PHYSICAL REVIEW B VOLUME 62, NUMBER 15 15 OCTOBER 2000-I

Core exciton energies of bulk MgO, Al_2O_3, and SiO_2 from explicitly correlated *ab initio* cluster model calculations

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(Received 22 December 1999; revised manuscript received 18 May 2000)

Ab initio cluster model wave functions are used to predict the existence of localized excited states in MgO, Al_2O_3, and SiO_2 arising from metal $2p$ core-level excitations. Theoretical values obtained at different levels of theory result in a quantitative agreement with experiment, and the use of different models permits us to quantify the different contributions to the final excitation energy. The most important contribution is atomic in nature; a meaningful zero-order approximation is that in MgO and Al_2O_3 the exciton can be assigned to a $M(2p^6)\rightarrow M(2p^5 3s^1)$-like excitation, where $M=\mathrm{Mg}$ or Al. For the atomic models, the singlet-triplet exchange in the excited configuration is in good agreement with experiment. In addition, the solid-state effects on this exchange energy predicted by experiment are well reproduced by the cluster models representing MgO and SiO_2, whereas a less clear situation appears in Al_2O_3. The open-shell orbital in the final state has, however, important contributions from the ions near the atomic site where excitation occurs. Nevertheless, the final state appears to be localized in space without any *a priori* assumption, the localization following from the hole-particle interaction implicitly induced in the final-state wave function. The Madelung field reduces the excitation energy with respect to the atomic value; the effect of neighboring atoms, mainly Pauli repulsion, acts in the opposite way; and electronic correlation effects decrease it again. In agreement with the covalent nature of SiO_2, the exciton cannot be simply understood as arising from a $\mathrm{Si}(2p^6)\rightarrow \mathrm{Si}(2p^5 3s^1)$ in a fully oxidized Si cation.

I. INTRODUCTION

According to the simplest textbook definition, insulators and semiconductors are characterized by a region of forbidden energy separating the occupied and unoccupied states.[1] This energy gap is evident in the optical spectra of these materials and can be rationalized in terms of the band theory of solids. In some cases, however, the optical spectra of these materials are not so simple, and well-defined spectroscopic features appear in the forbidden energy region. These features are evidenced by the onset of optical absorption at energies below the interband continuum threshold. The origin of this particular spectroscopic feature is interpreted as due to the formation of Frenkel excitons. It is customary to define the Frenkel excitons as point defects originated by an atom or ion of the lattice in an excited state.[1,2] In the independent-electron model version of band structure, the excitation of a single electron on a given site does not affect the electronic structure. Hence, one may argue that for most purposes it can be more convenient not to describe the exciton as a localized state. However, some other models invoke a local character of the excited state[3] with an additional interaction between the electron and the hole created in the final and initial one-electron states, respectively. Depending on the energy of the radiation used in the experiment, excitons can involve valence or core bands. A local *ab initio* valence-bond model has also been proposed to study the excitations that give rise to the band gap of alkaline-earth oxides[4] and a variety of excited states in $KNiF_3$.[5]

The description above provides a qualitative understanding of the electronic structure of insulators and semiconductors. Notwithstanding, a complete description requires a first-principles-based theoretical framework able to quantitatively reproduce the main features of the electronic structure of these materials including exciton energies. Unfortunately, this is a rather complicated problem and even the magnitude of the band gap cannot be easily reproduced by state-of-the-art first-principles band-structure calculations. In fact, *ab initio* Hartree-Fock periodic calculations largely overestimate the band gap, while density-functional periodic calculations based on the local-density approximation (LDA) lead to band gaps that are too small or even fail to predict the existence of a gap, resulting in an incorrect description of the properties of the material;[2,6] i.e., LDA often predicts metallic instead of insulating behavior.[7] Surprisingly enough, the use of cluster models permits us to obtain a qualitatively correct picture of some important features of the electronic structure of ionic solids.[3–5] The sacrifice on the extended nature of the system implicit in the cluster model approach is compensated by the possibility to obtain a more accurate description of the electronic structure of these systems, i.e., by making use of explicitly correlated accurate wave functions. Of course, this is only possible for narrow-band systems where the electronic structure is not dominated by periodicity. In the case of semiconductors, bulk and surface, the shortcomings of the LDA can be corrected by making use of the well-known *GW* formalism.[2,8] There are other formalisms that permit the study of excited states in extended systems.[2] Here, we will simply mention that another alternative and efficient approach is the use of two-particle Green's functions that enables an accurate description of excitonic effects in semiconductors and simple ionic insulators such LiF.[9]

The origin of the failure of the Hartree-Fock and LDA methods concerning the evaluation of the band gap and other features of the electronic structure related to excited states lies in the neglect or inappropriate treatment of dynamical correlation effects. For instance, the electronic structure of oxides and other strongly correlated systems is quite involved and several corrections[10] to the LDA are required if one wishes to stay within the density-functional theory (DFT) description. Here we quote the self-interaction-correction[11] and on-site Coulomb repulsion terms.[12] In principle, wave-function-based methods are able to introduce dynamical correlation in a systematic way, and its use is rather common in quantum chemistry. However, this becomes a very difficult approach when dealing with an infinite solid. Only very recently has it been possible to study the ground-state properties of crystalline solids by means of a correlated wave-function approach.[13] Therefore, the study of excited states of crystalline solids requires some additional approximation. The requirement of a correlated wave function can be fulfilled if one accepts to simplify the description of the material. A clue for the construction of an appropriate material model is given by the fact that, quite often, excited states of crystalline solids are sufficiently local in nature so that one can make use of the cluster model approach and still obtain meaningful results. Examples exist of the adequacy of the cluster model approach for excited states of ionic and covalent solids. Quantitative agreement between cluster model calculations and experimental results has recently been reported for relevant properties in a variety of systems. These include the *d-d* spectra of NiO, CoO, and similar transition-metal oxides,[14–17] core-level excitation spectra in NiO,[18] excited states of alkaline-earth oxides[4] or of $KNiF_3$,[5] the optical spectra of point defects in SiO_2,[19–23] the magnetic coupling of a series of wide-gap insulators[24,25] including superconductor parent compounds,[26] and even for the valence exciton of MgO,[3] where a localized picture might be less adequate.

Here, we extend the above studies based on the *ab initio* cluster model approach by showing that it is possible to reach a rather quantitative description of the core-exciton energies of MgO, Al_2O_3, and SiO_2. The motivation for this choice arises from the existence of well-characterized experimental data that suggest the existence of core excitons in these materials.[27] Based on the comparison with atomic excitation values, O'Brien *et al.* assigned the observed excitonic excitations to $M(2p^6)\rightarrow M(2p^5 3s^1)$ transitions, where M stands for Mg, Al, or Si. In addition, based on this atomic model and on the theoretical approach by Onodera and Toyozawa,[28] O'Brien *et al.* were able to quantify the spin-orbit splitting and the atomic exchange energy of the excitonic state. By comparing with atomic data, these authors found important solid-state effects. These solid-state effects are interpreted in terms of screening and already indicate that the states involved in the electronic excitation may differ from those invoked in the atomic model. This is in agreement with the analysis of the chemical character of these oxides and of their electronic structure. Both suggest that the screening effects imply a more complex electronic structure than that implicit in the atomic model. On the one hand, the assignment based on the atomic model requires assuming complete oxidation of Mg, Al, and Si. While this is very likely to be the case in MgO (Refs. 4 and 29–32) and Al_2O_3 (Refs. 31–33), it is hard to accept a Si^{4+} cation in SiO_2; in fact SiO_2 is better described as a largely covalent material. On the other hand, the atomic model suggests that the atomic character of the valence orbitals is preserved in the solid. This is in contradiction with the idea that the conduction band of these materials is highly delocalized. Theoretical evidence for the delocalized character of the conduction band has been reported for MgO based on both cluster models[34] and periodic Hartree-Fock calculations.[35] A result was already predicted in the pioneering work on Pantelides, Mickish, and Kunz on the electronic structure of MgO including second-order contributions for the electronic correlation effects on the excitation energies.[36] However, it is important to stress the fact that these periodic approaches are unable to predict the existence of excitons; the exciton peak on the experimental spectra has to be removed in order to obtain agreement between experimental and calculated optical spectra.[36] From the discussion above, to assume that an excitation from the metal $2p$ core level to the conduction band produces a change in the character of this band with the appearance of a rather localized state appears to be necessary. Theoretical work based on *ab initio* Hartree-Fock cluster model wave functions shows that the excitation from the orbitals that have mainly $O(2p^6)$ character to the first empty orbital of a cluster model results in an orbital that extends considerably beyond the model independently of the cluster size.[34] However, a completely different picture is obtained if the electron is excited from a core $Mg(2p^6)$ orbital—the excited orbital is now localized in the cluster region.[37] Notice that the hole-particle interaction assumed on the exciton model appears in the wave function description in a natural way without any *a priori* conjectures. Therefore, the only point left is to show that this *ab initio* cluster model wave-function approach is able to quantitatively predict the excitonic energies and, hence, provide a more precise description of the one-electron states involved in these spectroscopic features. This is indeed the main goal of the present work.

II. MATERIAL MODELS FOR MgO, Al_2O_3, AND SiO_2

Embedded cluster models of increasing size have been used to represent each material. For MgO we consider MgO_6, $Mg_{13}O_{14}$, and $Mg_{19}O_{14}$ clusters, whereas for Al_2O_3 the models are AlO_6 and Al_8O_9. The point symmetry of the clusters modeling MgO and Al_2O_3 is D_{2h} and C_3, respectively. The computer codes used in this work, as most of the quantum chemistry codes for explicitly correlated calculations, can handle point groups with nondegenerate irreducible representations only. Therefore, C_1 has to be used for cluster models representing sections of the corundum crystal. This low symmetry does not permit us to extend the cluster model as in the case of MgO. The number of electrons included in each cluster is that corresponding to the formal ionic charges; i.e., Mg^{2+}, Al^{3+}, and O^{2-}. However, one must notice that the N-electron wave function describing the electronic structure of these clusters contains enough variational degrees of freedom to allow a buildup of covalent character if this chemical effect leads to a lowering of the cluster energy in the ground or excited state. These clusters are further properly embedded to account for some of the effects due to the rest of the crystal. For MgO and Al_2O_3 the cluster is first surrounded by an array of point charges optimized to reproduce the Madelung field in a large region of space around the cluster center.[38] As usual, the effect of these point charges on the cluster electronic structure is taken into account by properly computing the required one-electron integrals. The use of point charges as the only embedding may have some limitations, especially because the exclusion effects with the rest of the crystal and its response to changes in the cluster electronic structure are ignored. Exclusion effects can be introduced in a rather direct way by substituting the point charges closer to the cluster region by a better representation of the real ions. For the cations a simple yet efficient approach consists in the use of total ion potentials (TIP's) as suggested by Winter and Pitzer.[39] However, the description of anions surrounding the atoms defining the cluster model requires a more sophisticated approach. Here, we used the *ab initio* model potentials (aiMP's) developed by Barandiarán and Seijo.[40] We must warn that, in contrast to the point-charge embedding, the cluster embedding with TIP's and aiMP's confines the electronic structure of the cluster within the space region defined by the cluster model itself. Therefore, the excited state is forced to be localized in the cluster region, and dramatic changes in the excitation energy may appear in response to the excessive Pauli repulsion introduced by the embedding. This will be discussed at length in the last section of this paper. Finally, it is necessary to admit that the response of the rest of the crystal is not included in the present models. Polarization and long-range effects can be of importance in the description of charged point defects but should not largely affect the present results. This is supported by results on recent studies of the optical spectra of *F* centers of MgO.[41,42]

In the case of SiO_2 it is not realistic to embed the cluster in an array of formal $+4$ and -2 point charges, although this approach has been used in recent work based on the approximate $X\alpha$ method.[43] In this case a good strategy, already used to model bulk and surface SiO_2,[19–21,44–46] consists in saturating the oxygen broken bond by embedding hydrogen atoms (see Ref. 47 and references therein). In principle, one would use a typical O-H distance of 0.98 Å. Nevertheless, the stability of results with respect to this parameter has been carefully checked by computing the electronic transitions at different values of the O-H distance. Two different clusters, SiO_4H_4 and $Si_5O_{16}H_{12}$ (or $SiO_4Si_4O_{12}H_{12}$ if one wishes to specify the atomic shells), have been used to represent the SiO_2 bulk crystal. The point group of both SiO_2 cluster models is also quite low, C_2, thus preventing the use of larger models. The reliability of these cluster models is supported by the excellent results reported by recent studies of the optical spectra of SiO_2.[19–22] Results in the forthcoming sections will show that the cluster models described above do also provide a meaningful representation of the systems of interest and permit us to reach an extensive description of the core excitons in this system.

In addition to the cluster models described above, relevant calculations have also been carried out for the Mg^{2+} and Al^{3+} cations in vacuo and embedded in the Madelung field, and for an isolated Si atom. The idea behind the use of these atomic models is to identify and to separate the atomic, electrostatic, and covalent contributions to the excitations of interest. Finally, we point out that since all cluster models used in this work aim to represent nondefective solids it is not necessary to proceed to optimize the geometry of these models. In fact, it is more appropriate to construct the models using the experimental crystal structure, thus avoiding possible artifacts. Therefore, the experimental structure has been used to construct the cluster models except for the embedding hydrogen atoms commented on above for models of the SiO_2 crystal. A schematic representation of the cluster models above described is given in Fig. 1.

III. ELECTRONIC STRUCTURE AND COMPUTATIONAL DETAILS

The electronic structure of the models described in the preceding section has been investigated by means of *ab initio* wave functions of different complexities. The simplest description is obtained from Hartree-Fock calculations on the ground and excited states. In all cases, the ground-state wave function is represented by a single closed-shell Slater determinant. The excited-state wave function is obtained by performing a restricted open-shell Hartree-Fock (ROHF) calculation for the electronic configuration in which a $2p$ core electron of Mg, Al, or Si is promoted to the lowest unoccupied molecular orbital (LUMO) of the totally symmetric irreducible representation. The two unpaired electrons are coupled to a singlet or triplet spin-wave function with the excitation to the singlet final state corresponding to the dipole-allowed transition. Notice that the energy difference between the singlet and triplet states together with the spin-orbit splitting is a key parameter in the interpretation of the optical spectra in terms of the theory of Onodera and Toyozawa.[28] This has been precisely the theoretical framework used by O'Brien *et al.*[27] to obtain an indirect experimental estimate of this exchange energy. In the cluster model approach this parameter can be obtained directly from the calculation of the singlet and triplet state energies corresponding to the excited configuration. In the forthcoming discussion it will be shown that good agreement between the calculated results and those reported in Ref. 27 exists, thus providing further support to the theoretical models used in this work.

The final states of $Mg_{19}O_{14}$ (or MgO_6 and $Mg_{13}O_{14}$), Al_8O_9 (or AlO_6), and $Si_5O_{16}H_{12}$ (or SiO_4H_4) cluster models are ${}^1B_{3u}$, ${}^1A$, and ${}^1B$ for the singlets and ${}^3B_{3u}$, ${}^3A$, and ${}^3B$ for the triplets, respectively. The final symmetry is only determined by the symmetry of the $2p$ core orbital chosen. For the Mg^{2+} and Al^{3+} cations without and with external Madelung field the ground state is also a closed shell and the excited state is the ${}^1P$ arising from the excited $2p^53s^1$ electronic configuration. In the case of SiO_2, a largely covalent material, the atomic reference is not clear at all. Nevertheless, the electronic state chosen as the initial state of the Si atom is the ${}^1S$ arising from a $2p^63s^23p^2$ orbital occupancy and the excited state is the ${}^1P$ arising from the $2p^53s^23p^24s^1$ electronic configuration. Another choice concerning Si^{4+} has also been considered. Following the standard notation, excitation energies obtained from energy differences calculated at the ROHF level of theory are referred to as change in self-consistent field (ΔSCF) energies.[48]

Electron-correlation effects are explicitly introduced by second-order perturbation theory, hereafter referred to as

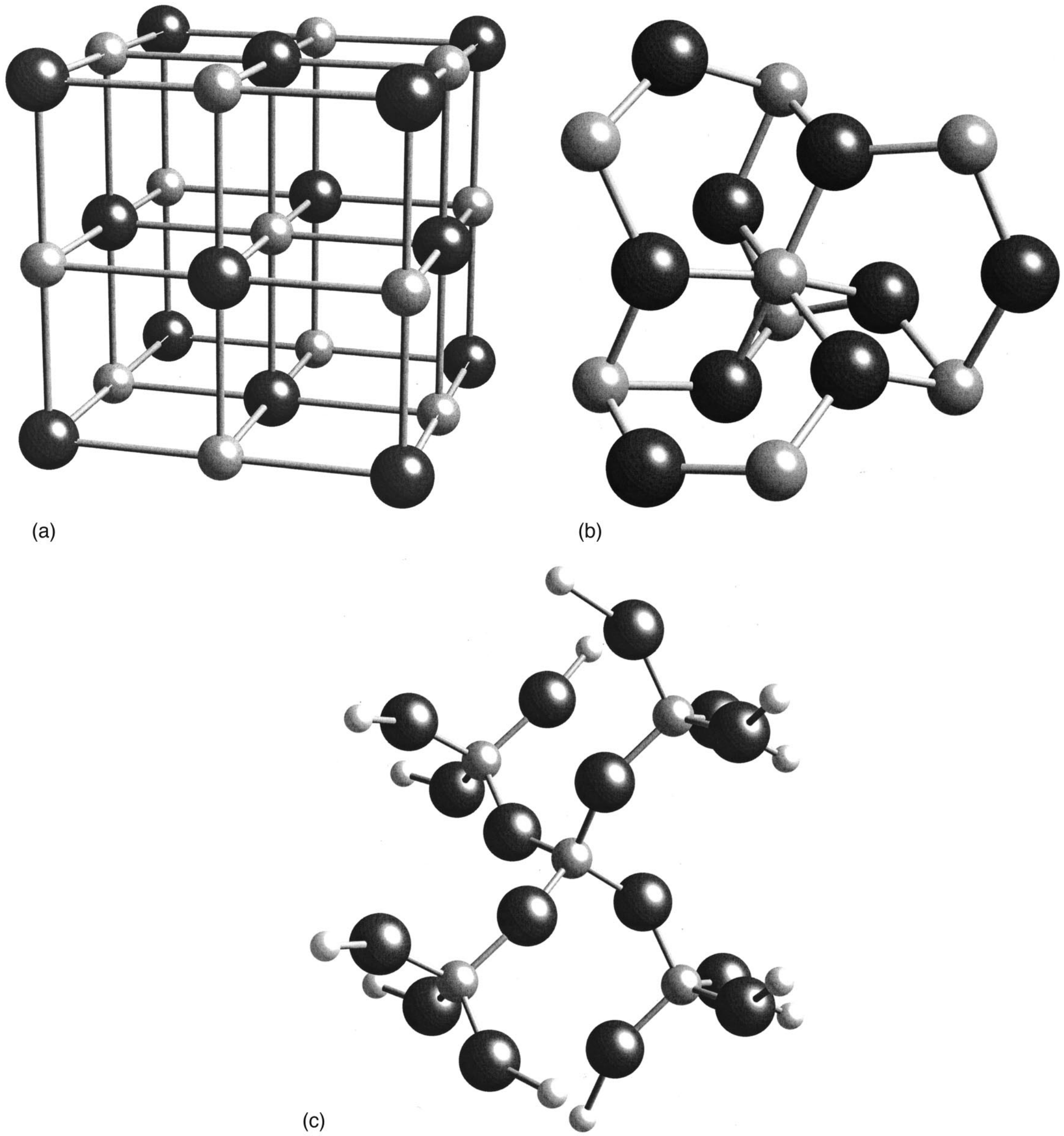

FIG. 1. Schematic representation of the clusters used to model MgO, Al_2O_3, and SiO_2. Dark spheres represent oxygens and light spheres metals. The embedding point charges are not shown.

PT2, by means of the complete-active-space PT2 (CASPT2) method developed by Andersson and co-workers.[49,50] This method can be applied to single and multideterminantal wave functions and reduces to the well-known second-order Møller-Plesset perturbation scheme[51] to electron correlation energy for closed-shell zeroth-order wave functions.[52] In order to apply the CASPT2 method to the ROHF wave functions described above it is convenient to view the ground- and excited-state wave functions as complete-active-space self-consistent field (CASSCF) wave functions with two active electrons in one active orbital (ground state) and two active electrons in two active orbitals (excited state). In all clusters, the $2p$ electrons of the metal atoms plus the $2s$ and $2p$ electron of oxygen are included in the second-order treatment of the correlation energy. An important feature of the CASPT2 method is its ability to take into account the orbital relaxation effects associated with the charge-transfer configurations that can mix with the excited-state configuration, causing a lowering of the excitation energy.[53] In the present case, however, one has to realize that possible charge-transfer configurations from the $O(2p^6)$ to LUMO have a very different energy compared to the $M(2p^6)$ to LUMO excitation, and hence this configuration mixing is really small.

The molecular orbitals used to construct the many-electron wave functions for the ground and core-level excited states have been expressed as a linear combination of atomic natural orbital (ANO), Gaussian-type functions[54,55] that are specially designed to accurately describe electron correlation effects while having a rather compact form. The ANO basis sets are derived from a large primitive set and contracted using a general scheme in which all primitive functions contribute to each contracted basis function. For all clusters a similar approach is followed in which the different shells of atoms are described differently depending on the distance to the central atom. The Mg, Al, and Si basis set used are de-

TABLE I. Net charge in the different atoms of each cluster shell derived from a Mulliken population analysis in the ground (GS) and excited (ES) states, respectively. The difference in net charge in both electronic states, Diff. is also given. The different shells correspond to $MgO_6Mg_{12}O_8$, $AlO_6Al_7O_3$, and $SiO_4Si_4O_{12}H_{12}$, respectively.

	Shell of atoms				
$Mg_{13}O_{14}$	Mg	O_6	Mg_{12}	O_8	
GS	2.11	−2.20	2.10	−2.01	
ES	1.30	−2.10	2.12	−2.00	
Diff.	0.81	−0.10	−0.02	−0.01	
Al_8O_9	Al	O_6	Al_7	O_3	
GS	2.72	−2.02	3.06	−2.02	
ES	2.61	−1.84	2.91	−1.99	
Diff.	0.11	−0.18	0.15	−0.03	
$Si_5O_{16}H_{12}$	Si	O_4	Si_4	O_{12}	H_{12}
GS	1.38	−0.92	2.48	−1.16	0.53
ES	0.46	−0.61	2.45	−1.14	0.49
Diff.	0.92	−0.31	0.03	−0.02	0.04

rived from the $(17s,12p,5d)$ set, whereas that of oxygen starts with a $(14s,9p,4d)$ primitive set. This basis set for the central atom is contracted to $(5s,4p,1d)$, that of the first shell of surrounding oxygens to $(4s,3p,1d)$, the next shell of metal atoms uses a $(4s,3p)$ set and the next shell of oxygen and other atoms a $(3s,2p)$ set. A $(2s)$ contraction of the $(7s)$ primitive set defines the basis set used to describe the embedding hydrogen atoms. The adequacy of these basis sets has been checked by comparing the results obtained with different contractions of these ANO basis sets on smaller cluster models. Moreover, results for these reduced clusters provide useful information about the convergence of the computed excitation energies with respect to cluster size (cf. Table II). All calculations have been carried out using the MOLCAS 4 suite of programs[56] implemented in Hewlett Packard J282 and J2240 workstations.

IV. RESULTS AND DISCUSSION

For the ground state of the different embedded-cluster models, the analysis of the LUMO shows that this orbital is delocalized with important contributions on the cluster edge atoms. This delocalized character of virtual orbitals is inherent to the Hartree-Fock approximation, and hence this observation does not bring any relevant information. In fact, the Hartree-Fock virtual orbitals describe a one-electron state that ''feels'' the effective field of the *N*-cluster electrons, and hence it is too diffuse and too high in energy. This is one of the key points why periodic Hartree-Fock approximation leads to too large a band gap. In the Kohn-Sham approach to DFT, the virtual orbitals do not have this limitation because they are solutions in exactly the same potential as the occupied orbitals.[57] This argument explains why contrarily to the Hartree-Fock method, DFT-based band-structure calculations may lead to a good estimate of the optical spectrum. Electronic structure calculations of semiconductors, based on LDA corrected for self-interaction by means of the GW method, provide a well-documented field. A meaningful Hartree-Fock representation of a one-electron state described by a virtual orbital can only be obtained by occupying it with at least one electron. However, the final orbital is no longer a virtual orbital and its character may change completely. For the case of MgO, it has been shown[34] that the singly occupied molecular orbital (SOMO), resulting from a HOMO→LUMO excitation in a $Mg_{13}O_{14}$ cluster, is completely delocalized, extending beyond the edges of the cluster model. Moreover, the delocalized character of this SOMO is found independently of the cluster size and is in full agreement with the delocalized nature of the conduction band in MgO. However, a completely different situation arises when the LUMO orbital is occupied as a result of a metal core→LUMO excitation. In this case the electron-hole interaction is large enough to give rise to an orbital localized in the cluster region. The electron-hole interaction is implicity accounted for in the Hartree-Fock (and in the more accurate PT2) cluster model wave function and the result provides evidence for the formation of a core exciton[37] even in the cluster model representation of the material.

Here, we extend the previous analysis to the study of core excitons on different cluster models representing MgO, Al_2O_3, and SiO_2. The main goal of this work is to study the character of the electronic state resulting from a $M(2p^6)$ →LUMO excitation and the different physical contributions to the excitation energy. The degree of localization can be roughly obtained by comparing the expectation value of the $\hat{r}^2$ operator acting on the SOMO with the cluster size. More precisely the comparison involves $\langle \hat{r}^2\rangle^{1/2}$ and the cluster size measured as the distance between the central atom and those at the cluster edge. For the largest cluster models used to represent MgO, Al_2O_3, and SiO_2 these distances are 3.64, 3.50, and 5.15 Å, respectively. The extent of the SOMO for MgO, Al_2O_3, and SiO_2 is 3.72, 5.29, and 3.98 Å. For MgO and SiO_2, the comparison of the two observables shows that the SOMO is reasonably localized inside the cluster region. However, the $\langle \hat{r}^2\rangle^{1/2}$ value for Al_8O_9 is perhaps too large to accept that it represents a state localized within the cluster. This limitation arises from too small a cluster model imposed by the lack of symmetry of this system. Nevertheless, the

TABLE II. ΔSCF and PT2 exciton energies (in eV) for the three compounds modeled with the clusters mentioned in the text. Small, medium, and big refers to MgO_6, $Mg_{13}O_{14}$, and $Mg_{19}O_{14}$ for MgO, whereas small and medium stand for the AlO_6 and Al_8O_9 clusters representing Al_2O_3, and SiO_4H_4 and $Si_5O_{16}H_{12}$ representations of SiO_2.

	MgO		Al_2O_3		SiO_2	
Cluster	ΔSCF	PT2	ΔSCF	PT2	ΔSCF	PT2
Small	52.1	50.7	78.7	77.2	108.8	107.0
Medium	55.0	53.9	78.3	77.5	109.5	108.0
Big	54.6	53.8				
Experiment	53.4		78.6		106.1	

charge distribution, cf. Table I, for the ground and excited states, obtained from a Mulliken population analysis, shows that the creation of the core hole and the addition of the electron to the SOMO essentially affect the anions closer to the atom where the excitation occurs. The absolute values of the charges in Table I have to be regarded with caution because of the well-known deficiencies of the Mulliken analysis and because basis sets of different quality are used to describe the cluster atoms depending on their relative distance to the atom being excited. Nevertheless, the data in Table I indicate a strong ionic character of MgO and Al_2O_3, in agreement with previous works,[30,33] and a covalent character of SiO_2, also in agreement with previous findings.[19] The important point here is, however, the similarities in the net charges of the more external shell of atoms in the ground and excited states. This is another strong indication of a rather local character of the SOMO. Notice, however, that the situation in Al_2O_3 is slightly different, pointing towards a more delocalized excited state, consistent with the $\langle \hat{r}^2 \rangle^{1/2}$ value for the SOMO.

Having established that the cluster models used in this work are capable of predicting the existence of excitonic states arising from a core→LUMO excitation the next step concerns the analysis of the excitation energies and its various physical contributions. The first point of the analysis concerns the results obtained from the single-determinant Hartree-Fock or ΔSCF description on the different cluster model representations of each material. From the summary of results presented in Table II, one can readily see that the performance of the ΔSCF description is surprisingly good except for the case of the smallest MgO cluster model. Here, it is worth pointing out that ΔSCF usually provides a very accurate description of core-level ionization energies in molecules and cluster model representations of several materials.[48] Before turning our attention to the role of electron correlation it is important to analyze the influence of the cluster model size. For MgO, the ΔSCF values are converged with respect to this variable within a 0.4-eV interval. For the other two materials we already commented that the lower symmetry of these systems precludes the use of very large cluster models, although results in Table II show that further extension of the models will only produce a modest change in the calculated excitation energy. The ΔSCF method usually overestimates excitation energies because the Hartree-Fock description of the excited states is always less accurate than that for the electronic ground state. Therefore, better agreement with experiment is expected when electronic correlation is accounted for through second-order perturbation theory.

Results in Table II show that this is indeed the case: calculated and experimental values are in better agreement when electronic correlation is included although the improvement is modest. The relative agreement between calculated and experimental values support the present cluster model approach and show that it is possible to interpret the experimental data and to reach a quantitative description from purely *ab initio* wave functions. The fact that electronic correlation effects are not essential to explain the experimental observations permit us to understand the excitation from an orbital-based model in which the key point is the localization of the excited orbital. However, it is important to realize that it is not necessary to assume the existence of a hole-particle interaction or the existence of a localized state. Both appear naturally in the cluster wave function of the final state, the cluster model being therefore the only hypothesis.

On the other hand, the error on the excitation energy for SiO_2 does also reflect the limitations of the embedding used. In fact, one must be aware that the O-H distance of the embedding hydrogen atoms constitutes an external parameter and, in principle, it is possible to monitor the excitonic energy by changing this O-H distance. Table III reports the effect of this geometrical parameter on the Hartree-Fock energy of the ground state and the PT2 excitation energy. These results clearly show that by choosing a particular O-H

TABLE III. Variation of the ground-state Hartree-Fock total energy, E_{tot}, and the PT2 excitation energy, E_{exc}, with respect to the O-H distance chosen for the embedding hydrogen atoms in the two cluster model representations of SiO_2. 0.98 (O-H) and 1.6 Si-O stand for the typical O-H distance in several chemical compounds and to the equilibrium distance between Si and O in bulk SiO_2, respectively.

d(O-H) (Å)	SiO_4H_4		$SiO_4Si_4O_{12}H_{12}$	
	E_{tot} (a.u.)	E_{exc} (eV)	E_{tot} (a.u.)	E_{exc} (eV)
0.8	−590.8822	108.1		
0.9	−590.9942	107.7	−2650.2159	108.1
0.98 (O-H)	−590.9970	107.0	−2650.2327	108.0
1.1	−590.9942	106.5	−2650.0093	107.6
1.2	−590.8140	105.2	−2649.6980	107.2
1.6 (Si-O)	−590.3712	101.8		

TABLE IV. Excitation energies (in eV) from atomic calculations in vacuum, vac, and in a Madelung field, Mad.

	MgO		Al_2O_3		SiO_2
	Mg^{2+} (vac)	Mg^{2+} (Mad)	Al^{3+} (vac)	Al^{3+} (Mad)	Si (vac)
ΔSCF	53.7	51.6	78.1	77.4	108.7
PT2	53.9	51.7	78.2	77.5	108.1

distance it is possible to obtain better agreement with experiment. However, this is not the choice of the present work, which takes the O-H distance leading to the minimum total energy. Hence, results in Table III are only aimed to provide a rough estimate of the influence of this parameter on the calculated excitation energies.

It has been suggested by various authors[27,28] that the excitation energies can be well approached by a model consisting of a single atom. The reliability of the atomic model has been investigated by separate calculations on single cations in different environments. In Table IV we report ΔSCF and PT2 calculations for the $2p^6 \rightarrow 2p^5 3s^1$ excitation of Mg^{2+} and Al^{3+} cations in vacuo and surrounded by a proper Madelung field and for the $2p^6 3s^2 3p^2 \rightarrow 2p^5 3s^2 3p^2 4s^1$ excitation of an isolated Si atom. Results in Table IV show that the order of magnitude of the excitation energy is already provided by the atomic calculation, in agreement with the theoretical model of Onodera and Toyozawa.[28] This fact strongly suggests that the nature of the exciton observed in MgO and Al_2O_3 is atomic in character. However, this simple description ignores important solid-state effects pointed out by O'Brien *et al.*[27] In both ionic materials MgO and Al_2O_3, the electrostatic field of the rest of the lattice decreases the excitation energy in a non-negligible way. When the ions surrounding the cation being excited are explicitly included, the excitation energy increases again due to the Pauli repulsion of the neighboring ions. Finally, electronic correlation effects in the solid, mainly due to the anions, are more important than those in the atoms and the excitation energy lowers again. The result of this delicate balance with Madelung field and electronic correlation lowering the excitation energy and the Pauli repulsion raising it is that the values obtained in the atomic calculations are very close to those obtained with the largest cluster models. This description contrasts with that obtained for SiO_2, where the opposite effects described above are less important because of the absence of a Madelung field and of the strong covalent character of the Si-O bonds. However, the trend is the same as for MgO and Al_2O_3, the excitation energy increases going from the atom to the cluster and decreases when electronic correlation effects are accounted for. The results discussed above for Si correspond to a neutral atom, and one may suggest that there is a substantial net charge on Si in SiO_2. In the limit of a Si^{4+} cation one has a $2p^6 \rightarrow 2p^5 3s^1$ excitation; the ΔSCF calculated value for this transition is 105.7 eV, not very far away from the value obtained for the $2p^6 3s^2 3p^2 \rightarrow 2p^5 3s^2 3p^2 4s^1$ of the neutral Si atom, which is 108.7 eV. This result shows that it is not appropriate to obtain a measure of the ionic character by looking at the atomic excitation energies only. This is in the line of previous investigations by Bagus *et al.*[48] for the core-level shifts of several materials. A careful analysis of the different physical effects contributing to the core-level shift enabled these authors to show that one cannot justify the shift in terms of a single physical mechanism like the ligand to metal charge transfer.

The results commented upon so far involve the allowed singlet-singlet transition only. However, from a computational point of view it is very simple to obtain the excitation energy to the triplet state and from this the exchange energy parameter involved in the theory of Onodera and Toyozawa.[28] First of all, we comment on the PT2 results for the atomic calculations and compare with available experimental data. The PT2 singlet-triplet splitting arising from the $2p^6 \rightarrow 3s^1$ transition in Mg^{2+}, Al^{3+}, and Si^{4+} is 0.56, 0.71, and 0.94 eV, respectively, in quite close agreement with the experimental values of 0.61, 0.80, and 0.99 eV. For the cluster model representations of MgO and SiO_2, the PT2 values are 0.20 and 0.14 eV. These values have to be compared with 0.25–0.5 for MgO and 0.18 eV for SiO_2 as reported by O'Brien *et al.*[27] from experimental data and using the theory of Onodera and Toyozawa.[28] The agreement between cluster model calculations and experimental results show that these finite representations of the extended systems are able to predict the solid-state effects on this important spectroscopic parameter. As it could be anticipated from the discussion above, the result concerning Al_2O_3 merits a separate discussion. The calculated singlet-triplet splitting is much smaller than the atomic value, indicating that the cluster model effectively reproduces the solid-state effects. However, the more delocalized character of the SOMO results in too small a value, $\leqslant 0.1$ eV, depending on the cluster model, the embedding scheme, and the basis set.

The above discussion strongly suggests that the use of cluster models embedded in point charges or atomic hydrogen atoms provide a reasonable picture of these solids. A point that deserves further discussion is the influence of embedding on the physics arising from these models and on the calculated transition energies. For MgO, we considered a more sophisticated embedding. The new model, $Mg_{63}O_{62}$, consists of a cube of two times the lattice parameter, i.e., 7.28 Å, and involves up to 125 quantum-mechanically treated ions, further extended with a proper array of point charges. In this larger cluster, the $Mg_{13}O_{14}$ unit is treated as before, whereas the next shells of ions are represented by potentials, TIP's for Mg^{2+} (Ref. 39) and aiMP's for O^{2-} (Ref. 58). The spatial extent of the SOMO estimated from the calculated value of $\langle \hat{r} \rangle^{1/2}$ at the ROHF level of theory is 3.06 Å, considerably shorter than 3.72 Å, the value obtained with the $Mg_{13}O_{14}$ cluster embedded in point charges. Notice that the resulting SOMO is well inside the cube of 7.28-Å side. However, the ΔSCF and PT2 values for the excitation energy are 56.6 and 56.1 eV, respectively. These values are significantly larger than those obtained with the $Mg_{13}O_{14}$ embedded in the point charges. The increase in the excitation energy results from too strong an orthogonality imposed between the quantum $Mg_{13}O_{14}$ cluster and the remaining ions represented by TIP's and aiMP's. Moreover, the localization of the SOMO is not predicted without constraints; the SOMO must be localized because of this orthogonality. A more realistic representation of the solid is obtained by adding basis functions to the TIP's representing the 30 nearest Mg^{2+} cations. This relaxes the strong orthogonality constraints and, in addition, permits the SOMO to further delocalize by using these basis functions. However, the ROHF-calculated value of $\langle \hat{r}^2 \rangle^{1/2}$ is 3.49 Å, slightly shorter than the value computed from the $Mg_{13}O_{14}$ cluster surrounded by point charges (PC's) and well inside the cube of 7.28 Å. This is a further strong confirmation of the localized nature of this one-electron state. Moreover, the ΔSCF and PT2 values for the singlet-allowed transition energy are 56.1 and 55.3 eV, respectively. The PT2 value is still 0.9 eV higher than the experimental value, whereas the value obtained from the model with the PC's is only in error by 0.4 eV. The present results show how difficult is to devise a proper embedding scheme free of artifacts. On the other hand, cluster models embedded in PC's perform extraordinarily well even for such complex excited states.

We close the discussion by pointing out that the present assignment of the electronic excitation leading to the appearance of the exciton in SiO_2 is different from that suggested by the authors of the original experimental investigation[27] and also by a previous theoretical work.[43] Both studies assume that the exciton also originates from a $2p^6 \rightarrow 2p^5 3s^1$ excitation on a Si^{4+} cation in a fully ionic system SiO_2, in clear contradiction with the chemical nature of this oxide. The systematic theoretical analyses presented in this section show that it is not necessary to assume a full oxidized Si atom to quantitatively predict the existence of an exciton in SiO_2. In addition, the origin of the exciton in SiO_2 is attributed to a $2p^6 \rightarrow 2p^5(\mathrm{SOMO})^1$ excitation involving an Si atom that is not fully oxidized rather than a $2p^6 \rightarrow 2p^5 3s^1$ excitation in a Si^{4+} cation. On the other hand, the present work adds further support to the ionic description of MgO and Al_2O_3 and to the assignment of the excitonic features to a $M(2p^6) \rightarrow M(2p^5 3s^1)$-like excitation in agreement with the proposal of O'Brien *et al.*[27] However, in spite of the apparent success of the atomic models, we must remark that, in all cases, the character of the SOMO in the final state cannot be described as an atomic orbital.

V. CONCLUSIONS

The existence of localized excited states in MgO, Al_2O_3, and SiO_2 arising from metal $2p$ core-level excitations is predicted from *ab initio* cluster model wave functions. The excitation energies leading to these localized excited states permit us to understand the appearance of excitonic features in the energy gap of these materials. Theoretical values obtained from computations carried out at different levels of theory permit us not only to reach a quantitative agreement with experiment but also to understand the role of different physical effects. The most important contribution is atomic in nature; a meaningful zero-order approximation is that in MgO and Al_2O_3 the exciton can be assigned to a $M(2p^6) \rightarrow M(2p^5 3s^1)$-like excitation. However, the open-shell orbital in the final state cannot be described as a $3s$ atomic orbital because it has important contributions from the ions near the atomic site where the excitation occurs. Nevertheless, the final state for MgO appears to be localized in space without any *a priori* assumption; the localization follows from the hole-particle interaction implicitly included in the final-state wave function. However, a significantly larger cluster model is required to obtain a completely localized final state in Al_2O_3. The Madelung field reduces the excitation energy with respect to the atomic value; the effect of neighboring atoms, mainly Pauli repulsion, acts in the opposite way; and, finally, electronic correlation effects decrease it again. The result of this balance is that the values obtained from the calculation on the free atom are close to those computed for the largest cluster models. For SiO_2 the situation is very similar but the exciton cannot be understood as arising from a $M(2p^6) \rightarrow M(2p^5 3s^1)$ in a fully oxidized Si cation. This assignment is in agreement with the covalent nature of this oxide and is at variance with $X\alpha$ calculations that claim good agreement with experiment on the basis of a fully ionic description of SiO_2.[43] Finally, it is worth pointing out that the decrease in the singlet-triplet energy in going from the atom to the solid observed by O'Brien *et al.*[27] is reproduced by the present cluster models, adding further support to the adequacy of the present theoretical approach.

In summary, the *ab initio* cluster model approach permits us to reach a quantitative understanding of the excitonic features on these materials, allows us to confirm previous assignments for MgO and Al_2O_3, and gives us suggestions to reinterpret the assignment concerning SiO_2. The present study adds further support to the cluster model approach as a useful tool for the study of these complex excited states in ionic solids.

ACKNOWLEDGMENTS

This work has been financed by the Spanish ''Ministerio de Educación y Ciencia'' CICyT Project No. PB98-1216-CO2-01 and, in part, by the Generalitat de Catalunya SGR1999-SGR0040 project. C. de G. acknowledges financial support through the TMR activity ''Marie Curie research training grants,'' Grant No. FMBICT983279 established by the European Community. Part of the computer time was provided by CESCA/CEPBA through research grants from the University of Barcelona.

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