Theoretical analysis of the bonding of oxygen to Cu(100)

Paul S. Bagus and Francesc Illas
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
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The chemisorption of O/Cu(100) has been modeled by a Cu₆O cluster; \textit{ab initio} self-consistent-field electronic wave functions have been obtained for this cluster. The bonding has been analyzed using several new theoretical methods: (1) the variation of the Cu₆O dipole moment with the distance of O from the surface; (2) the projection of the O orbitals from Cu₆O; and (3) the constrained space orbital variation (CSOV) method for the development of the bond. It is concluded that the bond is dominantly ionic but with a significant covalent contribution. Our results indicate that the excess charge on O is \(\sim 1.5\) electrons. We have computed the CSOV analysis for Cu₆O and for Cu₆ with point charges. The comparison of these two clusters has allowed us to have a definitive measure of the contribution of the Cu \(d\) electrons to the covalent bond. The total contribution of the \(d\) electrons to the bond is rather large (1.2 eV). Once the different contributions are separated, it is shown that purely electrical polarization effects account for \(\sim 0.5\) eV, while the direct participation of the \(d\) electrons in the covalent bond is \(\sim 0.7\) eV.

I. INTRODUCTION

The molecular-orbital (MO) cluster-model approach to surface chemistry and surface phenomena provides a way to study complicated surface processes and the chemisorption bond. The value of this approach relies on the fact that many properties of the adsorbate-substrate system are rather local in nature and thus reasonably well reproduced by cluster-model wave functions. We note that the specific values of features of the interaction, for example, the binding energy of the adsorbate, depend on the cluster size. However, the general character of the adsorbate-substrate bond can be described even with rather small clusters; see Ref. 1, and references therein for an extended discussion of this point. The cluster model has been used by Madhavan and Newton to study O/Cu(100). They used clusters containing as many as 25 Cu atoms; with cluster wave functions that included electron correlation effects, they were able to obtain good agreement with experiment for the heat of adsorption. The present work focuses on the nature of the O-Cu interaction and determines the degree of ionicity of the chemical bond. The bond obtained with the cluster wave functions is analyzed using new techniques recently developed for the characterization of the chemisorption bond. In particular, one of these techniques allows us to decompose the total interaction into the contributions from different terms. With this technique, the involvement of the \(d\) electrons in the bond has been determined; the contributions from pure polarization and from direct covalent effects have been separated. This point is of physical importance because it indicates the extent of the participation of the \(d\) electrons in the adsorbate-substrate covalent bond. This participation cannot, as we have shown in an earlier paper, be represented with a treatment in which the \(d\) electrons are included in a pseudopotential.

The chemisorption of atomic oxygen on the Cu(100) surface has been studied with a cluster model, which contains the metal atoms in the first and second layers, which are nearest to the adsorbed O atom. Oxygen was placed in a fourfold site which is the experimentally known site. The resulting model for O/Cu(100) is Cu₆O, see Fig. 1. The point group of Cu₆ and Cu₆O is \(C_{4v}\). The metal-metal distances have been kept at the bulk values, but the oxygen distance to the surface has been varied. \textit{Ab initio}, all-electron self-consistent-field (SCF) wave functions for Cu₆O were determined using a reasonable size basis set to describe the molecular orbitals. The properties of the potential curve for Cu₆O as a function of the distance of atomic O to the surface plane have been reported in a previous paper. The purpose of this paper is to analyze the nature of the Cu—O bond. Much of the analysis will be carried out with the O placed at 1.9 bohrs.

![FIG. 1. Representation of the Cu₆O cluster model for O/Cu(100); the O atom is shaded.](image-url)
above the surface plane; this distance is reasonably close
to the equilibrium SCF distance of O above Cu₅, zₑ = 1.78
bohrs. The analyses are carried out for the ⁵E electronic
state of Cu₂O, which has a singly occupied e shell and for
the ground state of the Cu₅⁺ cluster, which has a ³A₂
ground state with an e² open shell; see Ref. 6, and refer-
cences therein for further details.

Three techniques have been used for the analysis of the bond.
The first is based on the projection of O orbitals from
the Cu₂O wave function and it is described in Sec.
II. This technique provides information about the extent
to which the O orbitals are occupied for chemisorbed
O/Cu(100), and gives information about its effective ioni-
city. We shall show that the projections are consistent
with O anionic by ~1.5 electrons. The second technique
used to study the bond character is the nature of the
dipole-moment curve μ(z) for motion of O normal to the
surface; in particular, we will examine the slope and cur-
vature of μ(z). This method is described in Sec. III,
where we analyze μ(z) for Cu₅ interacting with a point
charge (PC) as well as with O. The analysis of the Cu₂O
and Cu₅ plus PC μ(z) curves also indicate an O anionicity
of ~1.5 electrons. Finally in Sec. IV we examine the partici-
ipation of the Cu 3d electrons in the Cu—O bond. This
is done by performing constrained variations where
the ability of the 3d orbitals to participate in the bond is
successively increased. We find that while the largest
part of the interaction energy between Cu and O is ob-
tained from the 4sp electrons, the Cu d electrons make
a significant contribution to the bond. Here also, we com-
pare Cu₂O and Cu₅ plus PC’s in order to determine the
nature of the d electron involvement in the bond; in par-
cular, its participation in covalent bonds.

We believe that the conclusions from our analysis for
SCF wave functions are qualitatively correct even though
we have not considered electron correlation effects.
Concern about the SCF description of the metal—O bond has
been expressed because only a small part of the inter-
action energies for cluster models of O/Ni(100),
O/Cu(100), and O/Ag(100) is obtained with SCF wave
functions. However, for the work in Refs. 7 and 10, the
interaction energy was calculated for dissociation into
neutral metal cluster and O units. It is well known that
this procedure does indeed yield poor SCF interaction en-
ergies for ionic systems. This is because the SCF ioniza-
tion potentials (IP’s), and, in particular, electron affinities
(EA’s) for the separated units are much smaller than the
experimental values. Thus, the error of the SCF Cu-O
interaction energy for Cu₂O does not arise because the SCF
description of the bond is incorrect. It arises because of
the poor SCF description on the IP of Cu₅ and the EA of
O. A good description of the interaction energy is given
by computing the SCF binding energy of Cu₂O with
respect to Cu₅⁺ and O⁻ units and correcting this value with
the experimental EA for oxygen and the experimental
IP for Cu₅ (or the work function for a Cu surface). For
Cu₂O, we obtain a SCF binding energy of 6.4 eV with
respect to the energies of Cu₅⁺ and O⁻. When this is
corrected with the work function of Cu(100), 4.6 eV,¹²
and the EA of oxygen, 1.5 eV,¹³ we obtain a binding ener-

gy, or Dₑ, of 3.2 eV = [6.4 − (4.6 − 1.5)]. This is smaller
than the binding of 5−6 eV estimated from experiment.²
This small value of Dₑ is not surprising because the pre-
cise value of Dₑ is difficult to determine with the cluster
model.¹⁴ However, the SCF Dₑ = 3.2 eV is ≥75% of the
value, Dₑ ≈ 4 eV, which is obtained with correlated
wave functions for Cu₂O.³,⁷,¹⁰ This ≤25% SCF error
arises because, as we shall show, the Cu—O bond has
some covalent character. This approach may have been
neglected in earlier work because the ionic character of
the bond has not been established until the present
work.

There are strong reasons to accept the SCF description
of the Cu—O bond, in particular, and the metal—O
bond, in general, as qualitatively correct. Given that this
is the case, we proceed with our discussion of the three
techniques for the analysis of the Cu—O bond.

II. ORBITAL PROJECTIONS

For the analysis of the ionicity of the Cu—O bond for
O/Cu(100), we use the projection of the O atomic orbit-
als, φᵢ, i = 1s, 2s, 2pₓ, 2pᵧ, from the Cu₂O wave function.
The expectation value P₁ of the projection operator for
φ, φ₁, is taken with the Cu₂O SCF wave function Ψ;

$$P₁ = \langle \Psi | \phi₁ | \Psi \rangle .$$  \hspace{1cm} (1)

The value of P₁ indicates the extent to which the orbital
φ is occupied in the total Cu₂O wave function Ψ, see
Ref. 15. Three different cases may be considered for P₁.
If P₁ ≈ 2, then φ is fully occupied in Ψ. If P₁ ≈ 0, then φ
is not occupied. The intermediate case 0 < P₁ < 2 indi-
cates that φ may be involved in a covalent bond with Cu.
In this case, it is necessary to consider that there is an
overlap between φ and the orbitals of the bare Cu₅ clus-
ter.¹⁵ It is possible to estimate the partial occupation of φ
in Ψ(Cu₂O), N₁, by taking this overlap into account by

$$N₁ = \langle \Psi(Cu₂O) | \phi₁ | \Psi(Cu₂O) \rangle - \langle \Psi(Cu₅) | \phi₁ | \Psi(Cu₅) \rangle .$$  \hspace{1cm} (2)

For the Cu₂O cluster with O at 1.9a₀ above the sur-
face, the projection of O orbitals from the Cu₂O wave
function was performed. This distance is close to the
equilibrium distance of O above Cu₅; the projections do
not depend strongly on the O distance from the Cu sur-
face and similar values are obtained for distances within
~0.25a₀ of the equilibrium. The SCF orbitals for neu-
tral O and anionic O⁻ have both been used for the pro-
jection to test if the choice of the O orbitals is important.
We find that the use of either set of orbitals, O or O⁻,
gives similar information about the character of the
Cu—O bond. This insensitivity to the choice of adsorb-
ate orbitals to be used for the projection is consistent with
earlier studies.¹⁵ The values of these projections are
given in Table I, where we also give the projections of the
O orbitals on the bare Cu₅ cluster.

We consider first the projections of the neutral O orbit-
als. The projections of the 1s and 2s are 2.00 and 1.99;
these orbitals are fully occupied. The projection of the 2p_o atomic orbital is 1.915 with only a 4% reduction from complete occupation. This small reduction arises in part from a change in the shape of the 2p_o orbital due to the oxygen ionicity in Cu_2O. When we project the O 2p_o orbital on Cu_2O, the projection is 1.964 or only 2% less than fully occupied. While the 2p_o orbital may be involved, to a small degree, in a covalent bond, it is essentially fully occupied. The projection of O(2p_o) on the bare Cu cluster is not negligible; ~0.25 for either O or O^- orbitals. However, this arises simply because the orbitals of interacting units overlap. Since the occupation of the 2p_x is so close to 2, it is not appropriate to use the correction of Eq. (2). On the other hand, the projection of the O(2p_x) orbital is 3.64 or 9% smaller than the complete occupation. In this case, the correction of Eq. (2) is appropriate to identify the polarity, or ionic character, to the Cu—O covalent π bond. The projection of O(2p_y) on Cu_2O is 0.22, leading to an estimate of the O(2p_y) of 3.43. It is, of course, impossible to completely separate ionic and covalent components of a bond when the orbitals on different subunits have a significant overlap. Thus, it is better to view the values using Eqs. (1) and (2) as providing bounds on the ionicity. Summing the O σ projections from Cu_2O, Eq. (1), and the π projections using both Eqs. (1) and (2), we obtain bounds on the O anionicity, ~q, of 1.33 < q < 1.55. Similar results are obtained from the projection of the O^- orbitals.

When there are ionic and covalent contributions to a bond, it is not possible to assign the bonding electrons uniquely to one subunit or another. However, the projections clearly indicate that O/Cu(100) is strongly ionic and there is also a significant covalent contribution, in particular, for the π bond. It also suggests that −1.5 is a reasonable estimate of the ionicity; other measures discussed in the following sections support this estimate.

III. DIPOLE MOMENT CURVES

As discussed elsewhere,^15^ the slope of the curve of the dipole moment versus the distance, in the region near the equilibrium bond distance, is an excellent indication of the ionicity of a bond. For an ideal ionic molecule denoted A^+B^- the slope of that curve is |−1|. Of course, this is an oversimplified model which does not include the effects of the polarization of A^+ by B^- and of B^- by A^+. In this section, we shall present an analysis of the dipole moment curve of Cu_2O, which takes this polariza-

### Table I. Projection of the O and O^- atomic orbitals on Cu_2O and on Cu_s.

<table>
<thead>
<tr>
<th></th>
<th>O/Cu_2O</th>
<th>O^-/Cu_2O</th>
<th>O/Cu_s</th>
<th>O^-/Cu_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>2.00</td>
<td>2.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2s</td>
<td>1.99</td>
<td>1.99</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>2p_x</td>
<td>1.91</td>
<td>1.96</td>
<td>0.09</td>
<td>0.16</td>
</tr>
<tr>
<td>2p_y</td>
<td>3.64</td>
<td>3.87</td>
<td>0.22</td>
<td>0.42</td>
</tr>
<tr>
<td>Total</td>
<td>9.55</td>
<td>9.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We consider the dipole-moment curves, μ(z) [here, μ is the z component of the dipole moment, the only nonzero component for the O/Cu(100) cluster model], for the motion of O normal to the surface. The curve is expanded in a Taylor series about z_e = 1.78a_0 which is the O equilibrium distance,

\[ μ = M_0 + M_1(z - z_e) + M_2(z - z_e)^2 + \cdots \]  

The Taylor expansions made using quartic polynomial fits to five points about z_e are given in Table II. We consider first the value of the dipole moment for Cu_2O at z_e, M_0 = +0.24 a.u. A simple formula is often used to relate the ionicity of an adsorbate to the difference between the surface dipole, or work function, for the bare and adsorbate covered surface. With this formula, the ionicity q is given by

\[ q = \frac{[\mu(\text{ads}) - \mu(\text{bare})]}{z} \]

The dipole moment of the bare Cu cluster is +0.004 a.u. and using the simple formula above O is positively charged by ~0.1 electrons. This is consistently obtained with the ionicity estimated above the projection operator. However, this simple formula neglects the polarization of the O and Cu_5 units; Pettersson and Bagus^16^ have shown that the change of the work function cannot be used as a guide to the ionicity of the adsorbate precisely because of these polarizations. Following the work of Nelin et al.,^15^ we shall show that the slope of the dipole-moment curve provides a useful indication of the adsorbate ionicity; one that is consistent with the results obtained by projecting the O character. We note, see Table II, that the dipole-moment curve is reasonably linear; the curvature M_2 is less than 1/3 of the slope M_1. This is a strong indication of an ionic bond. If the interactions were entirely ionic and if the polarization scaled linearly with adsorbate distance near the z_e, then the curvature M_2 would be zero. The fact that M_2 is not insignificant is consistent with an ionic bond which has some covalent character. The value of the slope should indicate extent of the ionicity but there is an uncertainty related to the polarization of Cu_5^+ and O^- . This can be seen by considering the dipole-moment curve for the motion of a test charge q normal to a metal surface. If the surface is not allowed to polarize in response to the test charge, then the slope of the dipole-moment curve is q. If, on the other hand, the surface is assumed to polarize and to form an image charge, the slope of the dipole-moment curve is 2q. The actual response of the Cu_5 cluster and the response of the oxygen anion put wide limits on our ability to relate M_1 = −1.2 to the O anionicity; we can only say that O

### Table II. Coefficients of the Taylor series expansions of the dipole-moment curves for the Cu_2O, Cu_5-PC1, and Cu_5-PC2 clusters; see Eq. (3). For Cu_5-PC1 and Cu_5-PC2, point charges of −1 or −2, respectively, interact with the Cu_s.

<table>
<thead>
<tr>
<th></th>
<th>Cu_2O</th>
<th>Cu_5-PC1</th>
<th>Cu_5-PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_0</td>
<td>0.24</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>M_1</td>
<td>−1.17</td>
<td>−0.70</td>
<td>−1.52</td>
</tr>
<tr>
<td>M_2</td>
<td>−0.36</td>
<td>−0.27</td>
<td>−0.47</td>
</tr>
</tbody>
</table>
has considerable anionicity. It is worth noting that the infrared adsorption-reflection intensity \( I \) for the vibration of \( O \) normal to the Cu surface is related to the slope of the dipole-moment curve by \( I \propto M \). It is possible, in principle, to determine \( M \) from measurements of \( I \) and this could provide experimental confirmation of our prediction of a large ionicity for \( O/Cu(100) \). Unfortunately, we are not aware of such measurements for \( O/Cu \).

In order to understand the polarizability of the \( \text{Cu}_5 \) cluster, we have obtained the dipole-moment curve for two clusters, where the \( O \) atom is replaced by a point charge. In the first case, \( \text{Cu}_5 \)-PC1, we place a point charge (PC) of \(-1\) above the \( \text{Cu}_5^{+} \); the total cluster is neutral. In the second case, \( \text{Cu}_5 \)-PC2, we place a point charge (PC) of \(-2\) above \( \text{Cu}_5^{+} \). The total cluster has charge \(-1\) because we do not wish to remove a second of the polarizable "conduction-band" Cu electrons. Our choice of total cluster charges will make the polarizability of the Cu substrate similar for \( \text{Cu}_5 \)-PC1, \( \text{Cu}_5 \)-PC2, and \( \text{Cu}_5 \)-O.

The general shape of the \( \mu(z) \) curve for \( \text{Cu}_5 \)-PC1 is similar to that of \( \text{Cu}_5 \)-O except that the slope and curvature, \( M_1 \) and \( M_2 \), are reduced by \( 30-40\% \). This suggests that a point charge with larger magnitude than \(-1\) is needed to represent the effective charge of \( O \) in \( \text{Cu}_5 \)-O. When the charge is increased to \(-2\) in \( \text{Cu}_5 \)-PC2, \( M_1 \) and \( M_2 \) are \( 30-40\% \) larger than for \( \text{Cu}_5 \)-O. A simple linear interpolation of the \( \text{Cu}_5 \)-O values for \( M_1 \) and \( M_2 \) between \( \text{Cu}_5 \)-PC1 and \( \text{Cu}_5 \)-PC2 gives an effective ionicity for \( O \) of \( \sim 1.5 \) electrons in agreement with the estimate obtained from the projection. These two tests give clear evidence for an \( O \) anionicity of \( 1.5 \). We turn now to an analysis of the contributions to the \( \text{Cu}--\text{O} \) bonding; in particular, the contribution of the \( d \) electrons.

IV. PARTICIPATION OF THE \( d \) ELECTRONS IN THE \( \text{Cu}--\text{O} \) INTERACTION

The constrained space orbital variation (CSOV) method provides a unique capability to separate the contributions to a chemical bond, including those arising from intranuclear polarization and from interunit charge transfer or covalent bonding.\(^{3,8}\) Our major concern for the CSOV analysis of the \( \text{Cu}--\text{O} \) bond is to quantify the importance of the \( 3d \) shell participation in the bond. As in the previous section, we compare the behavior of \( \text{Cu}_5 \) interacting with \( O \) and with a point charge \( q = -1 \), to represent the \( O \). The CSOV analysis applied to the \( \text{Cu}_5 \)-O and \( \text{Cu}_5 \)-PC1 clusters enables us to divide the \( d \) electron involvement in the bond into polarization in response to the charge on the \( \text{O} \) ion and into direct participation in the covalent chemical bond.

For the analysis of the \( \text{Cu}_5 \)-O and \( \text{Cu}_5 \)-PC1 clusters, the \( O \) or the PC is placed at \( 1.94a_0 \) above the Cu surface. The contributions to the bond are measured by the interaction energy \( E_{\text{INT}} \) taken with respect to the ionic limits. For \( \text{Cu}_5 \)-O the limits are \( \text{Cu}_5^{+} \) and \( O^{-} \) and \( E_{\text{INT}} \) is defined as

\[
E_{\text{INT}} = E(\text{Cu}_5^{+}; \text{O}^{-}; 3P) - E(\text{Cu}_5^{+}; 3A_2) - E(O^{-}; 3P)
\]  

(3)

and for \( \text{Cu}_5 \)-PC1 as

\[
E_{\text{INT}} = E(\text{Cu}_5^{+}; \text{PC1}; 3A_2) - E(\text{Cu}_5^{+}; 3A_2)
\]  

(4)

all the energies are computed at the SCF level. This choice of dissociation limits allows us to directly compare the \( \text{Cu}_5 \)-O and \( \text{Cu}_5 \)-PC1 results. It also avoids errors which arise from the limitations of the SCF description of the \( O \) electron affinity and the cluster ionization potential,\(^{9,11}\) and focuses on the chemical interaction between the ions. The results for the CSOV analysis for \( E_{\text{INT}} \) are given in Table III.

To start the CSOV process, we consider the interaction of the Cu 4sp conduction band with \( O \). This is accomplished by fixing the 140 Cu electrons corresponding to the Ar cores and the filled \( d \) shells of the Cu atoms as they are in the \( \text{Cu}_5^{+} \) cluster. We note that the choice of the \( \text{Cu}_5^{+} \) cluster \( d \) orbitals allows some small amount of \( d \) electron involvement in the Cu conduction band\(^{6,19}\) because of the \( d \rightarrow 4sp \) hybridization. However, this creates the correct conduction-band environment for the cluster and approximates that of the metal. In this first CSOV step, we vary, for \( \text{Cu}_5 \)-O, 13 electrons: the five Cu 4sp conduction-band electrons and the eight electrons arising from \( O \). The orbital space for this variation is the occupied \( \text{Cu}_5^{+} \) \( a_1 \) and \( e \) orbitals of the 4sp conduction band and the \( O \) occupied \( 1s \), \( 2s \), and \( 2p \) orbitals and the full set of virtual (or unoccupied) orbitals for both \( \text{Cu}_5^{+} \) and \( O \). For the \( \text{Cu}_5 \)-PC1 variation, four electrons are varied in the orbital space of the \( \text{Cu}_5^{+} \) \( a_1 \) and \( e \) conduction orbitals and all the virtual orbitals of \( \text{Cu}_5^{+} \). We chose this as a starting point because of the large ionic and covalent interactions of the Cu conduction band with \( O \). In other words, we do not attempt to separate this interaction into ionic and covalent contributions. Given the large overlap of the Cu conduction band with the \( O \) orbitals, such separation may, in any case, not be possible. We rely on the evidence obtained from the dipole-moment curves and the orbital projection to characterize the ionicity. At this step, the interaction of \( \text{Cu}_5 \)-O is 5.10 eV, with respect to the energies of \( \text{Cu}_5^{+} \) and \( O^{-} \) and the interaction of \( \text{Cu}_5 \)-PC1 is 7.99 eV with respect to the energy of \( \text{Cu}_5^{+} \); see Table III. The \( \text{Cu}_5 \)-O interaction energy is smaller because there is a nonbonding Pauli repulsion (or surface wall) between the \( O \) charge distribution and the Cu conduction-band charge;\(^{1,3,5,15}\) this repulsion is absent when the \( O \) is replaced by a point charge. We will see

<table>
<thead>
<tr>
<th>Step</th>
<th>Cu5-O</th>
<th>Cu5-PC1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.10</td>
<td>7.99</td>
</tr>
<tr>
<td>3</td>
<td>5.34/(0.25)</td>
<td>8.25/(0.26)</td>
</tr>
<tr>
<td>4</td>
<td>6.16/(0.81)</td>
<td>8.51/(0.25)</td>
</tr>
<tr>
<td>5</td>
<td>6.31/(0.14)</td>
<td>8.53/(0.02)</td>
</tr>
</tbody>
</table>

TABLE III. A CSOV analysis of the interaction energy \( E_{\text{INT}} \) of atomic oxygen and of a \(-1\) point charge with a Cu(100) surface cluster model, \( \text{Cu}_5 \)-O or \( \text{Cu}_5 \)-PC1; see text for the definition of the CSOV steps. The values reported correspond to the interaction with respect to the ionic limits in eV and the numbers in parentheses are the increase in \( E_{\text{INT}} \) relative to the previous step.
that the 5.1-eV interaction at this starting point is the largest contribution to the Cu-O interaction, ~80% of the total. However, the d electrons do make a significant, ~1 eV or 20%, contribution to the interaction. Electron correlation effects, as obtained, for example, through configuration interaction, would change the precise numerical values of the conduction-band 4sp and 3d contributions to the bond from the SCF values obtained in this work. However, there is overwhelming evidence both, in general, for cluster models of the adsorbate surface interaction and, in particular, for the O/Cu interaction that the SCF wave function gives a correct qualitative description of the bond.

We now turn to a variation of the 50 electrons arising from the closed Cu d shells. We fix the orbitals for the remaining 103 electrons (Cu2O cluster) or 94 electrons (Cu2-PC1 cluster) as they were in the CSOV step 1 wave functions. Two orbital spaces are used for the variation of the 50 Cu d electrons. In the first case, a virtual space is formed from the s, p, and d contracted basis functions for the Cu atom, which are in the region of space near the 3d shell. (Recall that the \( \langle r \rangle \) for the 3s, 3p, and 3d orbitals of the Cu atom are 0.723a_0, 0.757a_0, and 0.991a_0, respectively, as obtained from numerical Hartree-Fock wave functions. These have to be compared with \( \langle r \rangle = 3.331 \) for the 4s atomic orbital.) These virtual orbitals are added to the occupied 3d cluster orbitals to form the full orbital space for this variation denoted CSOV step 2A. Basically this step is performed to examine the polarization of the 3d electrons in the contracted or core region of space where they are distributed. For Cu2O, this CSOV step increases the interaction energy by 0.25 eV. This increase is likely to be due to the polarization of the d shell by the electric field arising from the adsorbate oxygen anion. We would expect that a similar change in \( E_{\text{INT}} \) would arise from replacing O by a point charge. We find that this is indeed the case for Cu2-PC1 where at the CSOV step 2A, \( \Delta E_{\text{INT}} = 0.26 \) eV.

We consider a more extended variation of the 3d orbitals in the CSOV step 2B. The orbitals, which are fixed, and the electrons, which are varied, are the same as in step 2A above. However, all of the Cu \(+\) and O virtual orbitals are included in the variational space for Cu2O. This step 2B allows the 3d electrons to hybridize with the Cu 4sp and O 2p orbitals and to form dative covalent bonds with O; this is in addition to the polarization of the 3d orbitals studied in the previous CSOV step 2A. For the Cu2-PC1 cluster, dative covalent bonding of the 3d with O is, of course, not possible; only 3d to 4sp hybridization can be induced by the electric field of the point charge. In Cu2O, the change in \( E_{\text{INT}}, \Delta E_{\text{INT}}, \) due to the 3d to 4sp hybridization and dative covalent bonding with O, is 0.81 eV; see Table III. In Cu2-PC1, \( \Delta E_{\text{INT}} = 0.25 \) eV, but, as noted above, only 3d to 4sp hybridization is possible here. In other words, at this step the d participation in the Cu—O bond contributes 0.56 eV to the interaction. As we noted above, the SCF wave function does not include correlation effects. In general, we expect that correlation effects will give an improved description of a covalent bond and will increase the d contribution to the Cu—O bond at this and future CSOV steps.

In the previous step, we have noted that we considered only d participation for dative covalent bonding with O. However, the d's can also participate in the covalent bonds between Cu 4sp and O. This can be studied by allowing rotation between the closed and open shells as obtained from the step 2B CSOV calculation. (For Cu2O, this mixing is important only for \( \epsilon^\prime \) symmetry where there is an \( \epsilon^\prime \) open shell; the \( \epsilon_\gamma \) symmetry contains only closed shells.) This closed-open mixing for the Cu2O CSOV step 3 contributes an additional 0.14 eV to \( E_{\text{INT}} \) due to d electron involvement in the Cu—O covalent bonding. The sum of the direct d involvement in the Cu—O bond from CSOV steps 2 and 3 is 0.70 eV = 0.56 (step 2B) + 0.14 (step 3). Finally, at step 4, we perform unconstrained full SCF calculations for Cu2O and Cu2-PC1; this is done to identify whether any important steps have been omitted from the CSOV sequence. We see that the improvements for \( E_{\text{INT}} \) for the full SCF over the last CSOV step are quite small, 0.04 eV for Cu2O and 0.02 for Cu2-PC1. Thus, the 0.7 eV given by the CSOV analysis is a correct measure of the contribution to \( E_{\text{INT}} \) due to the direct involvement of the Cu d electrons in the Cu—O bond. This is about 15% of the estimate of 5 eV for the heat of adsorption of O on Cu. We expect that the d involvement will become larger when electron correlation effects are included.

This value for the d involvement is larger than the one reported in previous work by Mattsson et al. and Wahlgren et al. This is because those works have not made a careful enough analysis of the d involvement and neglected some essential features of the interaction. Mattsson et al. have fixed the Cu cores as they are in the isolated atoms and have neglected the d hybridization to the Cu sp conduction band. Wahlgren et al. have not properly taken into account the large overlap between the Cu and O virtual orbitals. In effect, they have used Cu d orbitals to represent, albeit approximately, O atom character. We have been careful to avoid this source of error. In particular, our comparison of Cu interacting with a point charge has allowed us to clearly distinguish polarization from participation in the chemical bond. For Cu2O, the total d participation in the bond contributes 1.24 eV to \( E_{\text{INT}} \); this is the difference between \( E_{\text{INT}} \) for the CSOV step 1 and the full SCF. For the Cu2-PC1, the d contribution to \( E_{\text{INT}} \) is 0.53 eV and is due entirely to polarization of the d orbitals by the point charge representing O. The difference between Cu2O and Cu2-PC1, 0.7 eV, is the contribution to \( E_{\text{INT}} \) due to the presence of the O atom.

V. CONCLUSIONS

The bonding of atomic oxygen to Cu(001) with a surface cluster model has been analyzed by different techniques. It has been shown that this is a rather ionic bond with a net charge on the oxygen atom of about 1.5 electrons. This is supported by both orbital projection and dipole-moment curves. It has been found that the amount of d electron participation in the Cu—O bond is
about 0.7 eV. Our analysis supports the commonly held belief that the d electrons participate in the bond and provide an estimate for its energetic importance. In conclusion, the bond of atomic oxygen to a Cu(100) surface is rather ionic with a considerable participation of the d electrons in the bond.

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1Permanent address: Departament de Química Física, Facultat de Química, Universitat de Barcelona, E-08028 Barcelona, Spain.


9The oxygen basis set is (9s6p/4s3p) and was optimized to provide a fair description of both O and O-. For the Cu cluster atoms, the basis set was (14s9p6d/6s5p4d). The contraction scheme for the oxygen basis set was 6 + 1 + 1 + 1 + 1 + 1; for Cu it was 6 + 3 + 2 + 1 + 1 + 1 + 1, 6 + 1 + 2 + 1 + 1, and 3 + 1 + 1 + 1.


