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

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In the previous paper, the systematics of the binding energy of hydrogen and oxygen on transition metals were related to a few basic parameters characterizing such metals. In this paper we justify some of the approximation used in the previous paper through much more comprehensive numerical calculations. We also compare the calculated local density of states at the surface with ultraviolet photoelectron spectra.

I. INTRODUCTION

In the previous paper,[1] referred to hereafter as I, we derived a simple model in which we were able to reproduce the experimentally observed binding-energy trends for oxygen and hydrogen atoms on the transition metals. The experimental data, taken from a recent review by Toyoshima and Somorjai,[2] were summarized in the previous paper. The observed gross trends—binding energy decreasing from about 8 eV per oxygen atom on metals at the left-hand side of the transition series to about 4 eV per atom at the right-hand side, and smaller values for hydrogen—indicated that an explanation should be sought in terms only of the most basic parameters of the metals. This was the approach that we adopted in the previous paper.

In this paper, we examine and justify some of the simplifications that we introduced for the sake of computational convenience into the model of the previous paper. We now perform detailed computations of the adsorption of oxygen atoms on the 4*d* transition metals. Instead of using model local density of states (LDS) functions, we explicitly consider the metal crystal structure, and compute the local densities of states directly.

We demonstrate, among other things, in this paper that the details of the metal LDS are unimportant in the determination of the chemisorption binding-energy trends, confirming the approach that we took in the previous paper. We also show that the final chemisorbed LDS's generated by our calculations are in good agreement with experimentally observed UPS (ultraviolet photoelectron) spectra.

II. DESCRIPTION OF THE CALCULATIONS

The fundamental assumptions on which we base our calculations are the same as in the previous paper. We treat explicitly the interaction of the adatom orbitals with the *d* electrons of the transition metal. The role played by the metal *sp* electrons was discussed at length in the previous paper: The assumption we make is that the contribution of the *sp* electrons can be adequately expressed by considering their role in renormalizing the *d*-electron parameters and screening out charge imbalances, rather than by direct bonding to the adatom orbitals.

We cast our calculation of the interaction between the adatom and the metal *d* electrons in terms of the LDS of the relevant orbitals. The procedure we adopt is described in I and uses a tight-binding formalism. We require that the LDS's on the adatom and its neighboring metal atoms be found self-consistently, so that the orbital energy levels are compatible with the calculated charges. In addition, we insist that the total charge on the surface atoms (adatom plus neighbors) be the same before and after chemisorption.

Then the expression for the adsorbate binding energy is given by

$$\Delta H_{\text{bond}} = \sum_{i\alpha} \left[\int_{-\infty}^{E_F} (E - E_F) \Delta n_{i\alpha}(E) dE - \tfrac{1}{2} \Delta C_{i\alpha} (\tilde{N}_{i\alpha} + N_{i\alpha}) \right] , \qquad (1)$$

where $\Delta n_{i\alpha}(E) = \tilde{n}_{i\alpha}(E) - n_{i\alpha}(E)$ is the change in

LDS of the orbital $i\alpha$ due to chemisorption; $N_{i\alpha} = \int_{-\infty}^{E_F} n_i(E)dE$; and $\Delta C_{i\alpha} = \tilde{C}_{i\alpha} - C_{i\alpha}$ the change in the center of gravity (or orbital energy) of each LDS. This expression is a slightly different form of Eq. (2) of the previous paper.

It is not the purpose of this paper to produce more accurate values of ΔH_{bond} than we did in I, but rather to examine the effect on the previously calculated results of removing some of the simplifications that were introduced there. The approximations used in the last paper that are removed here are:

(i) Instead of fitting the moments of generalized LDS functions, we set up a lattice of metal atoms, plus an adatom, and compute the LDS's and their integrals directly.

(ii) The adatom p_z orbital is no longer made to be degenerate with the p_x and p_y orbitals when chemisorbed. The coupling of the p_z orbital to the metal orbitals is also different from that of the p_x and p_y. (We choose a particular adsorption geometry such that p_x and p_y remain degenerate.)

(iii) The individual orbitals on the metal atoms adjacent to the adatom are no longer degenerate, and their energy levels are all found self-consistently. The concept of metal group orbitals is not used.

(iv) We calculate explicitly the effect on ΔH_{ads} of the metal atoms that are second neighbors to the adatom.

Some specific approximations that are not changed from Paper I are:

(a) The treatment of the metal *sp* electrons. The same U parameters are used in the detailed computations.

(b) We assume that any net charge transfer to or from metal atoms that are second or further neighbors from the adatoms will be so small that it will not be necessary to allow their energy levels to adjust (and we find that this is indeed the case).

(c) The contribution to ΔH_{ads} from metal atoms remote from the adatom (>second neighbors) is not calculated directly (but is estimated to contribute less than 2% of the total).

III. CONSTRUCTION

In I, we defined the LDS for each orbital by specifying the first three moments in the tight-binding approximation and using a canonical LDS function. In this paper, we calculate physically realistic LDS functions, taking the structure of the metal crystal explicitly into account.

We construct a lattice, either bcc or fcc, of metal atoms, with an (001) face exposed. The metal atoms have d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, and $d_{3z^2-r^2}$ orbitals. The hopping integrals between orbitals on adjacent atoms are defined by three parameters $dd\sigma$, $dd\pi$, and $dd\delta$, and the direction cosines of the vectors joining the atoms. $dd\sigma$ is the Hamiltonian matrix element for a pair of orbitals with *s* symmetry about the axis that joins them, e.g., between a pair of $d_{3z^2-r^2}$ orbitals on atoms separated along [001]; $dd\pi$ corresponds to a pair of orbitals with *p*-type symmetry about the axis joining them, e.g., d_{xz} orbitals separated along [001]; and $dd\delta$ to *d* symmetry, e.g., $d_{x^2-y^2}$ orbitals separated along [001].

The Hamiltonian matrix element between any two orbitals on adjacent atoms is then given by a particular linear combination of $dd\sigma$, $dd\pi$, and $dd\delta$ according to formulas given by Slater and Koster.[3] $dd\sigma$ $dd\pi$, and $dd\delta$ are functions only of atomic separation, and we define them for nearest neighbors only for a fcc lattice, and for first- and second-nearest neighbors in a bcc lattice. Pettifor[4] has shown that taking the ratio $dd\sigma : dd\pi : dd\delta$ as $6:-4:1$ (the sign arising from the conventional way of writing the orbitals) gives band structures that agree well with those derived from more sophisticated calculations, so we take this ratio throughout.

Our metal band structure is therefore defined in terms of one parameter only, the $dd\sigma$, which is fitted to give the required bandwidth. For bcc lattices we take the second neighbor $dd\sigma$ to be 0.5 × the first-neighbor value. (Roughly speaking, the $dd\sigma$ should have a R^{-5} dependence, and the ratio of second-neighbor to first-neighbor distance in a bcc lattice is $2/\sqrt{3} \simeq 2^{1/5}$.)

We place the oxygen adatom above a center site on the (001) face of the metal. The adatom has p_x, p_y, and p_z orbitals, and because of symmetry, the p_x and p_y are degenerate. Two parameters $pd\sigma$ and $pd\pi$ are needed to define the hopping integrals to the metal orbitals, which are defined analogously with the metal-metal parameters. We consider hopping between the adatom and its nearest-neighbor metal atoms only.

A. Self-consistency equations

The adatom and its four nearest-neighbor metal atoms have between them a total of $3+5+5+5+5 = 23$ orbitals, not counting a factor of 2 for spin degeneracy. Because we have chosen a geometry with square symmetry, it turns out that out of the 23 there are in fact only seven inequivalent orbitals. On the adatom, the p_x and p_y remain degenerate, because of symmetry. The four metal atoms are in equivalent locations, and the five orbitals on any one of these atoms are equivalent to those of the other three.

We want to find the energy levels of all 23 orbitals on the surface atoms self-consistently. To do this, we need to write down the self-consistency equations [corresponding to Eqs. (15), (16), and (17) of I] for the seven inequivalent orbitals. Because we wish to calculate the self-consistent energy levels for each orbital on the surface atoms, we do not need to invoke the metal group orbitals we used in the previous paper, and we deal directly with atomic energy levels and charges.

The self-consistency equations satisfied by the energy levels of the seven nonequivalent orbitals are thus

$$\tilde{\epsilon}_a = \epsilon_a + U_a \sum_{\substack{\text{adatom}\\ \text{orbitals}\\ a' \neq a}} \Delta N_{a'} + U_{am} \sum_{\substack{\text{all neighboring}\\ \text{metal orbitals}}} \Delta N_m \ , \qquad (2)$$

where a stands in turn for the p_x and p_z adatom orbitals, and

$$\tilde{\epsilon}_i = \epsilon_i + U_m \sum_{\substack{\text{all orbitals}\\ \text{on same metal}\\ \text{atom, except } i}} \Delta N_{i'} + U_{am} \sum_{\substack{\text{all}\\ \text{adatom}\\ \text{orbitals}}} \Delta N_a \ . \qquad (3)$$

For the bare surface ϵ_{xy}, ϵ_{yz}, ϵ_{zx}, $\epsilon_{x^2-y^2}$, and $\epsilon_{3z^2-r^2}$ must be determined self-consistently by

$$\epsilon_i = C = Um \sum_{i' \neq i} [N_i - N_i(\text{bulk})] \ , \qquad (4)$$

where N_i(bulk) is the charge on orbital i of a bulk atom.

The energy levels of all metal orbitals that are not nearest neighbors of the adatom are fixed equal to C, the value deep in the bulk.

In these computations, we assume, as we did in I, that the charge transfer to metal atoms that are second and further neighbors to the adatom will be sufficiently small that it will not be necessary to allow their energy levels to adjust. We test this assumption, once the self-consistent solution for the "adjustable" atoms has been found (both for the bare surface and with the adatom), by calculating the charge transfer and total energy contribution of the metal atoms that are second-nearest neighbors of the adatom. For the geometry we are using there are eight nonequivalent second-neighbor orbitals; four on the atom directly beneath the adatom, and four on any one of the (four) metal atoms which are in the second layer and out to one side of the adatom. These orbitals, it turns out, have charge transfers of order only 0.002 electrons each due to chemisorption, and contribute between them a total amounting to less than 2% of ΔH_{ads} so the approximation is justified.

To compute the LDS's we use the recursion method of Haydock, Heine, and Kelly.[5] The technique and its applications are described in detail elsewhere.[6] The method, especially designed for systems with no translational symmetry, produces accurate and computationally cheap densities of states, together with their integrals, given a tight-binding Hamiltonian. The steps in the calculation are carried out on the computer by a series of now standard programs.[7]

IV. PARAMETERS

As we discussed in Sec. III, our metal band structure is entirely defined by the parameters $dd\sigma$, $dd\pi$, and $dd\delta$ which we take in the ratio $6:-4:1$. The bulk densities of states generated by these parameters are shown in Fig. 1, with $dd\sigma = 1.38$ eV for fcc and $dd\sigma = 1.47$ eV for bcc chosen to give bandwidths of 10 eV in each case. The spikes at the band edges are artifacts of the computation, and arise from the resolution of individual eigenvalues in the energy spectrum. These spikes are a well-known feature of the recursion programs. They do not usually contribute significantly to integrals over the density of states, which is what we are chiefly concerned with, and which is also what the recursion package calculates the most accurately. The spikes arise because of the abrupt cutoff of the d-band LDS at top and bottom of the band, and would disappear if the metal sp band were explicitly included in the LDS calculations.

In our chemisorption calculations, we adjust the parameter $dd\sigma$ (keeping the ratio $6:-4:1$ fixed) to give the correct d-band width of each metal, as specified by Watson, whose band parameters are listed in the previous paper. There is a small difficulty here, in that Watson specifies energies for the top, center of gravity, and bottom of each band, whereas in our present construction with $dd\sigma : dd\pi : dd\delta = 6:-4:1$, the band structure is completely specified by the center of gravity and the width. Rather than play around with the shapes of our own bands (by, for example, altering the $dd\sigma : dd\pi$ ratio) which would not have been a very rewarding task, we merely took the bandwidth, specified by Watson's top of band-bottom of band, as input together with the center of gravity.

The parameters for the adatom were discussed at length in the previous paper. We take $\epsilon_a - \epsilon_{\text{atomic}} = -13.6$ eV, $U_{\text{atomic}} = 12$ eV, and, in these calculations, we take $U_a = 4$ eV throughout.

The adatom-metal hopping parameters $pd\sigma$ and $pd\pi$ are not easy to estimate from first principles. Bullett[8] has a program for calculating Hamiltonian matrix elements between adjacent oxygen and transition-metal *atomic* orbitals, as a function of the interatomic separation. In his calculations, the electronic potential, but not the wave functions, are adjusted to allow for the overlapping electronic charge.

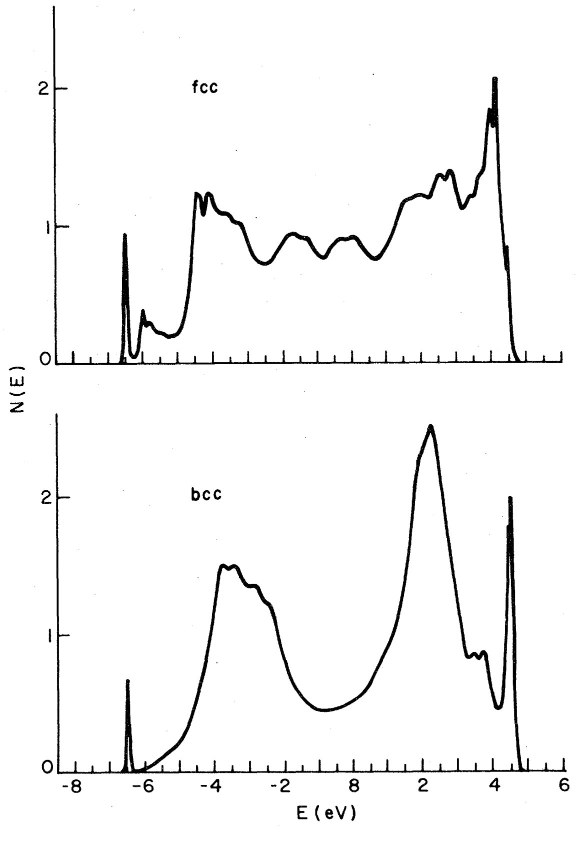

FIG. 1. Bulk density of states, calculated with the recursion method, for a bcc and a fcc lattice with parameters chosen to give a *d*-electron bandwidth of 10 eV.

Before we can arrive at values for $pd\sigma$ and $pd\pi$, we must know something of the metal-oxygen separation in chemisorption. There are experimental data available only for a very few cases [Ni(001), (110), and (111),[9] Fe(001),[10] Ir(110) (Ref. 11), and W(110) (Ref. 12)]. Extrapolating between these, it is not possible to estimate oxygen-metal bond lengths to better than 0.1 Å, and within this accuracy it is not possible to estimate $pd\sigma$ or $pd\pi$ to better than 8%. To this accuracy, $pd\sigma$ and $pd\pi$, as obtained from Bullett's programs, are constant across each row of the transition series, with $pd\sigma \simeq 1.5$ eV and $pd\pi \simeq -1.0$ eV.

How these values, derived from atomic orbitals, correspond to what we should use at a metal surface is not clear. The parameters we use in our model should correspond to the final charge states of the adatom and its neighboring metal atoms. Bullett's calculations are for neutral atoms, so we would expect to find some difference between his values and what we should really use. Because, in our calculations, the adatom and its surrounding metal atoms are neutral overall, it is reasonable to suppose that the values that we should use will not be very different from those quoted above. The figures given should be of the correct order of magnitude, and, in particular, the constancy across each series should be reproduced.

The parameter v that we used in the previous paper to describe the adatom-metal coupling is simply related to the $pd\sigma$ and $pd\pi$ of this paper. v^2, by construction, was equal to the sum of the squares of all the hopping matrix elements from an adatom orbital to all the neighboring metal orbitals, averaged over the different adatom orbitals. There is a result that the total sum of the squares of the hopping matrix elements between all the p orbitals of one atom and all the d orbitals of another is $(pd\sigma)^2+2(pd\pi)^2$ (not counting a factor of 2 for spin degeneracy), so that the average of this per p orbital is $[(pd\sigma)^2+2(pd\pi)^2]/3$, and v^2 is this quantity multiplied by the number of number of neighboring metal atoms, in this case four, so

$$v^2=\tfrac{4}{3}[(pd\sigma)^2+2(pd\pi)^2] \tag{5}$$

The values we take for $pd\sigma$ and $pd\pi$ in our computations were chosen to correspond to the value of v that we found to give the most appropriate numerical results in the previous paper. We took $pd\sigma=2.0$ eV and $pd\pi=-\tfrac{2}{3}pd\sigma$, using the approximate ratio found by Bullett. This corresponds to $v=3.2$ eV. Holding $pd\sigma$ and $pd\pi$ constant for the $4d$ series of transition metals is the best approximation we can make, and enables us to pay more attention to the other parameters in the calculations.

Since the available data on adsorption geometry are so sparse, we assume, for the sake of argument, that the geometrical arrangement of the adatom and its neighboring metal atoms is always the same as that for the O/Ni(001) system. The error involved in this approximation is much less than that caused by the uncertainty in $pd\sigma$ and $pd\pi$.

V. RESULTS

The results of our computations are shown in Fig. 2. We took fcc lattices for all the metals, and in addition calculated bcc Nb and Mo. The correspondence with the results of the model calculations of the previous paper (also shown in Fig. 2) is most satisfactory. (Because of the sharp cutoff at the top of the d band, we were unable, as in the previous paper, to obtain satisfactory results for Pd. The inclusion of the metal sp electron density of states would smooth out the band-edge singularity, and probably remove the difficulty.)

The similarity of Fig. 2 to the result shown in Fig. 4 in the previous paper demonstrates that the use of our model LDS function in that paper is quite adequate for the correct reproduction of the binding-energy trend for oxygen.

The very close similarity between the results for fcc and bcc Nb and Mo confirm that, of the metal parameters, it is the center of gravity of the band (which is the same for fcc and bcc, in the representation we have taken here) that is the dominant influence on the trend.

We expect the same qualitative dependence of the results of our computations in the input parameters (U_a, etc.) as we observed in our model calculations. The object of the present paper was not to produce more accurate values of ΔH_{bond}, which is not practicable, given the accuracy with which we can establish, for example, *pdσ* and *pdπ*, but to give an explicit demonstration of the validity of some of the approximations that we introduced into the model of the previous paper. Had we been concerned with numerically accurate values of ΔH_{bond} in this paper, we should also have taken into account the coupling of the adatom to the metal atom lying directly beneath it, and the fact that the geometrical arrangement of the atoms at a bcc (001) surface is necessarily different from that at a fcc (001) surface.

What we have shown by our computations in this paper is that the results of our previous model calculations are not dependent on: (a) using the canonical form for the LDS's instead of a full-blown calculation; (b) assuming the degeneracy of the adatom orbitals, and replacing their hopping interaction with the metal orbitals by a suitable average v; and (c) ignoring the contribution to ΔH_{bond} from the second neighbors to the adatom. These are the simplifications of the previous paper that we have explicity tested in this paper.

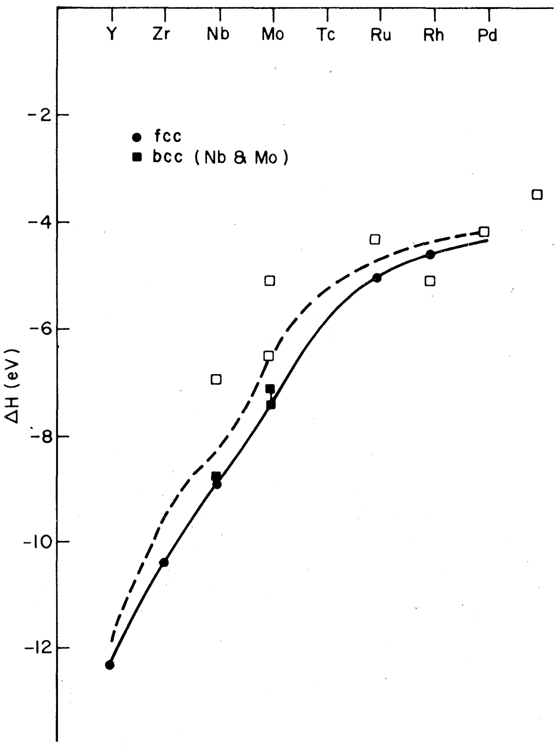

FIG. 2. Calculated binding energy for oxygen on 4*d* transition metals; solid line gives results using the methods of Paper I. Experimental results are also shown. For details of the geometry used in the present calculations, see text.

VI. COMPARISON WITH UPS EXPERIMENTS

We can test our detailed computation, and, by inference, our model calculations, by comparing the LDS's that we have calculated for the metal surfaces before and after chemisorption with the data available from photoemission experiments.

UPS experiments for the adsorption of oxygen on the transition metals almost invariably show oxygen-derived structure at around 6 eV below the Fermi level.[13,14] It is in fact quite remarkable how little this feature changes from one metal to the next. It is seen on metals as different as Ni [Ref. 14(a)] and W [Ref. 14(f)], for example. In the crudest analysis, prominent structure in the spectrum of the emitted electrons in UPS is to be directly identified with prominent structure in the surface LDS of the system under examination, although some allowance should strictly be made for matrix element, relaxation, and multiple-scattering effects.

In Figs. 3(a)–3(c), we show some of our calculated LDS's for the metals Y, Nb, and Ru using the parameters of Fig. 2. For each metal we show the LDS of the (self-consistent) bare surface atoms, summed over the constituent orbitals, and the final LDS of adsorbed atom plus neighboring atoms, again summed over all the constituent orbitals. In each case the graphs are normalized to unity. The reference energy in these graphs is the center of gravity C of the bulk metal band.

The density of state for the bare surfaces are different from the bulk densities of states (Fig. 2) because of the reduced number of neighbors of the surface atoms, and the LDS's for the different bare surfaces are different from each other because they are all determined self-consistently, according to the charge surplus or deficit at the bare surface.

The effect of adding the oxygen atom can be easily seen by comparing the two DOS graphs for each metal.

The feature to be noted in the final LDS's is that for all the metals, the oxygen-induced structure always lies at 7 ± 0.5 eV below E_F. This is very pleasing, and corresponds well to the different relative positions of $\bar{\epsilon}_a$ to E_F found in the previous paper. If we had chosen a larger value of U_a, e.g., 6 eV, we could have expected the oxygen-induced structure to move

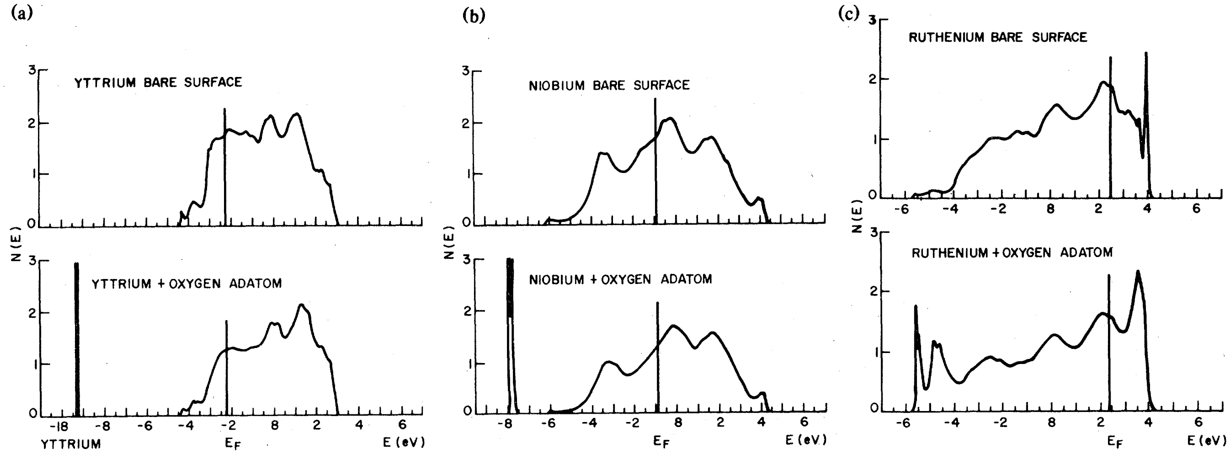

FIG. 3. Local density of states for the surface atoms of a few transition metals and the local density of states on adsorbed oxygen plus on neighboring transition-metal atoms. Results for (a) Y, (b) Nb, and (c) Ru are shown. Note the prominent peak, at 7 ± 0.5 eV below the Fermi energy, that appears after oxygen adsorption. The spike near the top of the band for Ru is an artifact of the truncation used in the recursion program.

up a volt or so in energy to give a numerical value closer to 6 eV below E_F. The fact that our calculated structure lies at the same energy with respect to E_F for all the metals we have studied is the important point, and lends extra credibility to our model. The sensitivity to U_a of the actual position of the oxygen-derived structure gives us another measure of the reasonable range of values for this parameter, and it is clear that unless U_a is within a volt or two of 5 eV, the structure in the LDS will lie in the wrong place. [Changing U_a from 4 to 6 eV typically shifts the final $\tilde{\epsilon}_a$ upwards in energy by about 1.3 eV, and changing $pd\sigma$ and $pd\pi$ to 1.6 and -1.2 eV (which would, from the results of the previous paper, give a larger upward shift in ΔH_{bond}) would shift the final $\tilde{\epsilon}_a$ upwards in energy by typically only 0.5 eV. The structure in the final LDS would move correspondingly.]

The oxygen-derived structure consists of two components, that from the p_x and p_y orbitals together having twice the weight of that from p_z.

For Y, the difference between p_x and p_z is so small that it is not noticeable in the LDS.

The extra spikes at the band edges for Ru both bare and with chemisorbed oxygen, are artifacts of the computer programs as we mentioned in Sec. IV above.

Where the oxygen-derived structure lies below the d band in energy in our model, it appears as a delta function. This is because we have only one adatom on the surface, so there is no dispersion in this energy level. The delta function would be broadened if there were many oxygen atoms on the surface, and by the presence of the sp-band density of states at the same energy, which we have ignored.

VII. CONCLUSION

We have in this paper explicitly tested and justified some of the simplifications that we introduced into our model calculations in the previous paper.

We have been able, in these two papers, to reproduce simultaneously both the experimentally observed data for heats of adsorption of oxygen and hydrogen atoms on the transition metals and also the oxygen-induced features of the surface density of states, as measured by UPS, at the correct energy.

Given the fundamental assumptions of the work—especially about the role played by the metal sp electrons—we have shown that our model calculations provide a consistent and useful picture of chemisorption. The assumption about the sp electrons is an untested one. In the literature our view is supported[15] by elaborate calculations on transition-metal surfaces; calculations on small clusters[16] tend to the opposite conclusion that direct bonding with the sp electrons of the metal atoms is important.

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