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P. S. Bagus, F. Illas, and C. Sousa

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Excited states of MgO: A cluster model study

P. S. Bagus
IBM Research, Almaden Research Center, 650 Harry Road, San Jose, California 95120

F. Illas
IBM Research, Almaden Research Center, 650 Harry Road, San Jose, California 95120
and Departament de Quimica Fisica, Facultat de Quimica, Universitat de Barcelona, C/Marti i Franques 1, 08028 Barcelona, Spain

C. Sousa
Departament de Quimica Fisica, Facultat de Quimica, Universitat de Barcelona, C/Marti i Franques 1, 08028 Barcelona, Spain

The character of low-lying excited states of MgO has been examined using cluster models of the MgO crystal. Several different clusters were used; in general, the clusters contained a central Mg atom, one or more shells of nearest-neighbor Mg and O atoms, and a large number of point charges to represent the Madelung potential in the space of the atoms explicitly included in the cluster. The excited orbital was occupied in two ways. First, an electron was added to a low lying excited level while the Mg^{2+} and O^{2-} anion levels were kept fully occupied. In the second way, an electron was excited from the oxygen $2p$ band into a low lying excited level. The excited orbitals, for both of these cases are very similar. Although the energetics of the excited states depended on the cluster model, in particular whether it was Mg or O terminated, the general character of the excited orbital remained the same. In all clusters, the excited state orbital was diffuse and delocalized. The excited orbital has no simple or direct relationship to the $3s$ orbital of Mg^{2+}. It is best described as a "conduction band" orbital. It extends up to and beyond the edge of the atoms explicitly included in the cluster. In our work, we did not find any evidence for localized excitonic states.

I. INTRODUCTION

Since the original work of Sugano and Shulman, nearly 30 years ago,[1] ground state and related electronic structure properties of ionic systems have been widely analyzed in terms of cluster model wave functions. In addition to the *ab initio* theoretical treatments, see, e.g., Refs. 2–12, there has also been extensive use of model Hamiltonians[13–19] where the Hamiltonian is parameterized with the use of experimental data. Zaanen, Sawatzky, and Allen have proposed a simple localized model to describe the band gaps and the electronic structure of transition metal compounds.[13] Based on this work, Torrance *et al.*[14–16] have proposed a simple ionic model to classify 76 oxides in terms of their electrical behavior. A localized model has also been used by Van der Laan *et al.*[17] to interpret the x-ray absorption spectrum of TiO_2. A closely related approach was suggested by Fujimori *et al.*[18,19] to interpret photoemission, optical–absorption and isochromat spectra of nickel compounds. Very recently an *ab initio* approach has been used to study ground state properties and optical excitations in the alkaline–earth oxides.[20,21] However, a detailed study of the character of the excited electronic states (or orbitals) in these oxides has not yet been carried out. It is the aim of the present work to examine, within the context of the cluster model approach, the character of these states. A major concern is whether the cluster model can provide an acceptable representation of the unoccupied "conduction band" (CB) levels. Further, we will address whether the O ($2p$) to CB excitations have an excitonic character.

Based on *ab initio* cluster model calculations for the ground state and for the electronic excited states, where an extra electron is added to the cation or transferred from the highest occupied molecular orbital (HOMO) mainly of oxygen $2p$ "band" character, to the lowest unoccupied molecular orbital (LUMO) it is a critical conclusion that this CB orbital does not have any clear or direct connection to the cation "ns" orbital. The reason there is no relationship between the CB and the Mg $3s$ orbital is that the space of the $3s$ orbital is, to a large extent, occupied by the O^{2-} anion charge distributions. In all clusters, the CB orbitals extend to the edge of the cluster and have significant amplitude in the region of the point charges used to provide a representation of the Madelung potential.

We demonstrate that the CB orbitals cannot be localized in the region of the cluster. They are delocalized over the entire cluster region and extend into the space where point charges (PCs) are used to represent the Mg^{2+} and O^{2-} ions. This nonlocal character is indicated by the $\langle r^2 \rangle$ which shows that the CB orbitals extend up to and beyond the outermost atoms contained in the cluster. This is true for all the clusters in a rather wide range of sizes that we have examined. Our cluster models range from the simplest one consisting of a single cation surrounded by an array of point charges, to larger clusters involving the first oxygen anion neighbors, MgO_6, the cations surrounding each anion of the previous cluster, $Mg_{19}O_6$, or a more compact cluster, $Mg_{13}O_{14}$, with three layers, each a square, consisting of nine ions. All these cluster models have been

embedded in an appropriate Madelung field represented by an array of point charges.

Since the MgO conduction band orbitals are delocalized, it may not be appropriate to use cluster models to describe excited states which involve occupation of these orbitals. On the other hand, the d orbitals of transition metals (TM) ionic crystals are localized.[12,13,18,19,22] It may, indeed, be appropriate to use clusters and the methods of quantum chemistry to describe excitations to these states. In particular, they will be appropriate for charge transfer processes between the ligand anion and the TM d levels and between the d levels of different TM cations.[21]

Our conclusions are obtained for MgO which represents a limiting case of extreme ionic character.[20,23-25] However, it has been proved that the nature of the chemical bond in alkaline-earth oxides does not change appreciably from MgO to BaO.[20,23-25] Thus, we feel that they are representative of the general situation in alkaline-earth oxides and, also, for excited levels in transition metal oxides which involve the participation of the diffuse outer ns/np levels of the cation as opposed to the localized d levels.

II. COMPUTATIONAL DETAILS

In this work we have used a variety of cluster models to represent bulk MgO. For comparative purposes we start with a single metal atom surrounded by a set of point charges chosen and optimized to represent the Madelung potential;[26] this cluster will be referred to as Mg(PCs). Our next model incorporates the six anions surrounding a given Mg cation. The resulting MgO_6 cluster model has also been surrounded by the corresponding array of point charges. Similar cluster models have been used in recent work to study the nature of the chemical bond in alkaline-earth oxides[20,23] and to interpret core level shifts in these materials.[24,25] Our next cluster model includes, in addition, the 18 Mg^{2+} cations surrounding each one of the O^{2-} anions of the previous, MgO_6, cluster model. The resulting model is denoted as $Mg_{19}O_6$ and was designed to provide two shells of fully coordinated ions. Hence the central Mg^{2+} and each one of the six O^{2-} anions surrounding it has all of its nearest neighbors. In order to avoid any possible bias arising from the particular way in which the $Mg_{19}O_6$ cluster was constructed we have also used a more compact model containing 27 ions arranged in a cube. This cube contains three ions on each edge plus ions at the center of each face and an Mg atom at the cube center. Thus, $Mg_{13}O_{14}$ contains four O^{2-} anions and five Mg^{2+} cations in the middle, or second layer, whereas the first and third layers contain five O^{2-} and four Mg^{2+} cations. In this case atoms are included in the cluster as groups of nearest neighbors of the central Mg; there are six O nearest neighbors, the 12 Mg second-nearest neighbors, and the eight O third-nearest neighbors.

For each cluster model, in each electronic state considered, we obtained *ab initio* self-consistent field (SCF) wave functions. The ionic nature of MgO is well established;[20,23] accordingly the number of electrons included in the electronic ground state SCF wave function is that corresponding to the fully ionic system. The LUMO orbital

TABLE I. Results for the cluster electronic state when one extra electron is added to the cluster LUMO; $\langle r^2 \rangle$ is the expectation value of the r^2 operator for the LUMO, r^2 (Mg-edge) is the square of the distance between the central Mg cation and the cluster edge ions, and EA is the cluster model electron affinity. Distances are in bohrs and energies in eV.

Cluster model	$\langle r^2 \rangle$	r^2 (Mg-edge)	EA
Mg^{2+} *(in vacuo)*	9.3	⋯	+14.70
Mg^{2+} (in PCs)	31.6	⋯	−1.88
MgO_6 (in PCs)	34.8	15.8	+2.05
$Mg_{19}O_6$ (in PCs)	116.0	63.1	−1.57
$Mg_{13}O_{14}$ (in PCs)	67.4	47.3	+0.80

was occupied in two different ways. In the first one we simply add one extra electron to the LUMO of a_{1g} symmetry; while keeping all the 2s and 2p levels of the Mg^{2+} and O^{2-} ions fully occupied. There is a reason for choosing an a_{1g} symmetry for the orbital to which the extra electron will be added. This is simply because a_{1g} is the symmetry of a 3s orbital on the central Mg atom in the cluster. In the second case we consider the electronic state where an electron is transferred from the HOMO of a_{1g} symmetry; which is mainly an orbital representing the oxygen 2p band, to the a_{1g} LUMO. We present results for the case where the two open shell electrons are coupled triplet although the character of the electronic state is not changed when a singlet coupling or an average coupling is used.

The SCF wave function for each one of the electronic states described above was obtained using a relatively large set of contracted Gaussian type orbitals, CGTOs. For atomic oxygen these sets contain 9s and 5p primitive GTOs contracted to 4s and 3p whereas for Mg we use 10s and 6p primitive GTOs contracted to 6s and 4p; these sets are represented as (9s,5p/4s,3p) and (10s,6p/6s,4p), respectively. The exponents and contraction coefficients are the same as previously used by Broughton and Bagus.[11] For the exterior 18 Mg atoms in the $Mg_{19}O_6$ cluster, two different contraction schemes, based on the same 10s and 6p primitive GTOs, were used. The first one is a minimal 2s 1p contraction and it is used simply to take into account finite size effects of the cations surrounding the six O^{2-} cluster anions. The second contraction is 4s 1p; here the additional two s-type contracted basis functions will allow for delocalization when the CB orbital is occupied. Unless we explicitly state otherwise, the $Mg_{19}O_6$ results given have been obtained with this latter, more flexible, Mg basis set. The SCF orbitals for the largest $Mg_{13}O_{14}$ cluster involved the use of 416 CGTOs.

III. RESULTS AND DISCUSSION

In this section we will describe the analysis of the electronic states which result when occupying a LUMO of the MgO crystal cluster model. First, we discuss the results which arise when an extra electron is added to the cluster models used to represent the MgO crystal. The overall situation can be easily understood by inspection of the data reported in Table I. The first interesting feature is the oscillation of the cluster electron affinity (EA) which some-

times is positive meaning that the system with one extra electron is more stable; in other cases the EA is negative and the additional electron is not stable. While at first sight this behavior appears to be fairly bizarre we see that the EA is positive for the oxygen terminated whereas it is negative for the Mg terminated clusters. As we discuss below, this ordering is a simple consequence of the physical nature of the state resulting when the extra electron is added to the cluster LUMO. Results for the LUMO $\langle r^2 \rangle$ show that, in all cases, the resulting orbital extends up to and beyond the cluster region; the CB orbital being delocalized may be artificially affected by the point charges surrounding the cluster. The electron added to the oxygen terminated clusters, MgO_6 and $Mg_{13}O_{14}$, is stabilized by the first, nearest, set of point charges which are positive. This stabilization occurs because the interaction of the diffuse electron charge cloud of the added electron with the nearby positive charges is attractive. The reverse is true for the Mg terminated clusters, Mg and $Mg_{19}O_6$, where the nearest set of point charges are negative.

From the results discussed above, there are many important consequences. The first one is related to the physical nature of the low lying electronic states of MgO. The picture that arises from our cluster model studies is that the resulting orbital is as delocalized as it can be. It does not have any clear or direct relationship to the Mg $3s$ atomic orbital and it is best described as a "conduction band" orbital. We must point out that our results are by no means biased to any particular description. In band theory, for instance, one assumes that the electronic states are delocalized and, hence, it is not possible to use the band structure formalism to describe localized, or excitonic states. On the other hand the cluster model can yield either localized or delocalized solutions depending on which is energetically preferable. The only constraint is that the cluster size and, in particular, the basis set used to describe the LUMO orbitals must be adequate to represent either localized or delocalized states; this is the case for the present clusters. The physical picture emerging from our study is that the "conduction band" orbital is delocalized. Then, it may not be appropriate to use cluster models to study the electronic states involving these CB orbitals. However, the use of cluster models of increasing size is precisely what has permitted us to draw such an important conclusion. Another consequence related to the present results is the fact that using point charges as an embedding scheme may or may not be appropriate to study certain electronic states; similar findings have been reported recently.[27,28] We must also point out that use of more sophisticated embedding schemes may be as misleading as the use of point charges. Let us take $Mg_{19}O_6$ as an example. If we use a minimal $2s$ $1p$ contraction of the $10s$ $4p$ primitive GTO set to describe the 18 Mg cations surrounding the MgO_6 cluster, we obtain a much more negative value for EA, -6.3 eV rather than -1.6 as reported in Table I. It is also important to examine the size of the LUMO as measured by the expectation value, $\langle r^2 \rangle$, of the r^2 operator. With the minimal $2s$ $1p$ basis set for the exterior Mg atoms in $Mg_{19}O_6$, $\langle r^2 \rangle = 33.0$ bohrs^2; this is considerably smaller

TABLE II. Results for the cluster electronic state when one electron is excited from the HOMO to the LUMO; $\langle r^2 \rangle$ is the expectation value of the r^2 operator for the LUMO, r^2 (Mg edge) is the square of the distance between the central Mg cation and the cluster edge ions, and Δ is the cluster model excitation energy. Distances are in bohrs and energies in eV.

Cluster model	$\langle r^2 \rangle$	r^2 (Mg edge)	Δ
MgO_6 (in PCs)	34.4	15.8	5.80
$Mg_{19}O_6$ (in PCs)	111.0	63.1	9.82
$Mg_{13}O_{14}$ (in PCs)	59.4	47.3	10.01

than the r^2 from the cluster central atom to the edge Mg atoms; 63.1 and it would appear that this orbital is localized. However, when the $4s$ $1p$ basis set is used for the 18 exterior Mg atoms, the $\langle r^2 \rangle = 116.0$ bohrs^2 becomes considerably larger and the orbital is clearly delocalized. The reason is that the $4s$ $1p$ basis set can now describe delocalized orbitals while the smaller $2s$ $1p$ was not sufficient and the orbitals described with this basis were forced to be localized. Using a minimal basis set for the second shell of Mg^{2+} cations has the same effect that using a pseudopotential or a model potential; see for instance Refs. 7 and 8. Hence, using an embedded cluster may not be adequate to study the MgO conduction band even if hundreds of model potentials are placed around the cluster region. This is because these potentials do not contain any basis functions; thus, the limited, central, basis set does not allow the CB orbital to become extended in space.

Next let us discuss the physical nature of the orbital that arises when one electron is transferred from the oxygen $2p$ "band" to the LUMO. The resulting electronic state has a "hole" in the anion $2p$ band and a "particle" in the conduction band. If the hole–particle interaction is strong enough an excitonic electronic state may appear which will be, possibly, localized around only a few atoms. The results in Table II report the $\langle r^2 \rangle$ value for the LUMO of the MgO_6, $Mg_{19}O_6$, $Mg_{13}O_{14}$ cluster models. In this case, the LUMO has a somewhat smaller extent than the one resulting when an extra electron is added to the cluster model. However, the $\langle r^2 \rangle$ values clearly indicate that the CB orbital extends up to and beyond the cluster region. The energy, Δ, required to move one electron from the O($2p$) valence band to the CB orbital is also reported in Table II. For the larger clusters the SCF calculated value of Δ is of the order of magnitude of the experimental band gap which is 7.8 eV[29,30] although it is much lower than the *ab initio* periodic Hartree–Fock value reported by Pandey *et al.*[31] However, because of the large edge effects found for the extent and energy of the CB orbital for different size clusters, see Tables I and II, considerable caution should be used in relating the cluster Δ to the MgO band gap. The most important consequence of the HOMO to LUMO excitations is that the excited orbitals are very similar to those obtained by adding one electron to a LUMO of the cluster. In both cases, the excited orbital is delocalized and in the conduction band. Moreover, our results do not indicate any excitonic feature for the excited electronic states studied. However, the existence of excitonic states cannot be completely ruled out on the basis of the present calcu-

lations. This is because we have only considered O(2p) holes which are delocalized over the O atoms in the cluster. For a localized O(2p) hole, the "hole–particle" interaction might be large enough to localize the excited state orbital. The fact that we have maintained O_h point group symmetry in our cluster calculations forces the O(2p) hole to be delocalized. However, if the point group symmetry used for the cluster calculations would have been lowered to C_{4v}, the localization of the O(2p) would have been a possibility; in this case the hole orbital could be either localized or delocalized. It would be useful to determine SCF wave functions for the excited states of MgO using lower symmetry constraints; this would permit more definite conclusions to be made about the existence of excitonic states.

IV. CONCLUSIONS

The character of the low-lying electronic states of MgO has been studied by means of *ab initio* SCF cluster model wave functions. In all cases we found that the low-lying orbitals are highly delocalized extending up to and beyond the cluster region. This is the case for the orbitals resulting when adding an extra electron to the cluster model and, also, when one electron is excited from a HOMO representing the oxygen (2p) valence band to the lowest CB orbitals. This delocalized nature of the CB orbital appears in a natural way when comparing results for clusters of increasing size and it is not forced as in periodic band structure calculations where delocalization is assumed.

The energetics concerning the cluster EA or the transition energy, Δ, depends on the cluster model used and, in particular, on whether it is Mg or O terminated. We have described some artifacts due to the point charges used to represent the Madelung potential; these artifacts are important for the MgO excited states.

We have not found any evidence of excitonic states in our cluster model studies. However, the existence of such states cannot be ruled out from the present calculations, largely because they involve a delocalized O(2p) hole. By lowering the constraints on the SCF wave function, the O(2p) hole may become localized. Indeed, localized O(2p) hole states were found for cluster models of CuO;[32] for the localized hole, the O(2p) binding energy was lower by ~1.1 eV than for the delocalized hole.[32] The localized O(2p) hole could lead to a large enough hole–particle interaction to form an excitonic state below the conduction band. Results for SCF cluster wave functions without the cubic, O_h, symmetry constraints are needed to draw stronger conclusions about the existence of excitonic states.

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