction between adatom and metal increasingly get populated. This further reinforces the trend.

A slightly better calculation would be to do the above, not with C, but with C_f, the mean energy of the filled part of the band. C_f has a trend in the transition-metal series similar to (but more slowly varying than) C.

The variation in the bandwidth W across the series is next in importance (after the mean *d*-electron energy, C or C_f) in determining the trend in the binding energy. Our conclusion from the calculations is that, other parameters remaining the same, a smaller W gives a larger binding energy. The leveling off of the binding-energy curve to the right of the series (even though C rapidly falls) is due to the decrease in W (see Table I) and the increasing importance of V relative to $|\epsilon_a - C|$ when the latter becomes small. This is due to two effects: C remaining the same, C_f is higher for a small W; also the alteration in the local density of states depends (besides on $\epsilon_a - C$) on V/W, being larger for larger V/W. Another way of stating the latter is that if the transition metals bond to each other very strongly (larger W) they have a correspondingly lesser tendency to bond with the adatoms.

The binding energy of course goes up with V. However, as discussed in Paper II, there seems to be only a small variation of V across the TM series. Here, the results are obtained with V held constant. V determines (along with the charge transfer and associated self-consistent Coulomb repulsion) the shape of the final local density of states. When $(\epsilon_a - C)$ becomes smaller, the role of V becomes correspondingly larger in determining the binding energy (see Fig. 7).

The binding energy of hydrogen on all the transition metals is much lower than that of oxygen (and therefore the variation across the series is much smaller) because of the smaller charge transfer to hydrogen since it has only one relevant unfilled orbital to begin with.

Note in Figs. 4–7 that we always get a significant bump in the binding energy near the middle of the transition-metal series. This reflects the fact that the cohesive energy of transition metals is maximum in the middle of the series, and correspondingly the binding to adatoms is hindered to some extent.

We now summarize the above discussion. The positions of the atomic levels of hydrogen and oxygen (and nitrogen) with respect to the *d* bands of the transition metals is such that the primary binding comes from transfer of *d* electrons from surface metal atoms to the adatoms,[20] and to low-energy bonding resonances induced on the metal atoms. However, there is a large enough hybridization of the adatom orbitals with the surface metal-atom orbitals that the local density of states of the metal atoms is significantly altered throughout the band. Correspondingly the metal parameters that determine the energy lowering due to charge transfer are the average position of the band with respect to the adatom orbitals $(\epsilon_a - C)$, and its overall width W. The alteration in the local density of states is largely determined by V and this parameter determines the binding energy for small $(\epsilon_a - C)$. The relative positions of the final local density of states are also significantly determined by charge transfer, and associated self-consistent Coulomb repulsion. But V as well as the Coulomb repulsion parameters set only the magnitude of the binding energy; the systematic trends are determined by the other parameters discussed above.

We have tried in this work to understand the binding-energy trends of simple atoms on transition metals. Through a simple physically motivated method, we have highlighted the essential parameters determining the binding energy. The major shortcoming of the work is that the parameters used, although reasonable, are not obtained from first principles. These can be obtained only through enormously difficult calculations and we do not expect that the physical picture obtained in this paper will be significantly altered through such calculations. Another shortcoming of the present work is that we have imposed local charge neutrality only for the electrons of the adatom and the *d* electrons of the metal, implying separately a "local" conservation of the *s*-*p* electrons of the metals, after their readjustment for screening purposes. This is more a difficulty of principle than a practical one, since the adatom binding energy is relatively insensitive to whether or not we imposed local charge neutrality.

As mentioned earlier, many of the assumptions in the present paper are checked in Ref. 2. We also compare there the position of the "chemisorption level" of these calculations with that deduced by photoemission spectra with satisfactory results.

ACKNOWLEDGMENT

We wish to thank Dr. R. E. Watson for kindly providing us the band parameters for transition metals calculated by him.

APPENDIX: CANONICAL FORM FOR LOCAL DENSITY OF STATES

This work relies heavily on the construction of local densities of states given their first few moments. We require a general function $n(\epsilon)$ containing three parameters which can be set to obtain the required moments.

$n(\epsilon)$ must have the properties of a LDS. In particular,

$$n(\epsilon)\geq 0 \quad \text{for all } \epsilon \ , \tag{A1}$$

$$\int_{-\infty}^{\infty} n(\epsilon)d\epsilon=1 \ , \tag{A2}$$

and all moments of $n(\epsilon)$ should be finite. The function we pick is the local density of states at the end orbital of a semi-infinite tight-binding linear chain. This function is continuous in the range $\epsilon=\pm\frac{1}{2}w$ and depending on the parameters may have split off δ functions on either side. It is given by

$$n(\epsilon)=\frac{m_2\Delta(\epsilon)/\pi}{[E-m_1-\hat{m}_2\Lambda(\epsilon)]^2+[\hat{m}_2\Delta(\epsilon)]^2}\ , \tag{A3}$$

where

$$\hat{m}_2=m_2+(m_1+m_3/m_2)(E-m_1)\ , \tag{A4}$$

$$\begin{aligned}\Delta(\epsilon)&=(8/w^2)(\tfrac{1}{4}w^2-\epsilon^2)^{1/2} \quad \text{for } |\epsilon|\leq\tfrac{1}{2}w\\ &=0 \quad \text{for } |E|>\tfrac{1}{2}w\ ,\end{aligned} \tag{A5}$$

and

$$\begin{aligned}\Lambda(\epsilon)&=8\epsilon/w^2 \quad \text{for } |\epsilon|\leq\tfrac{1}{2}w\\ &=\frac{8\epsilon}{w^2}-\operatorname{sgn}(\epsilon)\left(\epsilon^2-\frac{w^2}{4}\right)^{1/2} \quad \text{for } |\epsilon|>\tfrac{1}{2}w\ .\end{aligned} \tag{A6}$$

Equation (A3) satisfies all the required conditions, and further

$$\int_{-\infty}^{\infty}\epsilon n(\epsilon)d\epsilon=m_1\ , \tag{A7}$$

$$\int_{-\infty}^{\infty}(\epsilon-m_1)^2 n(\epsilon)d\epsilon=m_2\ , \tag{A8}$$

$$\int_{-\infty}^{\infty}(\epsilon-m_1)^3 n(\epsilon)d\epsilon=m_3\ . \tag{A9}$$

$n(\epsilon)$ to a semiellipse when $m_1=m_3=0$ and $m_2=\frac{1}{16}w^2$. Also $n(\epsilon-c)$ gives a band centered at c.

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