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Molecular-orbital theory of bonding in FeO and chemisorbed oxygen on Fe(100)

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A high-spin molecular-orbital study is made of $^7\Sigma$ FeO and O chemisorbed to Fe(100) in a small-cluster approximation. Bond lengths, force constants, binding energies, and electron energy levels are in promising agreement with experiment. Comparison is made to the low-energy electron diffraction study of Legg, Jona, Jepsen, and Marcus and the uv photoemission work of Brucker and Rhodin. It is suggested that correct theoretical structural determinations depend in a crucial way on occupying one-electron orbitals in the proper spin configuration.

I. INTRODUCTION

There are many computationally and conceptually realistic means for determining the energy levels of molecules and solids.[1] Finding structures of larger systems is more difficult because the variational theorem requires numerous calculations. Accuracy is a problem for all but the most difficult extended-basis-set procedures. A theory has been developed for approximating energy levels and structures for small and large molecules when self-consistency is relatively unimportant and when low-spin approximations are satisfactory.[2,3] More recently it was shown that atomic valence-electron ionization energy shifts are necessary for both nickel and oxygen atoms in a surface nickel oxide,[4] and it was suggested that ionic shifts should be the rule in strongly ionic systems. In this paper oxidized Fe(100) surfaces are considered. As in the case of O on Ni(100), valence ionization energy shifts are found necessary, but are insufficient for producing the correct surface structure. It is found that spin unpairing plays a crucial role in the structure of the surface iron oxide. At the same time it is shown how the simple one-electron molecular-orbital theory can be used for such systems.

The theory has the same form before and after approximate self-consistency and spin unpairing are implemented. The atomic-orbital parameters and orbital occupation schemes are affected, not the formalism. There are two conceptual steps,[2] which are worth repeating to provide the elements of discussion. First, rigid atoms are superimposed in a molecular configuration. On integrating the Hellmann-Feynman force, the energy of this system E_R is a sum of pairwise repulsive components:

$$E_R=\sum_{\alpha<\beta} -Z_\beta \int \rho_\alpha(r)(\vec{R}_\beta-\vec{r})^{-1}\,d\vec{r}\,, \tag{1}$$

where Z is the nuclear charge, ρ the complete charge density for an atom and, α and β are indices spanning the atoms in the molecule. The attractive energy components due to charge redistributions might also be evaluated using the Hellmann-Feynman force theory if the electron density function were available for all molecular geometries. A simple orbital theory provides an estimate of the attractive component directly and yields molecular orbitals and their energies and charge densities at the same time. To do this, a model molecular Hamiltonian, equal to the sum of atomic Fock potentials, is diagonalized, with approximations, over the atomic orbital basis set. The one-electron Hamiltonian matrix elements H take in this model the form

$$\begin{aligned} H_{ii}^{\alpha} &= E_i^{\alpha}+\sum_{\beta\neq\alpha}\langle\varphi_i^{\alpha}\,|\,V_\beta(r_\beta)\,|\,\varphi_i^{\alpha}\rangle \simeq E_i^{\alpha}\,,\\ H_{ij}^{\alpha\beta} &= E_i^{\alpha}S_{ij}^{\alpha\beta}+\langle\varphi_i^{\alpha}\,|\,V_\beta(r_\beta)\,|\,\varphi_j^{\beta}\rangle+\sum_{\gamma\neq\alpha,\beta}\langle\varphi_i^{\alpha}\,|\,V_\gamma(r_\gamma)\,|\,\varphi_j^{\beta}\rangle\\ &\simeq \tfrac{1}{2}K(E_i^{\alpha}+E_j^{\beta})S_{ij}^{\alpha\beta}\,, \end{aligned} \tag{2}$$

where φ are atomic orbitals with indices i and j, V are atomic Fock potentials, E are atomic ionization energies, and $S_{ij}=\langle\varphi_i\,|\,\varphi_j\rangle$, the overlap integral. In practice,[2,3] $K=2.25$ and the right-hand side of Eq. (2) is multiplied by $\exp(-0.13R_{\alpha\beta})$, where R is the internuclear distance. Solutions of Eq. (2) are molecular-orbital wave functions and corresponding energy levels. Electronic energies due to occupying these levels are added to E_R to produce working estimates of chemical binding energies and vibrational force constants when self-consistency is relatively unimportant, as for molecules considered in Refs. 2 and 3. Without self-consistency corrections, charge transfers are overestimated and, as shown for O on Ni(100) in Ref. 4, it is necessary to increase the valence ionization energies for the positive atoms and decrease them for the negative atoms to restore reasonable charge transfers in order to produce correct structure predictions. Further, the Sla-

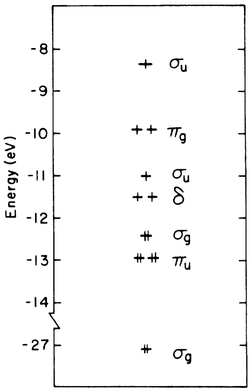

FIG. 1. Orbital energy levels for FeO in $^7\Sigma$ state.

ter exponents for O are decreased 0.3 in response to the negative charge on O. That for high-spin iron oxides the one-electron orbitals from this theory can be used is not unexpected because excited states have already been accurately treated for C_2, Ni_2, and Ni_3.[3]

II. FeO

The diatomic molecule FeO is isoelectronic to MnF and therefore is expected to have the same $^7\Sigma$ spectroscopic ground state,[5] though it is not reported in Ref. 5. From a calculation, as described below, the corresponding configuration is $\sigma_g^2\pi_u^4\sigma_g^2\delta_g^1\delta_g^1\sigma_u^1\pi_g^1\pi_g^1\sigma_u^1$ as shown in Fig. 1. This set of orbitals is a reasonable starting point for considering the molecular-orbital theory of other diatomics. The last σ_u level lies 1.5 eV above the π_g levels but is nevertheless occupied, creating a half filled set of levels in accordance with Hund's rule. Further evidence lies in consideration of the states of other molecules,[5] with question marks indicating predictions: $^2\Sigma$(ScO, TiN), $^3\Delta$(TiO), $^4\Sigma$(VO, TiCl), $^5\Pi$(CrO), $^6\Sigma$(CrF, MnO?), $^7\Sigma$(MnF, FeO?). These states follow from the orderly filling of the levels in Fig. 1 and noting the reversal of the neighboring δ and σ_u levels for ScO and TiO. For FeCl the state is $^4\Sigma$ because now that the shell is over half full the high-lying σ_u orbital loses its electron. CoO and NiO should be $^4\Sigma$ and $^3\Sigma$, respectively. CuO is $^2\Pi$, CuF $^1\Sigma$ as should be ZnO. Finally, ZnF is $^3\Sigma$ as should be GaO.

Standard parameters for O and Fe are in Table I, along with calculated spectroscopic properties for O_2 and Fe_2. Whereas the bulk iron parameters are used for the surface oxide studies in this paper, it is seen in Table I an improved Fe_2 binding energy is obtained when the 4*d* ionization energy is decreased 2 eV. Further, the $s\sigma_g$ to $s\sigma_u$ and $d\pi_g$ and $d\sigma_g$ to $p\pi_u$ transition energies are 3.37, 2.32, and 2.98 eV, similar to three observed adsorption bands observed for matrix isolated Fe_2.[6] An extensive study of transitions in Ni_2 and Ni_3 using this theory[3] showed the necessity of using free-atom 3*d* ionization energies. Thus for diatomics and small clusters one set of 3*d* ionization energies is appropriate while for the bulk the bulk values are appropriate. Intermediate sized clus-

TABLE I. Parameters used in the calculations. Calculated equilibrium distances R_e, force constants k_e, and dissociation energies D_e for O_2 and Fe_2 are also shown. See the text concerning parameter adjustments for the iron oxide studies. Experimental diatomic properties in parentheses are from Ref. 5.

	Principal quantum No., Slater exponent, and ionization energy (eV)		
Atom	*s*	*p*	*d*
O	2 2.246[a]–28.48[b]	2 2.227[a]–13.62[b]	3 2.4[c]–3.0[c]
Fe	4 1.7[c]–7.87[b]	4 1.7[c]–3.87[d]	3 5.35[e]–9.0[b]
Molecule	R_e (Å)	k_e (mdyn/Å)	D_e (kcal/mole)
O_2 $^3\Sigma_g$	1.22(1.2074)	10.3(11.76)	97.5(117.97 ± 0.45)
Fe_2[f] [$^7\Sigma$]	1.31, 1.30	2.4, 2.5	82, 36(24 ± 5)

[a] E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2686 (1963).

[b] Reference 14.

[c] Estimated.

[d] J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, J. Chem. Phys. 38, 796 (1963).

[e] The second exponent of this double zeta function is 1.8. The respective coefficients are 0.5366 and 0.6678.

[f] $\sigma_g^2\pi_u^4\delta_g^4\sigma_g^1\delta_u^1\delta_u^1\sigma_u^1\pi_g^1\pi_g^1$. In calculating the two-body repulsion energy one electron is placed in the 4*s* orbital. This is because the high-lying $s\sigma_u$ orbital is taken to be empty. The second set of calculated properties corresponds to using a free-atom 3*d* valence ionization energy for Fe as discussed in the text.

TABLE II. Calculated and experimental equilibrium bond length R_e, harmonic force constant k_e, and dissociation energy D_e for $^7\Sigma$ FeO. See the text for a discussion of this spectroscopic state assignment and parameters. Experimental values in parentheses are from Ref. 5.

R_e (Å)	1.67(1.626)
k_e (mdyn/Å)	4.15(5.67)
D_e (kcal/mole)	72[a](90.3 ± 5)

[a] Dissociating to neutral Fe d^6s^2 and O atoms.

ters should take an average.

Diatomic FeO is well described when the Fe valence ionization energies are increased 2.5 eV and decreased 2.0 eV for O. The bulk 3*d* ionization energy is used, this being greater than for the free atom and appropriate for the positively charged Fe ion. In the low-spin occupation the charge on O is + 0.42 while promoting electrons to the antibonding π_g orbitals in creating the $^7\Sigma$ state transfers charge to O, giving it − 0.35 electronic charge in a Mulliken definition. As the FeO bond length increases, more charge is transferred to O until a reversal sets in and neutral Fe and O atoms form. *Ab initio* calculations on AlO,[7] for example, show this behavior which has been encountered in many other ionic systems.[8] It is significant that bond lengths, stretching force constants, and dissociation energies are nearly correct in the constant valence ionization energy shift approximation. This means charge and valence-level adjustments occur at internuclear distances large enough for atomic overlap to be small.

III. O CHEMISORBED ON Fe(100): STRUCTURE AND CHARGE

Before studying the oxidized surface, some comments on the surface model are in order. The model consists, for the most part, of five Fe atoms, four in a square and one beneath. Unlike in the case of Ni, where the gap between the highest occupied and lowest unoccupied orbital energy level was 1–2 eV,[4] the gap for Fe clusters is small enough for a spin approaching the bulk value of ~2.25 μ_B per atom[9] if all levels in the *d* band contain at least one electron. Fe_2, whose calculated properties are in Table II, has a total spin of 6, as is seen in the molecular-orbital energy-level diagram in Fig. 2. This gives a spin per atom of 3 to be compared to the bulk value of 2.25. A five-Fe-atom cluster in the bulk geometry produces an energy-level spectrum shown also in Fig. 2 and has 12 unpaired electrons for a spin of 2.4 per atom, closer to 2.25. Finally, a nine-atom bulk cluster, wherein the atom beneath the other four in the previous five-atom cluster gains four neighbors forming a second plane has levels also depicted in Fig. 2 and has a spin of 2.67 per atom. What has been done is to occupy all the states in the well-defined *d* band and this requires spreading unpaired electrons over a range of about 0.5, 0.7, and 1.0 eV for the two-, five-, and nine-atom clusters. Electron interactions omitted in the molecular-orbital theory are responsible for the smearing of electrons over the 3*d* band of energies.

The imposition of high spin has a moderating effect on charge transfer among the atoms. The odd atom in the five-atom cluster has a charge of 2.46 in the low-spin configuration. In the high-spin case it becomes 0.13, which is much more reasonable. In the nine-atom cluster the charge on this atom decreases from 2.04 to 0.11. The charges on the other four second layer atoms changed from − 0.88 to 0.04 and the top layer change from 0.37 to − 0.07. Generally, it is seen that adapting high spin smooths out excess charge transfers by moving electrons to antibonding orbitals which put charge on those atoms which were neglected in forming the lower-lying bonding orbitals. The sign of an atom's charge depends on the orbital occupation assignment.

The interaction of an oxygen atom with the five-iron-atom cluster produces the binding curves in Fig. 3 with the fourfold site preferred. The equili-

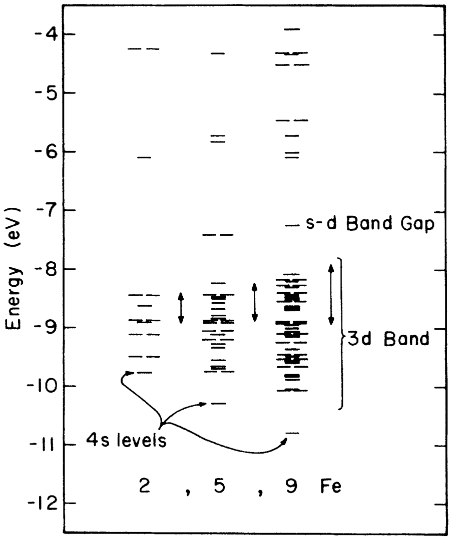

FIG. 2. Orbital energy levels two, five, and nine Fe clusters. The internuclear distance for Fe_2 is 1.31 Å, as calculated. Bulk geometries are used for Fe_5 and Fe_9. Singly filled levels are marked with vertical arrows.

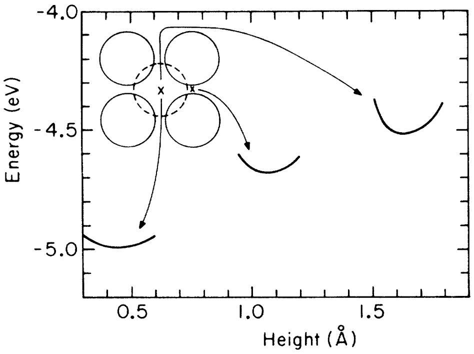

FIG. 3. Binding energy curves for O, on sites on a five-atom iron cluster, superimposable on the (100) surface, as shown. Oxygen is taken to be uncharged when infinitely far removed from the cluster. The one-coordinate site is over the single atom in the second layer.

brium distance from the surface of 0.48 Å is in acceptable agreement with 0.53 ± 0.06 Å from a low-energy electron diffraction determination.[10] For these calculations the Fe valence-state ionization energies (VSIE) were raised 1.5 and were lowered 1.0 for O. Increasing the VSIE for Fe by this amount, 1 eV less than for FeO, accords approximately with the 1:2 oxygen to iron ratio in the $c(2\times 2)$ half monolayer coverage. The decrease in the O VSIE by half as much then results in the same -0.35 charge on O as in FeO. As pointed out in Sec. IV, maintaining a 2 eV decrease in the O VSIE may fit the photoemission better, but with a reduced oxygen charge. There is little to be gained in further consideration of small ionization energy adjustments. Figure 4 shows the energy levels at equilibrium for the three possible symmetric binding sites and the high-spin occupations. As for the clusters, gaps between the *s* and *d* bands are evident. The structural preference is dependent on filling levels completely up to the energy gap, which in this case amounts to filling the FeO diatomic bonding orbitals. The top three levels for each structure in Fig. 4 are the same π_g and σ_u symmetry orbitals in Fig. 1. For the four-, two-, and one-coordinate sites there are, respectively, 12, 14, and 14 unpaired electrons for this cluster. Using a nine-atom cluster, with four more atoms in the second layer, and the binding distances calculated for the five-atom study, the binding energies are 2.9, 1.3, and 1.5 eV, with the same energy-level assignments. The fourfold site preference is maintained though the calculated binding energy is decreased, providing an illustration of the effect of model size on overall binding energy. Because of this dependence the emphasis is placed on relative binding energies for the sites.

IV. O CHEMISORBED ON Fe(100): ENERGY LEVELS

Comparison of the energy levels in the nine-atom Fe cluster with the experimental[11] Fe(100) photoemission spectrum in Fig. 5 shows similar widths. At about 1.5 L exposure to O_2, a $c(2\times 2)$ low-energy electron diffraction pattern appears[11] corresponding to half monolayer coverage, and for this the 5Fe+O spectrum is in qualitative agreement with the photoemission difference spectrum (also from Ref. 11, shown in Fig. 5). Slight shifts in the O and Fe VSIE levels could improve the agreement. If, for example, the O and Fe VSIE are decreased 2 and increased 1.5 eV, respectively, the O 2*p* levels lie at 5 eV beneath the Fermi level and the O charge is about -0.07. Something between these and the former shifts could put the 2*p* levels in exactly the correct position while maintaining a small O charge and the same distance from the surface. To do this would not provide further insight. The peak and levels at about 5.5 eV below the Fermi energy E_F are due to O 2*p* orbitals. The width of the experimental peak may be due to multiplet splittings.[11,12] The three highest filled levels in the cluster contain substantial charge on the oxygen due to antibonding mixing of its *p* orbital with the Fe surface orbitals from the upper part of the Fe^{2+} *d* band. This appears to give rise to the shoulder seen in the difference spectra at higher coverages around 1.5–2 eV below E_F.[13] It is believed that at in-

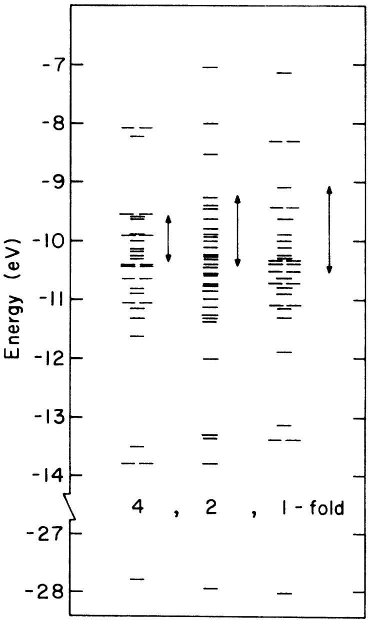

FIG. 4. Orbital energy levels for O at equilibrium on Fe_5 as in Fig. 3. Singly filled levels are shown with vertical arrows.

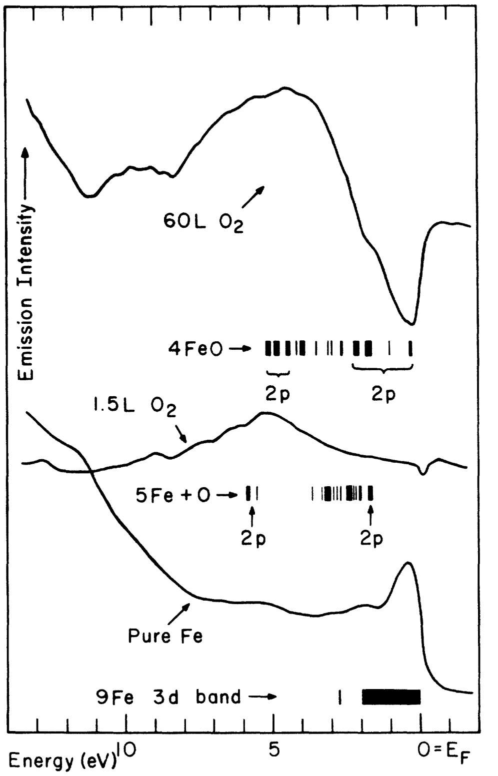

FIG. 5. Experimental Fe photoemission spectrum and difference spectra for 1.5- and 60-L exposure to O_2 at 300 °K as taken from Ref. 11. The calculated Fe_5+O in the fourfold binding site levels compare with the low-coverage spectrum and the calculated levels for $(FeO)_4$, with Fe in a square superimposable on the (100) surface, compare with the high-coverage spectrum.

creasing exposure to O_2 FeO islands nucleate and cover the surface prior to bulk oxidation.[11] At exposures of 4.7, and 60 L (1 langmuir = 10^{-6} Torr sec), emission from the Fe *d* band weakens the shoulder 1.5–2 eV below E_F becomes apparent. The energy levels of a bulk square array of 4 FeO bear this out as a comparison with the 60-L exposed surface in Fig. 5 shows. Larger cluster models would widen the calculated bands somewhat but not change their positions and would not fill in the weak O peak at 10 eV which is believed to be caused by electron "shakeup."[11]

V. SUMMARY AND DISCUSSION

A molecular-orbital theory which adds one-electron orbital energies to pairwise atom repulsions has been adapted to high-spin ionic iron oxides. This is accomplished by occupying all levels in the Fe 3*d* band with at least one electron and shifting VSIE levels in response to charge transfer. Agreement with experiment is promising. Other systems are obviously open to similar studies.

Further, this study suggests that structures for iron and other transition metal systems are strongly dependent on the unpairing of electron spins. Semiempirical one-electron theories and *ab initio* single-determinant and multideterminant treatments of these systems will need to recognize this to produce reliable results. It is important to learn experimentally the spin, structural, and electronic properties of clusters and surfaces for their own sake and to provide a guide to readily applicable theoretical procedures such as the one employed here. Although low-spin approximation may work some of the time, they cannot be counted on, and in the course of this study no parametrization scheme was found which would allow simultaneously the description of FeO and the surface oxide structure in the low-spin approximation.

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