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Small *ab initio* Cu(II) oxide cluster model with localized states and strong screening effects accompanying ionization

A. V. Kondratenko* and L. S. Cederbaum

Theoretical Chemistry Department, Institute of Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, D-6900 Heidelberg, Germany

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A neutral Cu(II) oxide CuO cluster with external point charges is studied in some detail. This cluster is small enough to allow the investigation of many-body effects by *ab initio* approaches. The electronic structure of the ground and low excited states as well as of core and valence ionic states of the cluster is discussed. We have thereby applied self-consistent-field, configuration-interaction, and Green's-function methods. The possibility is discussed that the cluster may serve as a model for solid-state Cu(II) oxides. The calculations show that the one-electron states of the cluster are strongly localized on either the copper or oxygen site. Strong screening effects are found to accompany the ionization of both valence and core metal levels of the cluster and result in many-electron shakedown satellites in the spectra. These effects are connected with an intense charge-transfer process from the occupied O $2p$ states to the vacant Cu $3d\sigma$ states in accord with predictions of non-parameter-free approaches (based on the Anderson impurity model, the Hubbard model, and other models) for the respective solid-state Cu(II) oxides. Connection is made with experimental x-ray-photoelectron and optical spectra. To substantiate the findings, the results of Green's-function calculations on ZnO and CuO$^-$ clusters are also discussed, which are of interest by themselves.

I. INTRODUCTION

For many years the right-hand-side transition $3d$-metal oxides have attracted attention in solid-state physics because widely used computational methods have very often failed to describe their electrical, magnetic, and spectroscopic properties. This situation still persists, for instance, for insulating monoxides of the right-hand side transition $3d$-metals, FeO, MnO, NiO, and CuO. For example, according to the standard local-density (LD) band theory the cupric oxide CuO has metallic electrical conductivity,[1-3] while in reality it is an antiferromagnetic semiconductor ($\varepsilon_{\text{gap}}=1.4$ eV, $T_{\text{Néel}}=230$ K), see Ref. 3 and references therein. In accordance with ideas of Mott[4] and Hubbard[5] this disagreement between LD band theory and experiment is roughly speaking due to the neglect of ground state many-electron correlation effects in standard LD band theory. On this ground the right-hand side transition $3d$-monoxides and similar compounds are referred to as highly correlated insulators or Mott-Hubbard insulators. The investigation of correlation effects in the ground state is a main task of the respective Mott-Hubbard insulator problem.[4-8]

There are additional many-electron aspects of this problem connected with the origin of fine structures in valence x-ray photoelectron spectra (XPS) of Mott-Hubbard insulators which could not be understood in terms of the LD band and cluster theories.[8-12] Generally speaking, one might expect that the LD band theory cannot reasonably describe the XPS of valence levels if it cannot describe the ground state of the system. Within the framework of the one-electron LD theory the valence XPS is intimately connected to ground-state electronic properties. It seems to be very important to understand why the one-electron LD band theory in its traditional forms does not correctly describe the ground-state properties of Mott-Hubbard insulators.

It should be mentioned that there are investigators who believe that, despite the fact that the LD band theory cannot describe the electrical and magnetic properties of the ground state of Mott-Hubbard insulators, the situation with the valence XPS is not so hopeless and use this method to calculate XPS of Cu(II) oxide-based high-T_c superconductors.[10,11,13]

The situation with XPS of core levels is more obvious because the extended fine structure here is a direct indication for strong many-electron effects which cannot be described in principle by any one-electron band theory. The appearance of this structure in the core XPS may serve as an indirect indication for strong many-electron effects in valence XPS, since the origins of these effects accompanying ionization of valence and core levels are related to each other. The occurrence of many-electron effects makes clear that it is necessary to investigate both the ground and highly excited ionic states of Mott-Hubbard insulators in detail. This applies in particular to high-T_c superconductors which are obtained by doping of Mott-Hubbard insulators. For instance, the LD band theory is unable to describe the electronic structure and the XPS of both the insulator La_2CuO_4 and the La_2CuO_4-based high-T_c superconductor $La_{1.85}Sr_{0.15}CuO_4$ with metallic conductivity above T_c.[9,14]

In order to describe the fine structure of core XPS,[15-22] valence XPS,[22-36] Auger electron,[20,35] x-ray absorption,[19,22,37–41] and x-ray emission[35,42,43] spectra of right-hand side transition 3*d*-metals compounds including Mott-Hubbard insulators and the respective high-T_c superconductors, alternative theories of electronic structure and of spectra have been developed. These approaches are based on the Anderson impurity model,[22,25,26,44–46] the Hubbard model,[23,24,28,35,36] the semiempirical cluster configuration interaction (CI) method,[30–34,47–49] and other methods.[9,50–53] Most of these approaches are collected in a recent book.[12] The underlying methods are based on the ideas of localized one-electron states (in contrast to the delocalized states as provided by the conventional band and cluster LD theories), and strong ligand-to-metal charge-transfer (CT) processes. The majority of these methods use the terms of cluster ligand-field (LF) theory where the valence one-particle basis states are either metal 3*d* or ligand *p* states. A possible hybridization between metal 3*d* and ligand *p* atomic one-particle states is believed to occur in the ground and ionized states of the system only as the result of CI mixing.

As a typical example we briefly mention the main features of the semiempirical cluster CI method used by Fujimori *et al.* on La_2CuO_4. According to Refs. 34 and 48 an adequate cluster of La_2CuO_4 is $CuO_6{}^{10-}$, the total ground state of which being represented mainly by a basis state with an electron configuration $3d^9L$, where L denotes the oxygen "band," that is, all the oxygen states with populations O $2p^6$. This basis state may mix with the basis state with an electronic configuration $3d^{10}\underline{L}$, where $\underline{L}$ denotes the oxygen band with one hole. The resulting final ionic states are determined as a mixture of the basis states $3d^8L$, $3d^9\underline{L}$, $3d^{10}\underline{\underline{L}}$. Using a CI-type semiempirical calculation to describe this mixture, an assignment of the valence XPS of La_2CuO_4 has been given which is in strong contradiction with the assignment predicted by LD theories. In the former calculations the first intense lines of the spectra have been ascribed mainly to $3d^9\underline{L}$ states and the second intense line to the $3d^8L$ states.

A similar assignment of the Cu(II) oxides valence XPS has been proposed by means of the Anderson impurity model,[22,25,26,27,29] the Hubbard model,[23,24,28,36] and other models.[53,54]

These many-electron methods leading to the latter assignment have also succeeded in describing fine structures of core XPS, x-ray absorption, and other spectra and, therefore, the underlying ideas became very popular especially among x-ray[55,56] and photoelectron[54,57–60] experimentalists. However, all these theories are "phenomenological" in nature and can describe the fine structure of the spectra quantitatively only when using a set of adjustable parameters. Consequently, the results of these non-parameter-free models are to be considered as only exploratory rather than confirmatory. Nevertheless, the central ideas of these non-parameter-free models, namely, the existence in Mott-Hubbard insulators of localized one-electron states and strong screening effects accompanying creation of a hole, seem to be very attractive and fruitful. In this paper we have, therefore, pursued the aim to develop an *ab initio* cluster model, which exhibits the localized one-electron states and strong screening effects accompanying ionization of core as well as valence metal levels.

II. CHOICE OF THE CLUSTER MODEL

To study a Mott-Hubbard insulator we have chosen Cu(II) oxide mainly because of its relevance in high-T_c superconductivity. As discussed in the Introduction, the cluster to be investigated as a model should fulfill several requirements. In particular, its one-electron states should be localized and strong screening effects should accompany the ionization of both metal core (Cu 2*p*) and metal valence (Cu 3*d*) levels.

Once the atoms constituting the cluster are specified, one has to determine the cluster's total number of electrons and to include in an appropriate way an external field to convey the influence of the crystal rest on the cluster. For Cu(II) oxide crystal one commonly uses a minimal standard cluster $CuO_6{}^{10-}$.[34,48,54,61,62] This cluster is chosen according to the traditional cluster approach rules. The six oxygen atoms in the cluster correspond to the sixfold coordination of the Cu in solid state Cu(II) oxides.[63] The number of additional electrons in the cluster is equal to ten according to the well-known ionic limit or formal valency model rules. By definition, the valence state of oxygen in any compound is two and the valence or oxidation state of copper, Cu(II), is calculated taking into account the chemical formula and electroneutrality principle. Thus, the oxidation state representation of the solid state oxide CuO is Cu(II)O(II) and, within the framework of the usual ionic limit model, its minimal cluster is $CuO_6{}^{10-}$, which can be imagined as the simple sum of one Cu^{2+} and six O^{2-} ions. It should be mentioned that solving a Schrödinger equation for the electronic structure of the cluster taking into account an external field goes beyond the ionic limit model. In particular, an accurate calculation results in atomic charges other than 2+ and 2− for Cu and O, respectively.

A main advantage of the traditional cluster approach is that one includes all the ligand atoms of the first coordination sphere of the metal atom, thus describing correctly the chemistry of this atom. This fact may be the main reason why the traditional cluster method has been shown by numerous calculations to be able to give a rather good description of the electronic structure and spectra of various transition metal compounds. However, for right-hand-side 3*d* transition-metal compounds this cluster approach seems to often fail in describing correctly the properties of both the ground and ionic states.[61,64,65] We believe that many problems of previous quantum chemical cluster investigations of right-hand-side 3*d* transition-metal compounds are partially connected with the too large negative charges chosen according to the traditional ionic-limit model. The additional electrons make the cluster a physically unreasonable and unstable system. The stabilizing external field can only partially compensate for the changes in the electronic system caused by these additional electrons. We believe that especially for such highly correlated solids as Mott-Hubbard insulators the traditional cluster approach is not adequate.

For this reason we have preferred in the present investigation to use neutral clusters for Mott-Hubbard insulators. The use of neutral clusters enables us to avoid ascribing to all atoms of the system integer oxidation states and as a consequence many additional electrons. This is particularly important for right-hand side transition 3*d* metal compounds for which the ideas about integer formal valencies of atoms in compounds seem to be inadequate.[1,66]

The choice of a neutral cluster is also important for studying oxidation (reduction) processes. These can be modeled by adding (removing) one electron from the electronic system of the cluster. Within the framework of a cluster approach this is a natural way to model doping processes such as the doping by $La^{3+}\rightarrow Sr^{2+}$ of the Mott-Hubbard insulator La_2CuO_4 leading to the metal $La_{1.85}Sr_{0.15}CuO_4$, which is known to be the first high-T_c superconductor.[67]

The above arguments allow us to choose smaller clusters which can be treated today by *ab initio* methods at a rather high level of accuracy taking thereby into account many-electron relaxation as well as correlation effects. Compared to the traditional approach a small cluster has the disadvantage that not all the ligand atoms of the first coordination sphere are included in the cluster. We would like to emphasize, however, that if the solid under consideration exhibits only weak covalent or hybridization effects but strong many-electron effects, the choice of a minimal cluster model seems rather adequate.

As a model of insulating Cu(II) oxides we consider here the smallest conceivable cluster CuO with two external point charges, 2− and 2+ (for technical details see next section). In order to avoid misunderstanding it should be mentioned that it is not *a priori* clear to what extent the results on our cluster CuO will be consistent with the properties of solid state Cu(II) oxides, in particular with the Mott-Hubbard insulator CuO. This paper mainly deals with the chosen cluster CuO as an *ab initio* cluster model exhibiting desired properties as localized one-electron states and strong screening effects.

III. METHODS AND TECHNICAL DETAILS

Two cluster model systems are studied in this work. The main system is a cluster CuO plus two stabilizing point charges: 2− on the side of the Cu atom and 2+ on that of O. The geometry is as follows (symmetry group of the system is $C_{\infty v}$): the interatomic distance Cu-O is chosen to be as in the CuO_2 plane in La_2CuO_4, i.e., 3.58 a.u.,[63] the distances between the copper atom and the point charge 2− and between the oxygen atom and the point charge 2+ are also equal to 3.58 a.u. The second cluster studied is ZnO. This cluster is investigated in connection with the so-called $Z+1$ model (see Sec. V A). Therefore, the geometry and external charges are taken to be the same as for the CuO cluster.

All the interesting states of the CuO and ZnO clusters were calculated by means of the self-consistent-field (SCF) method. For the states with the electronic configuration $1\pi^{-1}2\pi^{-1}$ the SCF wave functions consist of two determinants. In order to evaluate the role of CT and relaxation processes in screening effects we have performed calculations on all the relevant valence and core ionic states within the framework of the frozen-orbital approximation (FOA). In this approximation the molecular orbitals of the ground state of the cluster CuO are used to compute the ionic energies as a single configuration expectation value of the Hamiltonian.

For transition 3*d* systems an adequate treatment of correlation effects is believed to be very essential to obtain accurate excitations energies[68–70] and ionization potentials.[68–71] Therefore, CI calculations have been carried out for the most important neutral and ionic states. These calculations consist of single and double excitation CI with respect to the single-reference SCF configuration of the state in question. For the states with electronic configuration $1\pi^{-1}2\pi^{-1}$ we have performed double-reference singles-plus-doubles CI calculations in accordance with the two-determinant SCF wave functions. Excitations have not been allowed into the highest seven virtual orbitals constructed from the core atomic orbitals and having energy more than 900 eV. The CI calculations were repeated using the molecular orbitals of the ground state of the cluster CuO (referred to as CI-GS results in the following). The SCF and CI calculations were performed using the program package GAMESS.[72]

For the calculations on the anion CuO^- (anionic closed-shell state of the cluster CuO) and the cluster ZnO we have also used the Green's function (GF) method.[73–77] Let us briefly describe the main features of this method. For a system with a nondegenerate N-electron ground state $|\Psi_0^N\rangle$ the matrix elements of the so-called one-particle GF, $G(\omega)$, are in energy representation given by

$$G_{pq}(\omega)=\sum_n \frac{\langle\Psi_0^N|c_p|\Psi_n^{N+1}\rangle\langle\Psi_n^{N+1}|c_q^\dagger|\Psi_0^N\rangle}{\omega+A_n+i\eta} +\sum_n \frac{\langle\Psi_0^N|c_q^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|c_p|\Psi_0^N\rangle}{\omega+I_n-i\eta} .$$

Here $|\Psi_n^{N\pm1}\rangle$ denote the states of the $(N\pm1)$-particle system, and $c_q^\dagger$ and c_p stand for creation and annihilation operators of electrons in the SCF orbitals of the ground state. The pole positions of the G matrix constitute the ionization potentials I_n and electron affinities A_n and the residues give the pole strengths or spectroscopic factors $|\chi_n^p|^2$. All these quantities are directly related to experimental observables.

There exist several methods to evaluate the GF. In this paper we have used a method which is referred to as the third-order algebraic diagrammatic construction scheme, ADC(3).[75] The ADC(3) scheme has been found to be successful in the calculations of many molecules.[77] In the present applications the ADC(3) configuration space was constructed using 47 orbitals out of the 60 available SCF orbitals. Omitted are the six core orbitals and the highest seven virtual molecular orbitals with energy ≥900 eV. These are the counterparts to the six core orbitals and the molecular orbital related to the *s* combination of the Cartesian *d* functions. For completeness we mention that because of linear dependency problems the deletion of the latter Cartesian function from the basis set can be important for the transition $3d$-metal atoms on the right-hand side of the row.[78] In our case the presence of this function in the basis set has not led to such problems.

Let us now describe the basis sets used. Previous theoretical studies of transition-metal molecules indicated that rather extensive basis sets are required to account adequately for correlation effects.[68–70,78] Due to technical limitations we have used a medium-size basis set of double-ζ quality augmented by polarization functions. The Gaussian basis set of Cu (Zn) consists of Roos' *et al.*[79] $(12s6p4d)/[8s4p2d]$ basis set and two additional functions optimized to represent the $4p$ orbital. As recommended in Ref. 80 for molecules, the exponents are chosen as 0.232 597 and 0.069 298 (0.243 682 and 0.071 653 for Zn). Furthermore, we added to this set a set of d functions with exponent 0.1682 (0.1910 for Zn).[81] The oxygen basis set $(9s5p)/[4s2p]$ is based on Dunning's[82] double-ζ contraction of Huzinaga's primitive set.[83] To this basis set we have added a polarization d function with an exponent of 1.28.[84]

IV. GROUND AND LOW-LYING EXCITED STATES

A. *Ab initio* data

Let us first discuss the *ab initio* SCF results for the ground and some low-lying excited states of the CuO cluster, namely, for the four doublet states[85] which are the most probable candidates for the ground state of the cluster:

$$^2\Sigma(\mathrm{Cu}\ 3d\sigma^{-1}),^2\Pi(\mathrm{Cu}\ 3d\pi^{-1}),^2\Delta(\mathrm{Cu}\ 3d\delta^{-1}),\ \text{and}\ ^2\Sigma(\mathrm{O}\ 2p\sigma^{-1})\ .$$

The respective results are summarized in Table I. As can be seen from the table, the ground state of the cluster seems to be the $^2\Sigma(\mathrm{Cu}\ 3d\sigma^{-1})$ state[86] having the following electronic configuration:

$$1\sigma(\mathrm{O}\ 2s)^2 1\pi(\mathrm{Cu}\ 3d\pi)^4 1\delta(\mathrm{Cu}\ 3d\delta)^4 2\sigma(\mathrm{Cu}\ 3d\sigma)^1 3\sigma(\mathrm{O}\ 2p\sigma)^2 2\pi(\mathrm{O}\ 2p\pi)^4\ .$$

As indicated by the atomic orbital in parentheses, the molecular orbitals of the ground state are strongly localized. Obviously this state of the cluster has to be referred to as the ligand field (LF) state arising from a Cu $3d^9$ occupation of a Cu^{2+} ion having a single hole in the Cu $3d$ shell. In other words, in terms of holes the ground state of the cluster CuO has the configuration $2\sigma^{-1}$ or, more approximately, Cu $3d\sigma^{-1}$.

TABLE I. Total energies E_n and Mulliken analysis data for some states of the CuO cluster obtained by SCF and CI calculations as well as the orbital energies ε_n and ionization potentials I_n of the closed-shell cluster CuO^- obtained by means of the SCF and GF methods. For comparison the results of LD calculations and the experimental optical spectrum of the solid state Cu(II) oxide $\mathrm{YBa_2Cu_3O_{6.5}}$ are also shown. All energies in eV.

Cluster state characterization	SCF Atomic populations	Atomic charges	ΔE_n	CI ΔE_n	FOA $\Delta\varepsilon_n$	GF ΔI_n	Experiment solid $\mathrm{YBa_2Cu_3O_{6.5}}$ (Ref. 90) ΔE
CuO							
$2\sigma^{-1}\,{}^2\Sigma$ $3d^9L$	Cu $4s^{0.05}$Cu $4p^{0.15}$ Cu $3d^{9.02}$O $2p^{6.05}$	Cu$\cong+1.89$ O$\cong-1.89$	0.00[b]	0.00[b]	0.00[c]	0.00[c]	
$1\pi^{-1}\,{}^2\Pi$ $3d^9L$	Cu $4s^{0.07}$Cu $4p^{0.15}$ Cu $3d^{9.00}$O $2p^{6.05}$	Cu$\cong+1.88$ O$\cong-1.88$	0.41	0.36	2.21	2.36	1.7
$1\delta^{-1}\,{}^2\Delta$	Cu $4s^{0.07}$Cu $4p^{0.15}$ Cu $3d^{8.97}$O $2p^{6.05}$	Cu$\cong+1.89$ O$\cong-1.89$	1.22	1.24	2.82	3.34	2.7
$2\pi^{-1}\,{}^2\Pi$					4.37	4.26	4.7
$3\sigma^{-1}\,{}^2\Sigma$ $\cong 3d^{10}\underline{L}$	Cu $4s^{0.24}$Cu $4p^{0.12}$ Cu $3d^{9.66}$O $2p^{5.23}$	Cu$\cong+1.11$ O$\cong-1.11$	8.82	7.11	6.09	6.42	
CuO($X\alpha$)[a]							
$2\sigma^{-1}\,{}^2\Sigma$	Cu $4s^{0.21}$Cu $4p^{0.18}$ Cu $3d^{9.47}$O $2p^{5.27}$	Cu$\cong+1.11$ O$\cong-1.11$	0.00[d]				
$2\pi^{-1}\,{}^2\Pi$	Cu $4s^{0.31}$Cu $4p^{0.15}$ Cu $3d^{9.60}$O $2p^{5.04}$	Cu$\cong+0.91$ O$\cong-0.91$	-2.25				

[a] The results (Ref. 102) of the LD calculations are obtained by means of the $X\alpha$ discrete-variational method.

[b] The ground state total energies E_n calculated by the SCF and CI methods are -1714.3878 and -1714.8697 a.u., respectively.

[c] The orbital energy $\varepsilon_{2\sigma}$ and ionization potential $I_{2\sigma}$ of the cluster CuO^- are equal to 1.24 and 0.49 eV, respectively.

[d] Total energy of this state is -1710.0639 a.u.

The next state, the LF state $^2\Pi$ has the electronic configuration

$$1\sigma(\mathrm{O}\ 2s)^2 2\sigma(\mathrm{Cu}\ 3d\sigma)^2 1\delta(\mathrm{Cu}\ 3d\delta)^4 1\pi(\mathrm{Cu}\ 3d\pi)^3 3\sigma(\mathrm{O}\ 2p\sigma)^2 2\pi(\mathrm{O}\ 2p\pi)^4 ,$$

which in terms of holes corresponds to $1\pi^{-1}$ or approximately to Cu $3d\pi^{-1}$. This state has an energy of 0.41 eV above the ground state. The third LF state $^2\Delta(\mathrm{Cu}\ 3d\delta^{-1})$ has an energy of 1.22 eV. The fourth $^2\Sigma$ state lies 8.82 eV above the ground state and also has rather well localized one-electron states as do the ground $^2\Sigma$ as well as the excited $^2\Pi$ and $^2\Delta$ states. This state, however, should be referred to as a charge-transfer (CT) state, because it has the following electronic configuration:

$$1\sigma(\mathrm{O}\ 2s)^2 2\sigma(\mathrm{Cu}\ 3d\sigma)^2 1\delta(\mathrm{Cu}\ 3d\delta)^4 1\pi(\mathrm{Cu}\ 3d\pi)^4 3\sigma(\mathrm{O}\ 2p\sigma)^1 2\pi(\mathrm{O}\ 2p\pi)^4 ,$$

that is, $3\sigma^{-1}$ or O $2p\sigma^{-1}$. Note that this CT state is derived from a Cu $3d^{10}$ occupation of the ion Cu^+ and results from the transfer of one electron from the O 2*p* orbitals to the Cu 3*d* orbitals. It has been discussed in Ref. 87 that for right-hand side transition 3*d* metal compounds LF as well CT states may serve as a ground state. For instance, the ground state of the free molecule CuO [$R_{\text{Cu-O}}=3.2584$ a.u. (Ref. 88)] is a CT one, O $2p\pi^{-1}$.[68,69] The same is found in this work to be valid for our cluster CuO ($R_{\text{Cu-O}}=3.58$ a.u.) when the point charges are removed. Thus, the role of the point charges is to provide the cluster CuO system with the desired LF ground state Cu $3d\sigma^{-1}$, which can thus be a rather adequate model of Cu(II) oxides. As mentioned above all the cluster orbitals in these three states are essentially localized either on Cu or O sites. This is also reflected by the Mulliken population analysis and shows that the bonding in this cluster is very ionic on the *ab initio* SCF level.

Since electron correlation effects may be of great importance[70] for transition 3*d* metal molecules, we have augmented the SCF results on these states by CI calculations. The results of these calculations are also given in Table I. We find that correlation effects do not substantially change the results obtained at *ab initio* SCF level for the three LF states. The change in the relative energies (excitation energies) of the states when going from the SCF to CI level amounts only to 0.05 eV. The natural orbitals of these LF states computed on the CI level are found to be localized. All these features are due to the fact that the CI wave function is dominated by the respective reference SCF configuration in all these LF states. The coefficients C of these configurations are equal and amount to 0.96. In contrast to the LF states, the CI wave function of the CT $^2\Sigma(\mathrm{O}\ 2p\sigma^{-1})$ state is a mixture of the O $2p\sigma^{-1}$ ($C\cong0.91$) and Cu $3d\sigma^{-1}$ ($C\cong0.27$) configurations. This leads to a strong delocalization of the natural orbitals and to a deviation of the relative energy from the SCF one of about 1.71 eV.

We have also performed GF calculations on the closed-shell anion CuO^- of our cluster in order to obtain its ionization potentials I_n. These determine the relative total energies ΔE_n of the neutral states of the cluster CuO. According to these GF data which are shown in Table I the ground state of the cluster CuO is indeed the state $^2\Sigma(2\sigma^{-1})$, having the smallest ionization potential (0.49 eV). There are, however, quantitative differences between the GF and the CI and SCF data concerning the relative energies of the cluster CuO states as can be easily seen from Table I.

The GF results seem to be able to give reasonable estimates of the optical transition energies for Cu(II) oxides. Two *d-d* transitions are predicted which have energies 2.36 and 3.34 eV. Further splittings can be expected because of the crystal field. This is consistent with some of the interpretations of optical spectra of Cu(II) oxides, which have assigned the two broad peaks with energies 1.7 and 2.7 eV to *d-d* transitions.[89,90] Calculations using the model Hamiltonian method (cluster $\mathrm{CuO}_4{}^{6-}$) and *ab initio* second-order Moller-Plesset perturbation theory [clusters $\mathrm{Cu(OH_2)}_n{}^{m+}$] have been carried out for the *d-d* transitions and yield smaller values 1.4 eV (Ref. 53) and 1.3–1.8 eV,[91] respectively. SCF and CI seem to underestimate the *d-d* transition energies. For the first transitions we have obtained by means of SCF and CI methods, 0.41, 1.22, and 0.36, 1.24 eV, respectively. We notice the fact that the FOA data (orbital energies $-\varepsilon_n$) and GF data are in good quantitative agreement with each other and the experimental optical transition energies (see Table I). Finally, it is interesting to note that our CuO^- cluster is predicted by the GF approach to be stable with respect to electron loss and that the opposite is predicted on the SCF and CI levels of approximation.

In the literature the traditional point of view[89] is that the strong absorption broad peaks with energies above 3 eV in optical spectra of the monoxides are due to the ligand to metal CT transitions. On the grounds of our GF calculations we predict two CT transitions with energies 4.26 and 6.42 eV. The first of these transitions could be assigned to the peak at 4.7 eV in the experimental spectrum[90] of the solid. We are not aware of any optical measurements of Cu(II) oxides in the region close to and above 6 eV. As has been already pointed out[89] such an assignment of the optical data rules out the model for high-T_c superconductivity where the existence of low-lying CT excitations has been postulated to mediate the pairing of the holes.[92] It rather seems to support the models which assume pairing due to the exchange of spin excitations.[93,94]

B. LD theory results

The above *ab initio* results for the ground and low-lying excited states strongly contradict those of LD calculations discussed in the following. The LD band calculations carried out for Cu(II) oxides, as CuO,[1-3] La_2CuO_4,[95,96] etc., have yielded an essentially delocalized one-electron state picture.[14] A similar picture of delocalized orbitals has been obtained[61,97] using the LD $X\alpha$ discrete-variational[98] and $X\alpha$ scattered-wave[99] methods for the conventional CuO_6^{10-} and CuO_6^{9-} clusters. It is believed to be typical for solid-state transition-metal compounds as oxides, sulfides, etc., and, therefore, these compounds have been regarded as coordination compounds with three-dimensional spatial chemical bonds.[100,101] Our present results show a distinctly different picture than the traditional ones obtained with the LD band and cluster methods. We attribute the discrepancies to shortcomings in the LD exchange-correlation potential used and to the inadequate choice of the cluster (in the case of the cluster approaches). A closer investigation of these topics is beyond the scope of this paper. Nevertheless, we mention that we are inclined to the opinion that the LD approximation not only fails to give a good description of the electric (transport) and magnetic properties, but apparently also of the valence one-electron states structure of right-hand-side $3d$ transition-metal oxides.

A direct indication for this opinion are the results of calculations[102] performed by means of LD $X\alpha$ discrete-variational method on the same CuO cluster as studied in this paper. The results of these LD $X\alpha$ calculations are also collected in Table I and the computational details can be found elsewhere.[61,62] The ground state of the CuO cluster is a CT one, namely, $^2\Pi$ with the electronic configuration $2\pi^{-1}$. All the σ and π one-electron states are relatively strong mixtures of the O $2p$ and Cu $3d$ atomic orbitals in strong contradiction with our *ab initio* SCF and CI results on the same cluster. The state $^2\Sigma$ with the electron configuration $2\sigma^{-1}$ is found in the LD approach to have an energy about 2.25 eV larger than that of the state $2\pi^{-1}$ and it has strongly delocalized one-electron states of σ symmetry. Moreover, for both states the $X\alpha$ atomic populations are rather far from the respective integer numbers and the atomic charges are closer to 1 rather than to 2. According to LD band calculations[1] the Mulliken populations of the solid state CuO are as follows:

$$\text{Cu } 4s^{0.52}\text{Cu } 4p^{0.66}\text{Cu } 3d^{9.79}\text{O } 2s^{1.75}\text{O } 2p^{4.27} .$$

As can be easily seen, they are not close to our *ab initio* SCF results (see Table I) and seem to be rather far from reliable values too.

We conclude that the present CuO cluster treated by means of *ab initio* methods is a rather adequate model for Cu(II) oxides. It has the desired ground-state properties, namely, strongly localized one-electron states, appropriate Mulliken populations of Cu $3d$ and O $2p$ states, which are very close to the respective integer numbers 9 and 6, respectively, and meaningful values of other electronic structure characteristics such as atomic charges, etc.

V. VALENCE LEVELS IONIZATION

A. Theoretical ionization spectrum

In this section we discuss the valence ionic states of the CuO cluster. The ionic states obtained by ionizing core levels are investigated in the next section. The results for the total energies E_n and ionization potentials I_n of the valence hole states computed by the FOA, SCF, and CI methods are summarized in Table II.[85] In order to make clear the nature of the ionic states we use here two different types of notations. One in terms of holes (namely, the cluster's parent closed-shell one-electron states), for instance, $2\sigma^{-1}2\pi^{-1}\,{}^3\Pi$ which means that the state $^3\Pi$ of the ion CuO^+ has the electronic configuration

$$1\sigma^2 1\pi^4 1\delta^4 2\sigma^1 3\sigma^2 2\pi^3 .$$

The other one is the LF theory notation in which $3d^9\underline{L}$ means that this $^3\Pi$ state has one hole in the Cu $3d$ shell and one hole in the O $2p$ shells of the ligand atoms. Note that using the LF notation is meaningful as long as the calculations on the ionic states studied show that the localized one-electron states picture is valid and that the populations of Cu $3d$ and O $2p$ atomic orbitals are close to the respective integer numbers. This is indeed the case for most ionic states studied here. The exceptions are all the states with electronic configuration $1\pi^{-1}2\pi^{-1}$. In these states the σ orbitals obtained with the SCF method are strong mixtures of Cu $3d\sigma$ and O $2p\sigma$ atomic orbitals. Nevertheless, also in these cases the populations of Cu $3d$ and O $2p$ atomic orbitals are close to 9 and 5, respectively, and we may still use the notation $3d^9\underline{L}$.

Before discussing in some detail the theoretical ionization spectrum of the cluster we first recall that main lines correspond to ionic states where an electron is ejected from a one-particle state (orbital). Satellite lines correspond to ionic states where one electron is ejected and another one is excited. Satellite lines can appear in a photoelectron spectrum only because of correlation and/or relaxation effects and "borrow" their intensity from a (or several) main line. For a classification of satellites, see Ref. 103.

At first we discuss the results of our FOA calculations on the ionization potentials. As can be seen from Table II the ground state of the ion CuO^+ is the CT state $2\sigma^{-1}2\pi^{-1}\,{}^3\Pi$. Since the neutral ground state of the cluster is $2\sigma^{-1}$, the ionic ground state corresponds to the removal of an electron from the oxygen one-electron state 2π and thus to the 2π main line in the theoretical ionization spectrum of the cluster CuO. This result is consistent with the *ab initio* generalized valence bond calculations of Goddard *et al.*[65] and *ab initio* second-order Moller-Plesset perturbation theory calculations of Cartiss and Tam[91] on various clusters representing the $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ classes of high-temperature superconductors. It is also consistent with recent experimental observations[41] that the doped holes in the $YBa_2Cu_3O_{7-\delta}$ ($0 \le \delta \le 0.5$) are off-plane CuO_2 oxygen holes [provided, of course, that doping ($\delta \ge 0$) only implies the removal of electrons from the copper oxide]. Thus, the first ionization process leads to the creation of a hole in the O $2p^6$ shell (reduction of the oxygen by doping) rather than in the Cu $3d^9$ shell [oxidation of Cu or creation of Cu(III) atoms by doping]. The ionization of the metallic 2σ (Cu $3d\sigma$) open shell needs essentially more energy than that of the ligand 2π (O $2p\pi$) orbital. The ionization potentials of the respective states $2\sigma^{-2}$

and $2\sigma^{-1}2\pi^{-1}$ differ by 8.6 eV on the frozen orbital level of approximation.

The lower part of the theoretical ionization spectrum of the valence levels of the cluster CuO corresponds mainly to CT $3d^9\underline{L}$ states. The part of the spectrum at larger energy corresponds mainly to the $3d^8L$ states. It has to be referred to the main lines of the oxygen 2π and 3σ levels and to the satellites which are related to electronically excited states accompanying the ionization of the metallic levels 1δ, 1π, and 2σ. The upper part consists of the Cu $3d$ main lines 1δ, 1π, and 2σ, which, on the FOA level, have ionization potentials ranging from

TABLE II. Ionization potentials I_n of the CuO cluster calculated by the frozen orbital approximation (FOA), SCF, and CI methods. The division in four subgroups is done according to the results of the FOA. Note that many ionic states have similar energies and the ordering of these states may strongly depend on the method chosen.[g] For comparison the relative peak positions of the experimental valence XPS for the solid-state cupric oxide CuO are shown as well. Ionization potentials in eV.

Experiment (Ref. 2) Solid CuO peak	ΔI	State characterization	FOA[f] cluster CuO ΔI_n	CI-GS[f] cluster CuO ΔI_n	SCF cluster CuO ΔI_n	CI cluster CuO ΔI_n
D,E[e]	0.0	$2\sigma^{-1}2\pi^{-1}\,{}^3\Pi$ $3d^9\underline{L}$, main line 2π	0.00[b]	0.00[b]	0.00[b]	0.00[b]
		$2\sigma^{-1}2\pi^{-1}\,{}^1\Pi$ $3d^9\underline{L}$, main line 2π	0.08	0.09	0.06	0.08
		$1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^-$[g] $3d^9\underline{L}$, CT satellite of 1π	0.63	0.64	0.63 (−10.28[a])	0.41[d]
		$1\pi^{-1}2\pi^{-1}\,{}^3\Delta$ $3d^9\underline{L}$, CT satellite of 1π	1.62		0.64	
		$1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^+$ $3d^9\underline{L}$, CT satellite of 1π	0.66		0.66	0.68[d]
		$1\pi^{-1}2\pi^{-1}\,{}^1\Sigma^+$ $3d^9\underline{L}$, CT satellite of 1π	1.80		0.70	
		$1\delta^{-1}2\pi^{-1}\,{}^3\phi$ $3d^9\underline{L}$, CT satellite of 1δ			1.10[a]	
C	2.4	$1\pi^{-1}3\sigma^{-1}\,{}^3\Pi$ $3d^9\underline{L}$, CT satellite of 1π	4.02	3.97	3.51	3.34
		$2\sigma^{-1}3\sigma^{-1}\,{}^3\Sigma^+$ $3d^9\underline{L}$, main line 3σ	2.71	3.44	3.51	3.61
		$1\delta^{-1}3\sigma^{-1}\,{}^3\Delta$ $3d^9\underline{L}$, CT satellite of 1δ	3.97	4.36	4.04	3.84
B	6.9	$1\delta^{-1}2\sigma^{-1}\,{}^3\Delta$ $3d^8L$, main line 1δ	5.71	4.66	3.70	3.99
		$1\pi^{-1}2\sigma^{-1}\,{}^3\Pi$ $3d^8L$, main line 1π	6.70	5.31	4.11	
A	9.3	$2\sigma^{-2}\,{}^1\Sigma^+$ $3d^8L$, main line 2σ	8.60	6.40	5.76	4.51
		$1\pi^{-1}2\sigma^{-1}\,{}^1\Pi$ $3d^8L$, main line 1π	8.50	7.07	5.65[c]	
		$1\delta^{-1}2\sigma^{-1}\,{}^1\Delta$ $3d^8L$, main line 1δ	8.27	6.89	6.31	6.10
		$2\pi^{-2}\,{}^3\Sigma^-$ $\cong 3d^{10}\underline{\underline{L}}$, CT satellite of 2π	21.30	7.39	11.24	

[a] SCF calculations have been carried out with broken spatial symmetry (see text).

[b] Total energies E_n of the state $2\sigma^{-1}2\pi^{-1}\,{}^3\Pi$ calculated by FOA, CI-GS, SCF, and CI methods are −1713.9637, −1714.4859, −1714.0624, and −1714.5120 a.u. The respective ionization potentials are 11.54, 10.44, 8.85, and 9.73 eV.

[c] For these singlet states our SCF procedure did not converge. The energy of these states has been calculated with the molecular orbitals of the corresponding triplet states, $1\delta^{-1}2\sigma^{-1}\,{}^3\Delta$, etc.

[d] Results of double-reference CI calculations.

[e] This value 0.0 eV corresponds to the peak D. The value for the peak E is equal to −1.9 eV.

[f] The energies of the ionic states have been calculated with the molecular orbitals of the ground state of the cluster CuO (frozen orbitals). The ionization potentials are calculated on the single-configuration level (FOA) and beyond (CI-GS).

[g] According to a GF calculation on the cluster CuO$^-$ (Ref. 123) the state $1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^-$ is the ground ionic state, i.e., the ground state of the cluster CuO$^+$ (high-spin states have not been computed).

5.71 to 8.27 eV.

The most interesting feature of the theoretical ionization spectrum of the CuO cluster is that the computed satellites of the Cu 3*d* main lines are found to be shake-down satellites. In other words, their ionization potentials are smaller than those of the respective main lines from which they borrow their intensity. These main lines correspond to the ionization of the metal Cu 3*d* states of the cluster.

As has been discussed above the one-electron states of the CuO cluster are localized and the Mulliken populations are close to integer numbers. This enables us to interpret the calculated shake-down satellites in the spectrum as charge transfer satellites accompanying ionization of the Cu 3*d* levels (more precisely as ligand 2*p* to metal 3*d* states CT satellites). Thus, already the simple FOA calculations show that our cluster model exhibits strong electrostatic screening effects accompanying ionization of metallic 3*d* levels leading to shake-down satellites (with zero intensities on the FOA level, of course).

Let us now discuss the results of the SCF (ΔSCF) calculations on ionic states and their ionization potentials thus taking into account the relaxation effect, i.e., rearrangement of one-electron states of the cluster under influence of a created hole, accompanying ionization. As can be easily seen in Table II the relaxation effect does not essentially change the results obtained on the FOA level. According to the SCF data the ground state of the ion CuO^+ is also the CT state $2\sigma^{-1}2\pi^{-1}\,{}^3\Pi$. The Mulliken populations of this ionic ground state are as follows:

$$\mathrm{Cu}\ 4s^{0.09}\mathrm{Cu}\ 4p^{0.08}\mathrm{Cu}\ 3d^{8.98}\mathrm{O}\ 2p^{5.11}\ .$$

They are rather close to the integer numbers 9 for Cu 3*d* and 5 for O 2*p* orbitals and allow us to use for this state the LF notation Cu $3d^9\underline{L}$. As on the FOA level there are shake-down satellites of the Cu 3*d* main lines between the O 2*p* and Cu 3*d* main lines although the energy splittings between these two groups of main lines and between the Cu 3*d* shake-down satellites and Cu 3*d* main lines have become essentially smaller. A possible explanation of this effect is proposed later.

In order to clarify the effect of electron correlation on the discussed SCF results we have calculated several ionic states via CI. As can be seen from the respective data of Table II, with a few exceptions (see below) the correlation has proven to play here only a minor role concerning the interpretation of the ionic states and the photoionization spectrum. The correlation effects taken into account by single reference (two for electronic configuration $1\pi^{-1}2\pi^{-1}$) singles-plus-doubles CI calculations have not essentially changed the SCF wave functions of all the investigated states. Indeed, the coefficients of the respective reference SCF states in the CI wave functions are always more than 0.94 and the natural orbitals resemble the molecular orbitals.

Qualitatively similar results have been obtained when using for the CI calculations on the ionic states the molecular orbitals of the ground state of the CuO cluster (CI-GS data in Table II). We probably have to use more sophisticated methods in order to be able to take into account all important correlation effects for the valence ionic states of the cluster CuO.

In connection with this discussion we can report on a very interesting result obtained for the state $1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^-$ on the SCF level. We have succeeded in computing both the spatially broken and spatially correct SCF solutions for this state (see Table II). Breaking the spatial symmetry (C_{2v} instead of $C_{\infty v}$) shows up through the nonequivalence of the π_x and π_y one-electron states. While the $1\pi_y$ and $2\pi_y$ states are found to be localized either on Cu or O, the $1\pi_x$ and $2\pi_x$ are strong mixtures of Cu 3*d* and O 2*p* atomic states. The most interesting feature of the symmetry broken solution is that its energy is 10.91 eV lower than the energy of the proper symmetry solution. As can be seen in Table II, this covers 88% of the correlation energy of the state $1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^-$ computed by the CI method. Although being of interest by itself, this result also indicates that correlation and delocalization effects do play a role in these CT ionic states. The nature of these effects is not fully clear yet.

Lst us make some remarks concerning the relation between the ionic ground state of the cluster and the ground state of the respective solid-state doped Cu(II) oxides, high-T_c superconductors. As can be seen from Table II there are several CT states with energy close to the ionic ground state $2\sigma^{-1}2\pi^{-1}\,{}^3\Pi$ of the CuO cluster, for instance, the state $1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^-$. It is clear that the present methods are not sufficiently accurate to determine the ground state beyond doubt. It is very interesting to note that according to GF calculations (see Ref. 123) the above ${}^3\Sigma^-$ state is the ground ionic state of the cluster. Furthermore, the relative energies of the states may strongly depend on the field of external point charges. Our cluster model calculations are not adequate enough to make a definite conclusion on the nature of the ground state of the respective doped crystal. In particular, we cannot say which of the CT states of Table II with relative ionization potentials ranging from 0.00 to 0.70 eV is indeed the most probable candidate to clarify the microscopic mechanism of oxidation or doping the insulating Cu(II) oxides. For example, we can imagine that the most adequate candidate for this purpose is the CT state $1\pi^{-1}2\pi^{-1}\,{}^3\Sigma^-$ because it has delocalized σ one-electron states that could favor metallic conductivity (an insulator-metal or Mott-Hubbard transition) and superconductivity of the doped Cu(II) oxides. In such a case we assume that the nature of the states near the Fermi surface is complicated and it becomes necessary to revise our understanding of the microscopic mechanism of electrical conductivity because of the breakdown of the standard one-electron theory for states near the Fermi level. Of course, the states near the Fermi energy are those on which the attention is focused in high-T_c superconductivity studies.[27,41,47,49,53,106–111] The present results on the model CuO cluster indicate that the most probable candidates for the ground state of the ionized (or doped) species are the local triplet or singlet states of $3d^9\underline{L}$ character rather than those of $3d^8L$ character. This finding is consistent with the predictions of the Anderson impurity model,[27] of the model Hamiltonian cluster method,[53] and of the semiempirical cluster CI approach.[47]

B. Assignment of experimental valence XPS of the solid state Cu(II) oxides

It is interesting to compare our theoretical ionization spectrum of the cluster with the experimental valence XPS of the solid state Cu(II) oxides, for instance, of cupric oxide CuO. This comparison is made in Table II and Fig. 1. On the grounds of our theoretical results we assign the first band composed of the peaks *C*, *D*, and *E* of the experimental spectrum to the oxygen main lines 2π, 3σ, and the shake-down satellites of the copper $3d$ levels 1π and 1δ. The second band composed of the peaks *A* and *B* of the experimental XPS are mainly due to the copper 1δ, 1π, and 2σ main lines. As can be seen in Table II the results of the simple FOA calculations are in the best agreement with experimental relative ionization potentials for the solid-state oxide CuO. Moreover, according to the FOA data all the ionic states obviously subdivide into four groups with remarkable energy gaps, the latter being in good agreement with the energy distances between the experimental XPS maxima *D*, *C*, *B*, and *A*. On the grounds of these FOA data we can therefore do more detailed assignment of the fine structure of the experimental valence XPS as has been shown in Table II and Fig. 1. Note that GF calculation on the cluster CuO^- (Ref. 123) have yielded results that are in good agreement with the FOA data concerning the four remarkable energy gaps discussed above.

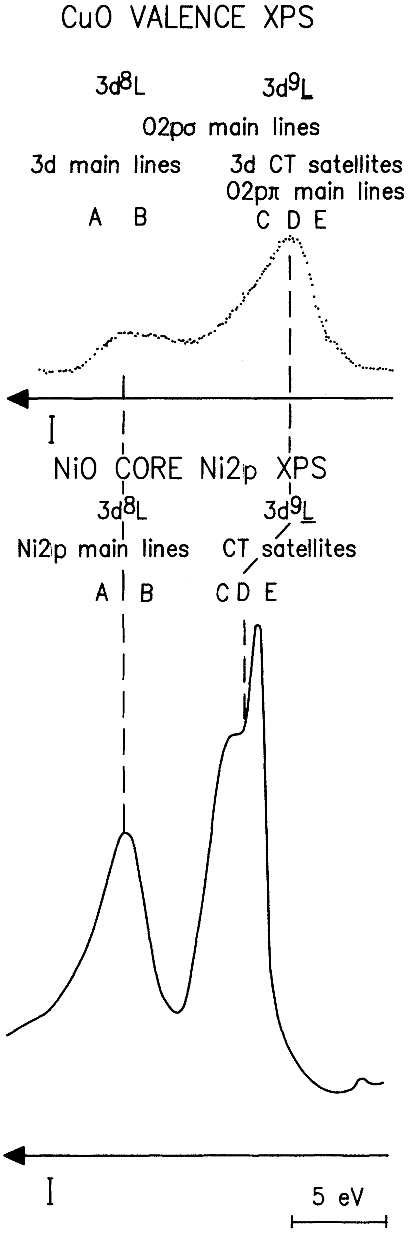

FIG. 1. Assignment of the bands of the experimental valence XPS of the solid-state oxide CuO (Ref. 2) and core Ni $2p$ XPS of the solid-state oxide NiO (Refs. 8 and 120) made according to the results of the *ab initio* cluster model.

The SCF method has yielded data on the cluster that are in worse agreement with experimental ones on the solid. For instance, according to these SCF data there is no energetical gap between the $3d^9L$ and $3d^8L$ states and the SCF theory seems to strongly underestimate the energy splittings between Cu $3d$ and O $2p$ main lines. As an explicit example we mention the $^3\Delta$ $(1\delta^{-1}2\sigma^{-1})$ $-{}^3\Pi(2\sigma^{-1}2\pi^{-1})$ splitting which is 3.7 eV on the SCF level and smaller by about 3 eV than the experimental *D*-*B* gap.

This underestimation with respect to experiment and the FOA and CI-GS data may be mainly due to the shortcomings of the present cluster model/or due to electronic correlation effects that we do not properly take into account with the present CI which builds on the SCF orbitals. Although the applicability limits of our cluster model are not clear yet, we are inclined to think that the lack of correlation effects is responsible for this underestimation of the Cu$3d$–O$2p$ splittings. In other words, the SCF method seems to be not particularly reliable for the right-hand transition-metal compounds. To support this opinion we quote results of our investigation of the molecule CuOH.[87] In this case we have found that the SCF splitting between the Cu $3d$ and O $2p$ main lines is smaller than the respective GF splitting by about 3.0 eV ($\cong 1.4$ eV for ZnO—see Sec. V). Moreover, the GF ionization potentials I_n are in good quantitative agreement with respective FOA ones, i.e., with Koopmans' values, $-\varepsilon_i$, for this closed-shell molecule. Thus, for this molecule the relaxation and correlation contributions to ionization potentials of Cu $3d$ levels are rather large by magnitude but of opposite signs and tend to compensate each other as in the case of ligand levels ionization.[74] We suppose that for Cu(II) oxides this compensation effect also exists at least partially, and therefore the FOA ionization potentials are in better agreement with experimental ones than the SCF values.

Concluding the comparison of our theoretical results with the experimental data, let us note that our assignment made on the grounds of calculations of the cluster CuO can be regarded only as a tentative one because of that we have not calculated XPS line intensities at all.

We conclude that our assignment of the experimental valence XPS bands (not fine structure) of the solid-state cupric oxide CuO made on the basis of energy calculations on the CuO cluster is consistent with the assignment made with the help of the non-parameter-free approaches based on the Anderson impurity model,[22,25–27,29,59] the Hubbard model,[23,24,28,36] the semiempirical cluster CI method,[30,34,47–49] and others[12,53] (see discussion in Sec. I). As far as the origins of the maxima *A* and *B* are concerned, this assignment is also in accordance with the conclusions made for oxide CuO (Ref. 104) and for high-T_c superconductors[58,105] on the grounds of resonant Cu $2p \rightarrow$Cu $3d$ XPS experiments. There, these maxima have been identified as arising from the $3d^8L$ states. It should be mentioned that the nature of the "mystery" peak *B* (see discussion in Ref. 36) deduced from these experiments is in contrast to the extended-Hubbard model-based interpretation.[36] According to this interpretation this peak has to be identified as arising from the states with two holes localized on nearest-neighbor oxygen atoms. Of course, such states cannot be described in our cluster model.

C. Determination of Coulomb and charge transfer parameters

It is of special interest to calculate *ab initio* the most important parameters of the Anderson impurity and Hubbard models, the ligand to metal charge transfer energy parameter Δ, and the Coulomb *d-d* interaction parameter *U*. Those are usually defined as follows:[29]

$$\Delta = E(3d^{10}\underline{L}) - E(3d^9L), \quad U = I_{3d} - A_{3d} ,$$

where I_{3d} and A_{3d} are the minimal ionization potential and electron affinity of the $3d$ level of the system:

$$I_{3d} = E(3d^8L) - E(3d^9L) ,$$

$$A_{3d} = E(3d^9L) - E(3d^{10}L) .$$

According to our GF data A_{3d} is equal to 0.49 eV (it is the ionization potential of the Cu $3d\sigma$ level of the CuO$^-$ cluster, see Table I). As an estimation of the I_{3d} we can use the CI ionization potential for the 1δ level of the CuO cluster which equals 13.72 eV. Thus, the *ab initio* estimate for the parameter *U* is 13.23 eV. To calculate the parameter Δ we use the GF ionization potentials of the 2π and 2σ levels of the CuO$^-$ cluster. We obtain the value 4.26 eV which can be related to the maximum 4.7 eV of the $YBa_2Cu_3O_{7-\delta}$ optical spectrum which has been assigned to CT transitions.[90] The values for *U* and Δ are satisfactorily consistent with those obtianed by fitting the results of the Anderson impurity [9.36 and 2.75 eV (Ref. 27)] and the extended Hubbard [10.2 and 1.0 eV (Refs. 35 and 36)] models to the experimental valence XPS data. In particular, the Coulomb parameter *U* is much larger than the CT energy parameter Δ. Therefore, we have to refer the modeled insulating Cu(II) oxides to the CT insulators on the grounds of the phase diagram of Zaanen *et al.*[29,112]

VI. CORE-LEVEL IONIZATION AND Z+1 MODEL

A. Green's-function results on the ZnO cluster

The method of GF can be used to calculate both the ionization potentials I_n and spectroscopic factors $|\chi_n^p|^2$ which are related to the relative intensities of XPS lines. The available approximation scheme discussed in Sec. III applies, however, to closed-shell systems only and cannot be used directly for CuO. According to the so-called $Z+1$ model, Cu core hole states of the CuO cluster are "similar" to valence hole states of the cluster ZnO with respect to their valence electronic structure. The GF calculation on the ZnO cluster can be carried out because it is a closed-shell system. The solid-state oxide ZnO is a wurtzite-type semiconductor[113,114] and is important by itself. It is worthwhile to discuss the results obtained for the ZnO cluster and to compare them with the experimental valence XPS data on solid ZnO (Refs. 113 and 114) and the core XPS of solid CuO.[2]

We have performed the SCF and GF calculations on the ZnO cluster (see Sec. III). According to our calculations the ZnO cluster has the following ground-state properties. The valence electronic configuration is closed-shell:

$$1\sigma(\mathrm{O}\ 2s)^2 1\delta(\mathrm{Zn}\ 3d\delta)^4 1\pi(\mathrm{Zn}\ 3d\pi)^4 2\sigma(\mathrm{Zn}\ 3d\sigma)^2 3\sigma(\mathrm{O}\ 2p\sigma)^2 2\pi(\mathrm{O}\ 2p\pi)^4 .$$

As indicated in parentheses all the one-electron states of the ZnO cluster are essentially localized as are those of the CuO cluster. The Mulliken populations are as follows:

$$\mathrm{Zn}\ 4s^{0.17}\mathrm{Zn}\ 4p^{0.15}\mathrm{Zn}\ 3d^{9.98}\mathrm{O}\ 2p^{6.06} .$$

We may conclude from these facts that the chemical bonding in this cluster (and probably also that in the respective solid-state oxide ZnO) is strongly ionic. The ground state can be referred to as a LF Zn $3d^{10}$O $2p^6$ or, equivalently, Zn $3d^{10}L$ state.

The results of the GF calculation on the valence hole states of the ZnO cluster, i.e., ionization potentials I_n, spectroscopic factors $|\chi_n^p|^2$ and relative intensities P_n of the theoretical valence XPS are collected in Table III and Fig. 2 together with the experimental valence XPS data of the solid-state oxide ZnO. The relative intensities P_n of the valence XPS lines have been calculated within the framework of the independent scatterers model of Gelius[115] thereby making use of spectroscopic factors computed by the GF method, the atomic orbitals Mulliken populations of the cluster's one-electron states, and the atomic photoionization cross sections calculated by the Fock-Dirac method.[116]

TABLE III. Theoretical valence XPS of the ZnO cluster calculated by the SCF and GF methods and the experimental valence XPS of the solid-state oxide ZnO. Shown are SCF orbital energies ε_p, ionization potentials I_n, spectroscopic factors $|\chi_p^n|^2$, and relative intensities P_n. All energies in eV.

Experiment (Ref. 113) Solid-state ZnO XPS band intensity	ΔI	State characterization	$-\varepsilon_p$	SCF^a ZnO cluster I_n	ΔI_n	GF ZnO cluster I_n	ΔI_n	$\lvert\chi_p^n\rvert^2$	P_n
C, weak	0.0	$2\pi(\mathrm{O}\ 2\pi)^{-1};3d^{10}\underline{L}$	11.62	8.90	0.00	10.45	0.00	0.92	7
B, weak	3.0	$3\sigma(\mathrm{O}\ 2p\sigma)^{-1};3d^{10}\underline{L}$	13.78	12.01	3.11	13.33	2.88	0.92	5
A, strong	5.8	$2\sigma(\mathrm{Zn}\ 3d\sigma)^{-1};3d^{9}L$	19.91			17.84	7.39	0.90	45
		$1\pi(\mathrm{Zn}\ 3d\pi)^{-1};3d^{9}L$	20.18			18.05	7.60	0.92	99
		$1\delta(\mathrm{Zn}\ 3d\delta)^{-1};3d^{9}L$	20.56	15.53	6.63	18.50	8.05	0.92	100
		$1\sigma(\mathrm{O}\ 2s)^{-1}$	31.85			26.40	15.95	0.12	5
						28.90	18.45	0.24	11
						29.10	18.65	0.06	3
						29.31	18.86	0.16	7
						29.63	19.18	0.26	11
						29.76	19.31	0.01	0.5

[a] The ground-state total energy calculated by the SCF method is −18 853.1762 a.u.

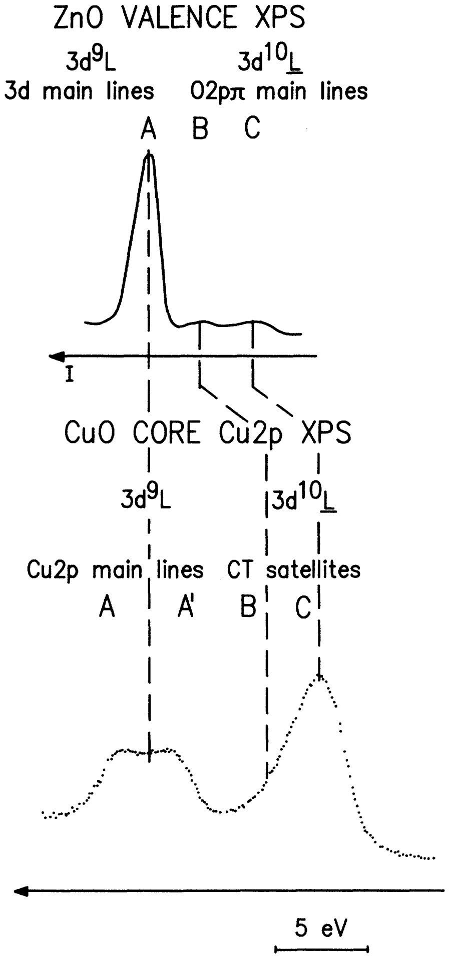

FIG. 2. Assignment of the bands of the experimental valence XPS of the solid-state oxide ZnO (Ref. 113) and core Cu 2*p* XPS of the solid-state oxide CuO (Ref. 2) made according to the results of the *ab initio* cluster model.

As can be seen from Table III, the theoretical XPS of the ZnO cluster consists of four band systems which can without difficulty be assigned to originate from definite one-electron states of the cluster. The outermost two bands (10.45- and 13.33-eV binding energy) are due to the 2π and 3σ states, respectively, having localized O 2*p* origin. In terms of holes the respective ionic states have the electronic configurations $2\pi^{-1}$ and $3\sigma^{-1}$ and in terms of LF notation they have the occupation configuration $3d^{10}\underline{L}$. The third band with energy ranging from 17.84 to 18.50 eV is determined by the 2σ, 1π, and 1δ one-electron states of Zn 3*d* and the respective ionic states are of $3d^9L$ type. The fourth band system extends from 26.40 to 29.76 eV and corresponds to multiple states all originating from the inner shell one-electron state 1σ(O 2*s*), i.e., all acquiring their intensities from the 1σ orbital. This band system is seen to have typical many-electron character.[103]

It can be concluded from Table III and Fig. 2 that the theoretical results on the cluster (energies and intensities) are in good agreement with the known experimental valence XPS of the solid-state oxide ZnO. This gives some evidence for having chosen an adequate cluster. On the other hand, the good agreement between theory and experiment allows us to use the theoretical data for the assignment of the experimental XPS as has been done in Table III and Fig. 2.

The most interesting feature of the theoretical data for the ZnO cluster is that the GF ionization potentials I_p are surprisingly close to the respective FOA ones, i.e., to the SCF ground-state orbital energies, $-\varepsilon_p$, for both the O 2*p* and Zn 3*d* levels of the cluster. Usually the ionization potentials of transition-*d*-metal compounds are about 5 eV smaller than the respective orbital energies ($-\varepsilon_p$) as far as *d* levels of these compounds are concerned.[117–119] These shifts result from substantial relaxation effects following the ejection of an electron from a localized *d* orbital. The fact that ionization potentials on the Koopmans' level ($-\varepsilon_p$) and on a more sophisticated level (here GF) can be approximately equal for $3d$ levels has been established by us in Ref. 87 for the molecule CuOH and the cluster CuO^- with an external positive charge $Q=+1$ which may serve as a cluster *ab initio* model for solid-state Cu(I) oxides. We have shown in Ref. 87 that this approximate equality between I_p and $-\varepsilon_p$ is a consequence of practically a total compensation of two large quantities with opposite signs: relaxation and correlations contributions to the ionization potentials of the localized $3d$ levels of the molecule and the cluster. Unlike the situation in localized core levels where the relaxation strongly dominates electron correlation effects, the correlation effects may be substantially enhanced in localized inner-valence levels for d^{10} compounds. Comparing the SCF and GF ionization potentials in Table III we can see that the situation for the ZnO cluster can be explained in analogy to the one for the Cu(I) oxides although the compensations seems to be more perfect in the latter systems. Thus, despite the fact that there is "good" agreement between the one-electron orbital energies and GF ionization potentials, we have to refer to the ZnO cluster (and probably also to the solid-state oxide ZnO) as a highly correlated system in the sense that there are large many-electron effects, relaxation, and correlation, accompanying ionization of the localized $3d$ levels.

Obviously, the SCF ionization potentials will strongly deviate from the exact ones for systems which exhibit the above discussed compensation effect. For instance, for the 1δ level of the cluster ZnO this deviation is equal to about 3.0 eV (see I_n in Table III). The O $2p\pi$–Cu $3d\delta$ splitting on the SCF level is smaller than the respective GF value by about 1.4 eV (see also discussion in Sec. IV B).

In conclusion let us note that the assignment of the experimental valence XPS of the solid-state ZnO made in Table III and in Fig. 2 is consistent with the traditional one[114] made on the grounds of empirical tight-binding band method calculations. Our *ab initio* cluster calculations thus support the traditional point of view on the electronic structure of the practical important solid-state oxide ZnO.[113,114]

B. Core hole states of the CuO cluster

On the grounds of the $Z+1$ model and the GF results on the valence XPS of the ZnO cluster we can now assign the core Cu $2p$ XPS of the CuO cluster. The experimental spectrum is depicted in Fig. 2. The first two overlapping peaks in the spectrum correspond to $3d^{10}\underline{L}$ states and the higher peaks A and B to $3d^9L$ states. Taking into account that the ground state of the CuO cluster has the configuration $3d^9L$, we may conclude that the first two overlapping peaks in the core XPS are shake-down satellites due to CT from O $2p$ to Cu $3d$ and that higher lying peaks (7–8 eV above the first peaks) correspond to the removal of a single electron without additional excitations. As expected, the present assignment of the solid-state XPS is consistent with that made on the grounds of the Anderson impurity and the Hubbard model based approaches[12,20–22,35] and of other non-parameter-free approaches.[2,9,15,54]

In order to support the results of the preceding subsection we have also carried out SCF calculations on the five core hole states of the CuO cluster constituting the Cu $2p\sigma$ XPS. The SCF data on the cluster and the experimental Cu $2p$ XPS data for the solid-state CuO are collected in Table IV. It seems that there is rather good agreement between theory and experiment. The agree-

TABLE IV. SCF data for core hole states of the CuO cluster and the experimental Cu $2p_{3/2}$ XPS of the solid-state cupric oxide CuO. Ionization potentials I_n in eV.

Experiment (Ref. 2) Solid-state CuO			FOA cluster CuO	SCF cluster CuO
XPS band	ΔI	State, characterization	ΔI_n	ΔI_n
C,B	0.0[c]	Cu $2p\sigma^{-1}2\pi^{-1}\,{}^3\Pi$ $3d^{10}\underline{L}$, CT satellite $2\pi\rightarrow 2\sigma$	0.00[a]	0.00[a]
		Cu $2p\sigma^{-1}2\pi^{-1}\,{}^1\Pi$ $3d^{10}\underline{L}$, CT satellite $2\pi\rightarrow 2\sigma$	0.07	0.02
		Cu $2p\sigma^{-1}3\sigma^{-1}\,{}^3\Sigma$ $3d^{10}\underline{L}$, CT satellite $3\sigma\rightarrow 2\sigma$	2.82	3.07
		Cu $2p\sigma^{-1}3\sigma^{-1}\,{}^1\Sigma$ $3d^{10}\underline{L}$, CT satellite $3\sigma\rightarrow 2\sigma$	2.90	3.16
A'	$\cong$7.5	Cu $2p\sigma^{-1}2\sigma^{-1}\,{}^3\Sigma$ $3d^9L$, main line Cu $2p\sigma$	17.32	7.68[b]
A	$\cong$10.0	Cu $2p\sigma^{-1}2\sigma^{-1}\,{}^1\Sigma$ $3d^9L$, main line Cu $2p\sigma$	20.95	10.97

[a] The total energy of the state Cu $2p\sigma^{-1}2\pi^{-1}\,{}^3\Pi$ calculated by the FOA and SCF methods are -1679.1928 and -1679.6371 a.u. The respective ionization potentials I_n are 957.66 and 945.57 eV.

[b] For this ${}^3\Sigma$ state our SCF procedure did not converge. The energy of this state has been calculated with the molecular orbitals of the corresponding singlet state Cu $2p\sigma^{-1}2\sigma^{-1}\,{}^1\Sigma$.

[c] This value 0.0 eV corresponds to the peak C.

ment with the GF results of the $Z+1$ model described in the preceding subsection is also satisfactory. For instance, both the SCF on the core level of CuO and the GF on ZnO lead to splittings between the shake-down satellites and main lines which are similar and agree satisfactorily with the respective experimental parameter of about 9.0 eV for the Cu $2p$ XPS of the solid-state CuO. Of course, the singlet-triplet splittings are not accounted for in the $Z+1$ model. These splittings are small for the $3d^{10}\underline{L}$ states and substantial for the $3d^{9}L$ states. Consequently, the peak A in the spectrum of ZnO splits into the peaks A and B for CuO (see Fig. 2).

Although the electrostatic screening is correctly described by the FOA (CT satellites have become shake-down ones), this approximation overestimates substantially the splittings between the main lines and the shake-down satellites. Here, the SCF method leads to values that are in good agreement with experimental ones. The nature of this phenomenon is clear. In contrast to the case of valence ionization where relaxation and correlation effects are of the same order of magnitude but often of opposite signs, the relaxation effect is the dominating many-electron effect for ionization of core levels. Note that the possibility of occurrence of shake-down satellites in core XPS on the FOA level due to electrostatic screening has been first shown for the N $1s$ XPS of paranitroaniline.[124]

C. A comment on the core XPS of NiO

The data obtained for the cluster CuO valence hole states can be used to assign bands of the core Ni $2p$ XPS of the solid-state oxide NiO.[8,120] Thereby we follow the $Z+1$ model used above. Namely, the valence hole states of the cluster CuO can be related to the core hole states of the cluster NiO, and, in turn, the latter states can be used for assigning the solid-state oxide NiO Ni $2p$ (and Ni $1s$ too) XPS. We tentatively assign the first band system in the Ni $2p$ XPS (Ref. 120) ($I \cong 854$ eV) to the shake-down CT satellites and the second band system ($I \cong 862$ eV) to the Ni $2p$ main line (see Fig. 1). Note that the Cu-O distance in the CuO cluster used here (3.58 a.u.) is smaller than the Ni-O distance in the solid-state NiO (3.93 a.u.). The details of the geometry corrected calculations can be found elsewhere.[121]

VII. BRIEF SUMMARY

In this paper we have discussed a small *ab initio* cluster model of Mott-Hubbard insulators [Cu(II) oxides] which exhibits localized one-electron states. With the help of *ab initio* many-electron calculations which have been performed by means of SCF, CI, and GF methods it has been shown that the electronic structure of such a system with localized one-electron states is highly interesting. In particular, the creation of a hole on either the valence or core metal levels causes strong screening effects through the CT from occupied O $2p$ states to Cu $3d\sigma$ states vacant in the ground state of the cluster. Due to these effects there appear in the valence and core XPS of the cluster shake-down satellites. The *ab initio* results obtained in this paper are generally (not in the details) consistent with the data obtained earlier with the help of non-parameter-free approaches for the Cu(II) oxides, i.e., the Anderson impurity model, the Hubbard model, and so on. And thus, of course, they are in strong contradiction with the results of one-electron LD band and cluster methods. This gives evidence about the inability of the LD theory to describe adequately the ground, low excited neutral, and ionic states of Cu(II) oxides and may be of Mott-Hubbard insulators in general.

Although the Cu(II) oxides are referred to as highly correlated systems, the ground and ionic states under consideration can be partially described rather well by the SCF method since the studied many-electron correlation effects did not change drastically the SCF wave functions of most states. This conclusion was made by studying the structures of the computer CI wave functions. Our finding is in contrast to the suggestion of the non-parameter-free models[27,31–33,122] about the strong configuration interaction in the ground and ionic states. We would like to emphasize, however, that in these models one cannot distinguish between mixing of basis states and true correlation effects since the SCF is not computed, and the correlation energy is defined with respect to the restricted (spin and spatial symmetry) SCF level.[125]

In the present investigation on the CuO cluster we have used a moderate basis set and moderate-quality CI. We have thereby assumed that the presence of the external charges and the present choice of a neutral CuO justify the above treatment, while for molecules and negatively charged models with transition-metal atoms a better treatment is necessary.

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*Permanent address: Institute of Inorganic Chemistry, Siberian Branch of the U.S.S.R. Academy of Sciences, Lavrentiev av. 3, Novosibirsk 630090, U.S.S.R.

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[86] The ground state of the cluster CuO without point charges is the CT state O $2p\pi^{-1}$ and when the effects of the external point charges are taken into account, the ground state becomes the LF state Cu $3d\sigma^{-1}$. Unfortunately we could not make SCF calculations on the O $2p\pi^{-1}$ state for the cluster CuO with two point charges 2− and 2+ because of convergence difficulties. But it has been done for the LF state Cu $3d\pi^{-1}$ with the same symmetry. This is an indirect indication for the fact that the state O $2p\pi^{-1}$ is of higher energy than Cu $3d\pi^{-1}$. Moreover, we have carried out SCF calculations on the cluster CuO with two point charges 1− and 1+ and have obtained that for this system the state O $2p\pi^{-1}$ has higher energy ($\cong 0.15$ eV) than the state Cu $3d\sigma^{-1}$. On these grounds we assume that the state Cu $3d\sigma^{-1}$ is indeed the ground state of the cluster CuO with the point charges 2− and 2+.

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