Ab initio valence-bond cluster model for ionic solids: Alkaline-earth oxides

A. Lorda, F. Illas, and J. Rubio
Departament de Química Física, Facultat de Química, Universitat de Barcelona, C/Martí i Franques 1, 08028 Barcelona, Spain

J. B. Torrance
IBM Research Division, Almaden Research Center, 650 Harry Road, San José, California 95120-6099
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A linear *M*-O-*M* (*M* = metal, O = oxygen) cluster embedded in a Madelung field, and also including the quantum effects of the neighboring ions, is used to represent the alkaline-earth oxides. For this model an *ab initio* wave function is constructed as a linear combination of Slater determinants written in an atomic orbital basis set, i.e., a valence-bond wave function. Each valence-bond determinant (or group of determinants) corresponds to a resonating valence-bond structure. We have obtained *ab initio* valence-bond cluster-model wave functions for the electronic ground state and the excited states involved in the optical-gap transitions. Numerical results are reasonably close to the experimental values. Moreover, the model contains the ionic model as a limiting case and can be readily extended and improved.

I. INTRODUCTION

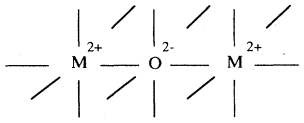
The interest in the electronic structure of transition-metal oxides has been largely stimulated by the discovery of superconductivity at high temperatures.[1-3] It is well known that these oxides are members of a broad class of perovskites and simple transition-metal oxides that may or may not exhibit metallic conductivity and only under very special conditions behave as high-T_c superconductors.

A convenient starting point to understand the electronic structure of these kinds of ionic systems is provided by the framework developed by Zaanen, Sawatzky, and Allen.[4] In this approach, the band gap of a given system is given in terms of two parameters: U and Δ. The U parameter corresponds to the $d_i^n d_j^n \rightarrow d_i^{n-1} d_j^{n+1}$ excitations of the Mott-Hubbard theory,[5] where "i" and "j" denote two transition-metal sites and n the number of transition-metal d electrons. On the other hand, Δ corresponds to the charge-transfer energy $d_i^n \rightarrow d_i^{n+1}\underline{L}$, where $\underline{L}$ denotes a hole in the anion band. Both parameters, U and Δ, are taken into account in the Anderson model Hamiltonian.[6]

Usually U and Δ are taken from experiment,[4] although there have been some attempts to compute them directly by means of *ab initio* theory of electronic structure. A clear example of this approach is the cluster-model study of NiO reported recently by Janssen and Nieuwpoort.[7] The only problem in this approach arises from the fact that both excitations, U and Δ, are computed by considering that the two sites involved are infinitely far away from each other. As a result, their ionized cluster becomes charged and it is necessary to take into account the bulk polarization. In the work of Janssen and Nieuwpoort, this is done in a semiempirical way through the classical Claussius-Massotti relation.

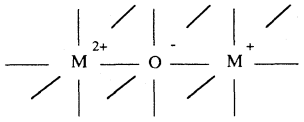
It is also possible to consider that U and Δ correspond to local excitations, as in the ionic model of Torrance *et al.*,[8] where these parameters are computed from experimental data for the ionization potential of the metals, assuming a value of -7.7 eV for the electron affinity for O^-, including the Madelung potentials, and taking into account explicitly the Coulomb interaction between the electron and hole. This simple model enabled Torrance *et al.*[8] to classify 76 oxide systems as either (1) insulating with large Δ and large U, or (2) metallic with small Δ, or (3) metallic with small U.

The oversimplified picture arising from the ionic model of Torrance *et al.*[8] should be more properly treated by some model of the electronic structure theory in order to include important effects that are neglected by this very simple model. In particular, the valence-bond (VB) theory[9] appears to be especially well suited because for an ionic divalent system (such as MgO, for instance), the ground-state wave function will be dominated by the



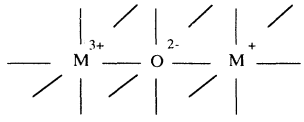
(1)

resonating valence-bond component. In the VB framework an excited electronic state can be schematically depicted as



(2)

for the state corresponding to a charge-transfer Δ or



(3)

for those states corresponding to a U excitation energy. The electronic ground state will be a mixing of these (and other) components and the same applies to the electronic states dominated by Δ and U. Now, if we omit the coupling between the different resonating VB components, the VB model reduces to the simple ionic model of Torrance *et al.*[8] If we use a cluster model, with the adequate embedding scheme, and a basis set to explicitly describe the wave functions corresponding to the resonating VB structures (1), (2), and (3) and compute the expectation value of the energy, for each one of these wave functions, we will have an *ab initio* extension of the ionic model. Subsequent improvements of this model are straightforward by including the coupling between the different VB determinants (through a variational configuration-interaction approach), the more important quantum effects of neighboring ions (QENI) and the effect of the external correlation.

Unlike band-structure calculations, the resulting VB wave function is explicitly correlated and from the very beginning the many-body nature of the electronic system is taken into account. By a correlated wave function we mean that the (VB) N-electron function is not an eigenfunction of a Hamiltonian which can be written as a sum of monoelectronic operators (as in the Hartree-Fock theory).

In this paper, we will introduce the cluster *ab initio* valence-bond model and apply it, as a first step, to the simple oxides of the alkaline-earth elements. Finally, we recall the similarity between the present model and the one used by Fujimori and Minami.[10] The important difference between the present work and Ref. 10 lies in the *ab initio* (parameter-free) nature of our model where all the matrix elements are explicitly evaluated.

II. THE CLUSTER MODEL FOR SIMPLE OXIDES

In this work we use a small cluster model containing three atoms surrounded by a set of 340 point charges (PC's) or 336 point charges and 4 pseudopotentials to describe the oxygen nearest-neighbor metal atoms not included explicitly in the model (see Sec. V). The model contains two metal atoms and one oxygen (Fig. 1) and the number of electrons explicitly involved in the calculation is the one corresponding to M^{2+} and O^{2-} although the resulting model (real atoms plus the PC's) has zero net charge. The set of PC's has been optimized to reproduce the Madelung potential in a large set of points on spherical surfaces centered on each cluster atom, plus a set of points on the lines connecting next nearest neighbors, and imposing zero charge for the resulting system. Only the PC's corresponding to sites other than those where the real atoms are have been optimized and symmetry conditions on equivalent sites have been imposed in the optimization process. It is worth pointing out that the Madelung potential calculated along any other arbitrary direction differs in less than 0.001 hartrees from the exact potential obtained through the use of the well-known Ewald techniques.

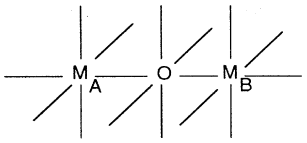


FIG. 1. Schematic representation of the cluster model used to represent alkaline-earth oxides.

A limitation arising from the limited cluster size is that Δ energies correspond largely to excitations to nearest neighbors whereas U corresponds to local excitations between second-nearest neighbors. Consequently, the values of U and Δ calculated in our M-O-M model may differ from those calculated for the other geometries. For example, MO_6 and MO_4 clusters have no excitation corresponding to U, while the nearest metal-metal distance (which affects the value of U) is closer for the M_6O and M_4O clusters than our M-O-M model. However, in this work, our interest is focused on the presentation of the model and its performance to reproduce the optical band gap at different levels of approximation. The systems we deal with are clearly charge-transfer insulators and the effect of U will be of minor importance, especially for the calculated value of the energy Δ.

A final point to be stressed is that the small cluster size discussed here can be readily extended to larger clusters and we can use the same computational framework presented in the forthcoming sections (see Sec. X).

III. THE VALENCE-BOND MODEL SPACE

The electronic configuration dominating the electronic ground state corresponds to $1s^2 2s^2 2p^6$ for oxygen (behaving as O^{2-}) and $(n-1)p^6 ns^0$ for the alkaline-earth metal atoms (behaving as M^{2+}). If the metal atoms are labeled A and B and no label is used for oxygen, the electronic ground state will be dominated by the

$$|\cdots p_{z_A}\overline{p_{z_A}}\cdots p_z\bar{p}_z\cdots p_{z_B}\overline{p_{z_B}}\rangle \tag{4}$$

Slater determinant, corresponding to the resonating VB component indicated in (1). In (4), χ and $\bar{\chi}$ represent the alpha and beta spin orbitals, respectively. Because our cluster model has three atoms lying along the z axis, we will consider local charge transfer along the z direction only. The Slater determinant denoted by (4) can then be abbreviated as

$$|z\bar{z}\rangle\ . \tag{5}$$

It is worth pointing out that in the VB formalism the Slater determinants are constructed from pure atomic orbitals. Hence, $p_{z_A}\overline{p_{z_A}}\cdots p_{z_B}\overline{p_{z_B}}$ is a set of atomic orbitals whose explicit form will be considered in the next section.

Corresponding to the VB resonating structure (2), we can construct the following VB Slater determinants:

$$\begin{aligned} &|z\overline{s_A}\rangle\ , \\ &|\bar{z}s_A\rangle\ , \\ &|z\overline{s_B}\rangle\ , \\ &|\bar{z}s_B\rangle\ , \end{aligned} \tag{6}$$

for a total z component of the spin angular momentum (S_z) of zero. In (6) s_A and s_B are the ns atomic orbitals (AO's) of the cation which are not occupied in (5). These determinants correspond to a single excitation from either z and $\bar{z}$ to the empty spin orbitals of the cation.

For the VB resonating structure labeled (3) we can construct the following VB Slater determinants:

$$\begin{aligned} &|p_A z\bar{z}\bar{s}_B\rangle \equiv |p_A\bar{s}_B\rangle \ , \\ &|\bar{p}_A z\bar{z}s_B\rangle \equiv |\bar{p}_A s_B\rangle \ , \\ &|p_B z\bar{z}\bar{s}_A\rangle \equiv |p_B\bar{s}_A\rangle \ , \\ &|\bar{p}_B z\bar{z}\bar{s}_A\rangle \equiv |\bar{p}_B s_A\rangle \ . \end{aligned} \tag{7}$$

Finally, we consider the valence-bond contributions corresponding to neutral oxygen. There are two different ways to construct resonant forms with neutral oxygen, namely,

$$M^{2+}\text{–}O^0\text{–}M^0 \tag{8}$$

and

$$M^{+}\text{–}O^0\text{–}M^{+} \ . \tag{9}$$

The VB Slater determinants associated with (8) are

$$\begin{aligned} &|p_A\bar{p}_A s_B\bar{s}_B\rangle \ , \\ &|p_B\bar{p}_B s_A\bar{s}_A\rangle \ , \end{aligned} \tag{10}$$

and those corresponding to (9) may be written as

$$\begin{aligned} &|s_A\bar{s}_A\rangle \ , \\ &|s_B\bar{s}_B\rangle \ , \end{aligned} \tag{11}$$

and we recall that z and $\bar{z}$ are not occupied in either (10) or (11).

The final valence-bond model space contains the Slater determinants (5), (6), (7), (10), and (11), having dimension 13×13. It is important to point out that depending on the orbital basis set used to construct the VB Slater determinant, the resulting secular equations must include (or not include) explicitly the overlap between them. In the next section we will show how the orbital basis set is constructed and orthogonalized. The N-electron VB basis set is then orthogonal. Because this basis set directly uses Slater determinants, it is not spin or symmetry adapted. The transformation of the VB basis to a spin and symmetry adapted basis is straightforward although it is not convenient from the computational point of view.

Once the VB model space is constructed we define the projection operator $\hat{P}_s$ as

$$\hat{P}_s = \sum_{k\in \mathrm{VB}} |k\rangle\langle k| \ , \tag{12}$$

where $|k\rangle$ is one of the 13 Slater determinants and S is the VB model space. Next, we solve the secular equations (the orthogonal VB problem)

$$\hat{P}_s\hat{H}\hat{P}_s|\psi_m\rangle = E_m|\psi_m\rangle \tag{13}$$

which lead to the eigenfunctions of the electronic Hamiltonian in the VB model space basis set. These eigenfunctions are of the form

$$|\psi_m\rangle = \sum_{k\in \mathrm{VB}} C_{mk}|k\rangle \ . \tag{14}$$

To solve (13) a number of matrix elements H_{ij} have to be computed. This is done without introduction of any empirical parameter provided each $|k\rangle$ VB determinant is constructed from an atomic orbital basis set and the set of integrals necessary to evaluate H_{ij} computed within the AO basis set.

IV. THE ATOMIC ORBITAL SET

To construct the VB Slater determinants, it is necessary to have a set of (orthogonalized) atomic orbitals. If the system we are concerned with is an ionic crystal, it would be logical to use as atomic orbitals those of the cation and anion in the crystal. These orbitals are obtained by performing a Hartree-Fock self-consistent-field (SCF) calculation of the M^{2+} or O^{2-} anion in the Madelung field. Technically, this is done by surrounding the ion by the set of point charges used to obtain a proper simulation of the Madelung potential and expanding these orbitals in a basis set of contracted Gaussian-type orbitals (CGTO's).

The CGTO basis set for the cations is the one reported by Huzinaga[11] for the M^{2+} cations augmented with two s primitive GTO's, to represent the outer s orbital of M (not occupied in the dication), and one p primitive GTO. The exponents of these functions were obtained in an even tempered way. For O^{2-} we use a basis set optimized for O^- (Ref. 12) and used previously to study the core-level shift in MgO.[12] Details about basis-set quality and contraction schemes are given in Table I.

Once the CGTO basis set is defined, a SCF calculation is carried out for a cluster model consisting of the ion and the set of point charges used to represent the Madelung potential. The resulting set of atomic orbitals is, of course, orthogonal. However, the AO set of each atom in

TABLE I. Atomic basis set used to describe the atomic orbitals of M^{2+} and O^{2-} (3*1 stands for 1+1+1 and so on).

	Primitive GTO	CGTO	s contraction	p contraction	d contraction
O^{2-}	11s 7p	5s 3p	5,2,1,2,1	4,2,1	
Mg^{2+}	9s 5p	6s 3p	3,1,2,3*1	3,2*1	
Ca^{2+}	12s 8p	8s 5p	3,1,2,1,2,3*1	3,1,2,2*1	
Sr^{2+}	15s 11p 4d	8s 6p 1d	4,3,2,1,2,3*1	4,1,2,1,2,1	4
Ba^{2+}	18s 14p 7d	9s 6p 2d	4,2*3,2,1,2,3*1	4,2*3,1,2,1	4,3

our cluster (1) for the simple oxides is not orthogonal to the AO set of the other cluster-model atoms. An orthogonal set is obtained by first using the Löwdin procedure to orthogonalize the AO's of both metals and then a Schmidt orthgonalization is carried out between O^{2-} AO's and those of the M^{2+}-···-M^{2+} cluster which at this step are an orthogonal set), taking care not to mix core and valence orbitals. The resulting set is orthogonal, but contains some orthogonality tails. An analysis of the electron density associated with each orthogonal AO reveals that the tails are indeed very small although they increase from Mg to Ba. The implication of these orthogonality tails will be described in Sec. VIII.

Using this set of orthogonal AO's, the resulting set of VB Slater determinants, constituting our model space, is also an orthogonal set and can be solved by using standard configuration-interaction (CI) techniques.

V. INTRODUCTION OF QUANTUM EFFECTS OF NEIGHBORING IONS

In the previous section we have described how to obtain the AO's of the ion in the crystal. This set of AO's is only an approximation to the set we would like to have. This is because there are quantum effects of neighboring ions (QENI), other than Madelung ones, that must be considered. In particular, it is necessary that the AO's of the cluster ions be orthogonal to the other ions in the lattice. QENI does affect both orbital energies and orbital shapes (see, for instance, Refs. 13 and 14). The effect on the cations is very small because of the contracted nature of the AO's of a positively charged atom. On the contrary, QENI is very large for O^{2-}, especially for the $2p$ AO's. A simple way to (partially) take QENI on the O^{2-} into account is to obtain the O^{2-} AO's in a cluster model where the nearest-neighbor cations of O^{2-} have been replaced by pseudopotentials.[15-17] This is precisely the approach we have used to introduce QENI in our cluster model. This leads to a set of AO's for O^{2-} that contains the dominating QENI on the atomic-orbital shape. The resulting $2p$ orbitals for O^{2-} are indeed very close to those obtained using more sophisticated approaches as the *ab initio* perturbed-ion method.[13]

Another quantum effect due to the neighboring ions on the cluster model we use may arise from the set of integrals computed in the given basis set. In fact, if we replace the point charges nearest to O^{2-} by pseudopotentials (as done above) the one-electron integrals for the given basis set will be different and closer to those obtained if the cluster model were larger.

In this work we have explored both kinds of QENI by explicitly substituting the oxygen nearest-neighbor point charges by pseudopotentials. We can see their effect by simply performing the calculations by explicitly including them or not (see Table IV).

VI. EXTERNAL CORRELATION EFFECTS

The VB wave functions (14), although they are explicitly correlated wave functions (they are not eigenfunctions of an independent-particle Hamiltonian), arise from an expansion that may be too limited to account quantitatively for the energy differences between the different electronic states. This is particularly true for the excited electronic states chosen to represent the Δ and U transitions. A way to improve this description is to consider each $|\psi_m\rangle$ function as a zero-order wave function and use perturbation theory to improve both the wave functions and energies.

In order to apply perturbation theory to each $|\psi_m\rangle$ we must realize that from the basis set used there exists a virtual space that is made up of all the remaining orbitals not occupied in any of the VB Slater determinants entering in the definition of $|\psi_m\rangle$. Then we can generate single and double excitations on the Slater determinants by substituting one or two occupied orbitals (in a given determinant) by one or two virtual orbitals. This may be expressed as

$$|k_a^r\rangle = r^+ a|k\rangle$$

or (15)

$$|k_{ab}^{rs}\rangle = r^+ s^+ ba|k\rangle ,$$

where a and b are the annihilation quasiparticle operators (for occupied orbitals) and r^+, s^+ the corresponding creation operators. If all the occupied orbitals are considered as active, the number of generated determinants of the type (15) may be enormous. Moreover, it is unlikely that excitations from the core levels will be important to describe the electronic transitions we are interested in. Accordingly, the active occupied orbitals are those corresponding to the $(n-1)p$ shell plus the ones of the $2s$ and $2p$ shells of oxygen. In our small cluster model this gives rise to $6+6+8=20$ active electrons.

The zero-order Hamiltonian is then defined as

$$\hat{H}^0 = \sum_{m \in \mathrm{VB}} E_m |\psi_m\rangle\langle\psi_m| + \sum_{I \notin \mathrm{VB}} E_I^0 |I\rangle\langle I| , \tag{16}$$

where $|I\rangle$ can be any of the determinants defined in (15) and $E_I^0 = \langle I|\bar{H}|I\rangle$. With this definition the perturbation operator is

$$\hat{V} = \hat{H} - \hat{H}_0 \tag{17}$$

and the first-order wave function is obtained as

$$|\psi_m^{(1)}\rangle = \sum_{I \notin \mathrm{VB}} \frac{\langle\psi_m|\hat{V}|I\rangle}{E_m - E_I^0}|I\rangle = \sum_{k \in \mathrm{VB}} \sum_{I \notin \mathrm{VB}} C_{mk} \frac{\langle k|\hat{H}|I\rangle}{E_m - E_I^0}|I\rangle \tag{18}$$

leading to a second-order energy

$$E_m^{(2)} = E_m + \sum_{k,l \in \mathrm{VB}} \sum_{I \notin \mathrm{VB}} C_{mk} C_{ml} \frac{\langle k|\hat{H}|I\rangle\langle I|\hat{H}|l\rangle}{E_m - E_I^0} \tag{19}$$

for each one of the electronic states belonging to our VB model space.

We refer to external correlation as the energy contribution of those VB Slater determinants not included in the VB model space, although a precise definition of correlation it is not possible in this case because the starting wave function $|\psi_m\rangle$ is not derived from a Hartree-Fock

calculation.

Because only second-order contributions are included, it is possible that the second-order energies for different states Δ or U are not balanced. This can be solved by introducing formally a variational class among those $|I\rangle \notin \mathrm{VB}$, although this has not been done in the present work.

The perturbation theory above corresponds to the Epstein-Nesbet partition of the electronic Hamiltonian and the overall procedure is closely related to the configuration interaction by perturbative selective iteration (CIPSI) algorithm[18–20] used in molecular electronic structure calculations. A point that must be commented on when dealing with extended systems concerns the size consistency of the method used. The wave function corresponding to the configuration interaction in the model space is not size consistent because it is a truncated CI expansion. However, many of the unlinked terms introduced by the normalization of the CI wave function on the model space are eliminated after including the second-order contribution through Eq. (19). If the barycentric Moller-Plesset partition of the electronic Hamiltonian is used, Malrieu has shown[21] that the second-order energy given by Eq. (19) grows, in the limit of an infinite number of particles, as $(\frac{2}{3})N$ (N being the number of particles). For the Epstein-Nesbet partition a comparable analytical study is not available. However, a recent study by Rubio *et al.*[22] shows that, for practical cases involving up to 56 electrons, both partitions behave similarly and the error introduced by unlinked terms is less than 1%. In the present case we use a limited model to represent an extended system and energy differences used to compute the optical gap from local excitations involve a constant number of electrons. Hence, it is very unlikely that the present results will be affected by size-consistency effects.

Finally, let us say that if a VB model space of dimension 13 is used and 20 electrons are considered active, the number of VB determinants $|I\rangle \notin \mathrm{VB}$ is around 700,000 and their contribution to the energy of a given state $|\psi_m\rangle$ is given in Eq. (19).

VII. A NUMERICAL TEST OF GROUND-STATE ENERGIES

In order to have an estimate of the performance of the *ab initio* valence-bond wave function, we compare here the total energy for the ground state of our cluster model as obtained from different approaches.

A first reference can be obtained by performing a Hartree-Fock calculation for the closed-shell Slater determinant (4) and comparing the result with the energy expectation value obtained when the orbitals entering into the definition of (4) are fixed to their atomic (orthogonal) shape, as described in Sec. IV. These energies are reported in Table II as E_{SCF} and H_{ii}, respectively. It is remarkable to see that at the simple H_{ii} level (where only the diagonal elements of the representation of the electronic Hamiltonian in the valence-bond model space) the calculated energy lies only $\sim 5\times 10^{-3}$ hartrees (~ 0.14 eV) above the Hartree-Fock energy of MgO, CaO, and SrO, and 5×10^{-2} hartrees (~ 1.4 eV) above the SCF value for BaO. This difference between both values is due to the covalent bonding contributions that permit the AO's of the metal to mix with those of the anion and, also, to the static polarization of the orbitals of a given atom due to the presence of the other cluster atoms.

Next, we consider the VB energy (E_{VB}) which is obtained by the diagonalization of the **H** matrix in the valence model space. The main effect is to permit the dionic VB determinant (5) to mix with the Δ and U valence-bond components. By including this configuration interaction, the energy with respect to the SCF is somewhat smaller but here electronic effects other than covalent and static polarization contributions are also included.

Finally, we consider the external correlation effects ($E_m^{(2)}$), arising from the second-order contribution of all the VB generated determinants, following Eq. (19). In this case, we include also covalent and polarization contributions and the more important instantaneous electron-electron interactions not already included in the model space. A detailed analysis of correlation effects in extended systems has been reported by Malrieu and coworkers.[23,24] These authors also show for convenience a valence-bond wave function to rationalize the different physical contributions to correlation energy.

If we were to be interested in ground-state properties only, a Hartree-Fock calculation followed by either the variational configuration interaction or by using Eq. (19) with only one Slater determinant in the model space will be surely enough and equivalent to the results reported here at either E_{VB} or $E_m^{(2)}$ levels. However, because our interest lies in the determination of the nature of the optical gap and its evaluation, we have to deal with excited electronic states as well. For these electronic states, it is not clear which electronic state has to be considered if a delocalized (molecular-orbital) basis set is used. This is because the corresponding **H** matrix will surely have eigenvalues lying below the one we are interested in. These intruder states correspond to excitations on a given atom without any charge transfer. The main advantage of the VB wave function is that we know from the very begin-

TABLE II. Ground-state total energy of the MO oxides (M = Mg,Ca,Sr,Ba) obtained at different levels of theory (see text). All energies in atomic units.

	E_{SCF}	H_{11}	E_{VB}	$E_{\mathrm{VB}}^{(2)}$
MgO	−525.349 183	−525.344 855	−525.345 912	−525.667 276
CaO	−1519.946 769	−1519.941 729	−1519.944 141	−1520.176 811
SrO	−6567.667 889	−6567.662 441	−6567.676 032	−6567.905 331
BaO	−16249.830 049	−16249.815 413	−16249.817 626	−16250.048 268

ning that the ground state is of the form (5) and also that the excited states are dominated either by combinations of the VB Slater determinants (6) or (7).

VIII. THE IONIC MODEL AS A LIMITING CASE

It is well known that if all the interactions other than purely the electrostatic ones are neglected, the energetics of an ionic system can be extracted from a very simple ionic picture. This will be the case if the lattice parameter is increased somehow with respect to its equilibrium value.

From a purely ionic point of view, the states described by the structures described in (2) in the Introduction will lie at energies given by

$$\Delta_0 = \left[e\Delta V_M - \frac{e^2}{a} \right] - (I - A) , \tag{20}$$

where $e\Delta V_M$ is the difference in the electrostatic energies (Madelung potential) between the cation and the anion, I is the ionization potential of M^+, and A is the electron affinity of O^- (see Ref. 8). A plot of Δ_0 versus $1/a$ will give a straight line with equal slope for all the oxides from MgO to BaO.

In our cluster model, if we do not consider any mixing between the different resonating structures we will be left with the diagonal elements of the **H** matrix. These elements provide an estimation of the energy of each VB component and give us an *ab initio* ionic model. To test this idea we have carried out calculations of these H_{ii} elements at different values of the lattice constant (from $1.3r_e$ to $1.8r_e$) where we know that the ionic model holds. These calculations are carried out using the same AO set orthogonalized at the corresponding geometry. A plot of H_{ii} versus $1/a$ gives indeed a straight line and the slope of this line is very close to the one obtained using the ionic model (see Table III). The small deviations in SrO and BaO are due to the orthogonality tails which cause the resonating structures defined in (2) (i.e., M^{2+}–O^-–M^+) to not correspond strictly with the result of the calculation. In fact, the orthogonality tails put a part of the electron density of the anion near the cation and the resulting structure is M^{2+}–$O^{\delta-}$–$M^{\delta+}$ with δ being somehow smaller than one. This explains the deviation of the calculated slope from the one obtained using a purely ionic model. On the other hand, the fact that the calculated H_{ii} plotted versus $1/a$ is a straight line clearly shows that our model reduces to the ionic model at large distances.

TABLE III. Slope of the representations of Δ_0 and H_{ii} vs $1/a$. Results are in (eV/Bohr).

Oxide	Slope
MgO	165.5
CaO	163.9
SrO	154.1
BaO	135.4
Ionic model (Δ_0)	163.0

IX. THE OPTICAL GAP

Now we want to compute the energy difference between the electronic ground state and the first excited state. From the point of view of VB theory it is clear that the states to be considered are those represented by the resonating VB components defined in (1) and (2) in the Introduction. However, we have to recall that our cluster model has left-right symmetry and an inversion center. Consequently, the four VB determinants representing Δ states (if no VB mixing is considered) are classified as either symmetrical (S) or antisymmetrical (A) with respect to a 180° rotation, and as triplet or singlet spin adapted. From the four VB determinants we obtain four VB states that are symmetry and spin adapted that can be represented as ^1S, ^3S, ^1A, and ^3A. The electronic transition permitted by the dipole selection rule is from the ground state to the ^1A electronic state.

In order to gain a deeper insight into the nature of the optical band gap it is interesting to perform the calculation at different levels. If we ignore the interaction between the different VB components we are left with the H_{ii} elements and our model reduces to the ionic model (vide supra). However, there are two different ways of obtaining these H_{ii} elements (using the same basis set) depending on whether the QENI is included or not in the calculation via both orbital and integral effects.

From the summary of results reported in Table IV it is seen that the values calculated for the optical band gap at the H_{ii} level *(ab initio* ionic model) are indeed very close to those obtained from a purely ionic model such as that used in Ref. 8. The inclusion of QENI produces a large decrease in the calculated band gap, although no other effect is included in the calculation. In fact, at this step we have an ionic model plus a representation of the quantum effects of the neighboring ions.

The next step is to allow a VB mixing between the different VB resonating structures. The overall effect of this mixing of di-ionic, monoionic, and neutral (on the anion) VB components is a further decrease of the calculated band gap in the right direction, although the results are less affected than when QENI is considered. At this point, it is important to realize that the orbitals used to describe all the resonating VB structures are those obtained from the electronic ground state. In the electronic states dominated by Δ resonating components, it will be more adequate to use M^+ to describe the outer *ns* atomic orbitals. This effect is partially taken into account by including external correlation. Thus, allowing single and double excitations on the active electrons of each VB determinant in our model space permits the AO's to be accommodated to each instantaneous electron-electron situation. The global result is a large decrease in the calculated band gaps again in the direction of the experimental values (Table IV).

Because each electronic state is described by an adequate N-electron wave function, the difference between the calculated band gap and the experimental value will arise mainly from the limited cluster model we are using. A simple way to estimate the extension of the model is to assume that the bandwidth of the Δ states can, in principle, be approximated by the energy difference between

TABLE IV. Calculated optical gap at different levels of theory assuming that the electronic states involved are the electronic ground state and the proper state dominated by the M^+–O^-–M^{2+} valence-bond components. Results are in eV.

Optical gap	MgO	CaO	SrO	BaO
Ionic model (from Ref. 8)	18.23	16.39	14.81	13.54
H_{ii} (*ab initio* ionic model without QENI)	18.1	14.0	12.0	8.3
H_{ii} (*ab initio* ionic model with QENI)	15.7	12.4	11.3	9.0
VB (valence bond in model space)	15.1	11.8	10.6	8.3
VB+2nd order	12.2	9.3	7.9	5.9
VB+2nd order+ estimated of bandwidth	10.9	8.0	6.2	4.8
Experimental value (Refs. 21 and 22)	7.7–7.8	6.8–7.1	5.8–6.0	3.8
ab initio Hartree-Fock band theory (Ref. 23)	17.6	15.9	14.9	
ab initio Hartree-Fock band theory plus second order on the one-electron levels (Ref. 23)	8.2	7.7	7.1	

the lowest and highest states among those representing Δ. To avoid possible artifacts arising from an unbalanced perturbation correction to the different electronic states we have estimated the Δ bandwidth directly from the **H** matrix eigenvalues in the VB model space. The final result, considering this estimated bandwidth, is reasonably close to the experimental values.[25,26]

Finally, we would like to compare our results with those reported recently by Pandey, Jaffe, and Kunz.[27] These authors have used *ab initio* Hartree-Fock band theory to compute the optical gap of MgO, CaO, and SrO. They also include a detailed and very interesting discussion about the failure of the Hartree-Fock one-electron levels to represent electronic transitions and show how these one-electron levels can be approximately corrected by using second-order perturbation theory. Results from Pandey's work have been included in Table IV for comparison. Unfortunately, details about the basis-set quality are not given in 27, the only information being the use of a set of 35 plane waves. It is remarkable to see how close the values derived from H_{ii} without QENI are to the *ab initio* Hartree-Fock ones. Moreover, the better description of the optical band gap achieved at the VB level indicates the superiority of this approach. This better description is due to the use of an explicitly correlated N-electron wave function for both ground and excited electronic states. It is also worth pointing out that after extensively including correlation effects, both approaches converge fairly well to the experimental values. A valuable feature of the present approach is that it can be systematically improved by extending the one-electron basis set, using a larger cluster model, expanding the model space, and taking into account correlation effects at higher order of perturbation theory. All these improvements are possible and are currently being investigated in our laboratory.[28] Some of these improvements are further discussed in Sec. X.

X. A COMMENT ON CLUSTER-SIZE EFFECTS

Even assuming that the physics involved in the determination of the optical gap may be well described by a model based on local excitations, one may wonder whether the results depend or not on the cluster size. This possibility can be explored by using a larger cluster model. In this section we will report results obtained for MgO using a larger cluster model containing explicitly one central oxygen atom and four metal atoms plus two total ion potentials and the remaining 336 point charges used to represent the Madelung field. When using the Mg_4O cluster model (of D_{4h} punctual symmetry), the number of electronic states corresponding to structures (1), (2), and (3) is larger than that for the small cluster because of the possible spin combinations and the larger number of active orbitals and electrons. If the model space for Mg_4O is constructed by keeping the ground-state closed-shell determinant, and only those determinants in which an electron from O^{2-} has been transferred to the 3s atomic orbital of one of the cations, we have 25 determinants. This choice leads to a model space which is as close as possible to that used in the smaller cluster model. The energies of these electronic states have been computed by diagonalization of the Hamiltonian matrix in the model space and further improved by second-order perturbation theory using Eq. (19).

For Mg_4O we have studied the ground state and the 24 electronic states corresponding to a Δ excitation. The model space contains 25 determinants and the number of determinants included at the second-order level of perturbation theory is ≈ 5 millions.

The symmetry permitted transitions leading to the optical gap are now from the $^1A_{1g}$ ground state to either $^1A_{2u}$ or ^1E_u. It has to be pointed out that within this model space there are two different states of ^1E_u symmetry and that only the lowest one will be considered here.

TABLE V. Calculated optical gap for Mg_2O and Mg_4O at different levels of theory assuming that the electronic states involved are the electronic ground state and the proper state corresponding to a local excitation from O^{2-} to Mg^{2+}. Results are in eV.

Level of theory	Mg_2O	Mg_4O
VB (Valence bond in model space)	15.1	14.4 (from $^1A_{1g}$ to $^1A_{2u}$)
		14.7 (from $^1A_{1g}$ to ^1E_u)
VB+2nd order	12.2	12.4 (from $^1A_{1g}$ to $^1A_{2u}$)
		12.2 (from $^1A_{1g}$ to ^1E_u)

Results for the two electronic transitions compatible with the optical gap are reported in Table V and compared with those obtained using the smaller model.

Analysis of the results in Table V show that the transition energies obtained through both models are very close. The important point is the similarity between the results obtained in the model space and the equal importance of external electronic correlation effects. Hence the overall description of the electronic transitions leading to the optical gap do not seem to depend on the cluster size, at least when going from Mg_2O to Mg_4O. It is very unlikely that results will be changed by further increase of the cluster size to Mg_6O.

The point we want to stress is once again the usefulness of the model to identify different physical contributions; contributions that given the local character of the process seem not to be largely dependent on the cluster size.

XI. CONCLUSIONS

In this work we have presented a cluster model approach to studying the electronic structure of ionic systems and applied it to simple oxides of alkaline-earth elements. The cluster model contains explicitly the Madelung fields and the more important QENI.

Using this cluster model, an *ab initio* valence-bond wave function is constructed to describe the electronic structure of the ground state and, also, of the excited electronic states involved in the electronic transitions leading to the optical gap. These valence-bond wave functions are explicitly correlated and can be indeed used as a multireference zero-order wave functions in a perturbation framework. The main advantage of using these VB wave functions lies in the physical description they contain. In this approach, it is straightforward to construct accurate wave functions which are directly related with simple physical ideas arising from a crude model as a starting point. In fact, if no coupling between the different VB components of the **H** matrix is considered, the model reduces to the ionic model but from an *ab initio* point of view where the energy of each ionic structure is directly computed as an expectation value using no approximations in the Hamiltonian and without introducing parameters in the evaluation of the matrix elements. A further advantage of the model is that it permits us to explore separately the different contributions to the optical gap. Starting from the *ab initio* ionic model, the result is improved by successively introducing different physical contributions such as QENI, mixing of different valence-bond components, by performing a configuration interaction in the model space, and including external correlation effects through perturbation theory.

For the alkaline-earth oxides we obtain a reasonable description of the optical gap at a quantitative level. Our results are very close to the experimental values and in good agreement with the recent *ab initio* Hartree-Fock band calculation of Pandey *et al.*[27] after including the correlation correction. Thus, both approaches agree in the large importance of correlation effects to properly describe these optical excitations. However, the important point is not the ability to reproduce more or less accurately the experimental results but the possibility of exploring the importance of the different physical contributions.

The cluster *ab initio* valence-bond model for ionic systems introduced here can be readily extended and its application to other oxides, particularly those containing transition-metal atoms, is being actively explored in our laboratory. We hope this model will provide a novel and useful way to explore the electronic structure of these fascinating systems.

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