

Calculation of the band gap energy of ionic crystals

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The band gap of alkali halides, alkaline-earth oxides, Al_2O_3 and SiO_2 crystals has been calculated using the perturbed-ion model supplemented with some assumptions for the treatment of excited states. The gap is calculated in several ways: as a difference between one-electron energy eigenvalues and as a difference between the total energies of appropriate electronic states of the crystal, both at the HF level and with inclusion of Coulomb correlation effects. The results compare well with experimental band gap energies and with other theoretical calculations, suggesting that the picture of bonding and excitation given by the model can be useful in ionic materials.

Keywords: Cluster model; alkali halides; oxides; band gap

El salto de banda de cristales haluro alcalinos, óxidos alcalinotérreos, Al_2O_3 y SiO_2 , se ha calculado utilizando el modelo del ion perturbado complementado con algunas aproximaciones para el tratamiento de los estados excitados. El salto se calcula de varias maneras: como una diferencia entre autovalores de energía monoeléctricos y como una diferencia entre las energías totales de estados electrónicos cristalinos apropiados, tanto al nivel HF como incluyendo los efectos de correlación de Coulomb. Los resultados están en buen acuerdo con las energías de salto de banda experimentales y con otros cálculos teóricos, lo que sugiere que la visión que da el modelo del enlace y las excitaciones puede ser útil para materiales iónicos.

Descriptores: Modelo de cúmulo; haluro alcalino; óxidos; salto de banda

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1. Introduction

The increasing interest which is presently observed in luminescent materials is due to their numerous technological applications, namely, luminescent lighting and preparation of lamp phosphors, nuclear spectroscopy, laser science, or the construction of two-dimensional detectors for use in medical screens and crystallography, to mention a few [1]. The calculation of the properties of those materials requires a model for the material and a computational model. The first one concerns the modelling of the crystal of interest. The computational model concerns the level of theory used in the calculations. The calculation of the electronic properties of doped ionic crystals (or crystals containing vacancies) at an *ab initio* level is still a challenge for the computational methods normally used for crystalline solids or molecules. The reason in the first case is the breaking of the translational symmetry by the presence of the defect. This enters in conflict with Bloch's theorem, which is the basis of the solid state calculations. A solution to this problem is to use a supercell geometry, in which a cell simulating a small region of the crystal containing the defect is repeated periodically [2]. There is the danger

of interaction between the defects if the supercell is not large enough. The use of molecular methods in real space requires also a large number of atoms to be treated in a selfconsistent way [3]. so the available techniques do not handle easily this problem. Those molecular methods replace the whole crystal by a cluster, but the role of the surface should not be overlooked even for large clusters. An intermediate approach is provided by embedded cluster models, in which the impurity is surrounded by a small fraction of the crystalline environment, and the rest of the crystal is simply described by point charges. This approach has been already applied to the problem of luminescent impurities [3]. Evidently, the description by point charges only gives an approximate representation of the bulk. In summary, a large number of atoms is needed for simulating an ionic crystal containing an impurity, and even in such a case the inherent problems of the cluster surface and the description of the infinite bulk should be faced. Thus, a model that gives a better description of the impurity-lattice and cluster-lattice interactions is desirable. The ideas of the theory of electronic separability (TES) developed by Huzinaga and coworkers [4–6] should be useful in this context. The TES supplies a natural framework to develop accurate schemes for dealing with the cluster-lattice interaction. The

perturbed ion (PI) model [7], based on the TES, was developed for the study of ionic crystals or, more in general, for crystals formed by atoms with closed shells, and has been later extended to free clusters of the same materials [8, 9].

We plan to apply the PI model to study luminescent centers in ionic crystals. As a first step, we use the PI model in this paper to calculate the band gap of pure alkali halide, alkaline-earth oxide, Al_2O_3 and SiO_2 crystals. All these materials are important in the field of luminescence and also in other fields ranging from catalysis to magneto-optical devices. The calculation of the energy band gap of these materials is important for several reasons: first of all, the impurity levels of the doped crystals are located in the band gap of the pure crystal. Furthermore, the gap is a very important quantity in the first step of the scintillation process, namely, absorption of radiation leading to formation of electron-hole pairs. This step influences the global efficiency of the scintillator. Last but not the least, it is also important from the theoretical point of view, as it gives information on the quality of the model. Well known are the difficulties of density functional theory to describe band gaps. A large body of work exists on the calculation of the band gaps in these materials using the traditional methods of band theory [10–24], and we compare our results to a representative set of band calculations. Although we obtain a better global agreement with experimental gaps than many *ab initio* band structure calculations, our intention here is not to compete with those well established solid state methods. Instead, we only intend to show that the PI model affords an accurate description of the band gap within the framework of a cluster-like approach, which is considered a convenient approach for the study of doped crystals.

The structure of the paper is as follows: In Sect. 2 we present the PI model for ionic crystals, showing how several problems concerning the cluster approximation are circumvented. Since the PI model is originally formulated in a Hartree-Fock (HF) framework, we also discuss the introduction of Coulomb correlation. Section 3 describes the calculation of the gap. Results are presented for the above mentioned crystals and the trends obtained are discussed in comparison with experiment and other calculations. Finally, Sect. 4 summarizes our conclusions.

2. The perturbed ion model

2.1. Theory

The PI model has been developed for systems (pure crystals, crystals with defects, or finite clusters) formed by weakly correlated one-center electronic groups, the prototypical systems being ionic crystals, like the alkali halides, formed by closed-shell ions. Therefore, according to the theory of electronic separability [4–6], the wavefunction of the system can be expressed as an antisymmetrized product of the local wavefunctions describing each group. If these local wavefunctions satisfy strong-orthogonality conditions [25, 26], the total energy

is the sum of intragroup, or net energies, and intergroup, or interaction energies:

$$E_{\text{system}} = \sum_R E_{\text{net}}^R + \frac{1}{2} \sum_R \sum_{S(\neq R)} E_{\text{int}}^{RS}, \quad (1)$$

where the R and S sums run through local groups. All the contributions to E_{system} due to a group A can be collected in an effective energy defined as

$$E_{\text{eff}}^A = E_{\text{net}}^A + \sum_{S(\neq A)} E_{\text{int}}^{AS} = E_{\text{net}}^A + E_{\text{int}}^A, \quad (2)$$

but it should be noted that E_{system} is not a simple sum of the effective energies since the interaction energies are then counted twice. So the additive energy of a group A is defined as

$$E_{\text{add}}^A = E_{\text{net}}^A + \frac{1}{2} \sum_{S(\neq A)} E_{\text{int}}^{AS} = E_{\text{net}}^A + \frac{1}{2} E_{\text{int}}^A \quad (3)$$

and then the total energy of a system formed by a groups of type A , b groups of type B , etc. can be written

$$E_{\text{system}}(A_a B_b \dots) = a E_{\text{add}}^A + b E_{\text{add}}^B + \dots \quad (4)$$

In practice, for ionic crystals the local groups will be identified with the closed-shell ions.

Group wavefunctions are obtained by minimizing their effective energies if strong orthogonality conditions are satisfied among the group wavefunctions. This restricted variational procedure can be successive and iteratively applied to all the different groups, in order to determine fully consistent group wavefunctions and the best system wavefunction compatible with the initial assumption of separability. When the wavefunction of a particular group is being determined, the wavefunctions of all the other groups are considered frozen.

The effective energies can be expressed as expectation values of appropriate effective Hamiltonians. For group A

$$E_{\text{eff}}^A = \langle \psi_A | H_{\text{eff}}^A | \psi_A \rangle = \sum_{S(\neq A)} Z^A V_H^S(R_{AS}). \quad (5)$$

The group-wavefunction ψ_A is a Slater determinant. The first term in Eq. (5), namely $\langle \psi_A | H_{\text{eff}}^A | \psi_A \rangle$, collects the energy associated to the electronic cloud of group A , and the second term gives the interaction between the nucleus A , of charge Z^A , and the Hartree potential of groups $S(\neq A)$. $R_{AS} = |\vec{R}_A - \vec{R}_S|$ indicates the distance between the two nuclei. The effective Hamiltonian H_{eff}^A can be written as a sum of several terms

$$H_{\text{eff}}^A = \sum_{i=1}^{N_A} T(i) - \sum_{i=1}^{N_A} Z^A r_{iA}^{-1} + \sum_{1 \leq j < i \leq N_A} r_{ij}^{-1} + \sum_{i=1}^{N_A} \sum_{S(\neq A)} [V_{\text{eff}}^S(i) + P^S(i)], \quad (6)$$

with $r_{iA} = |\vec{r}_i - \vec{R}_A|$ and $r_{ij} = |\vec{r}_i - \vec{r}_j|$. The i and j -summations run over the N_A electrons of group A . The first three terms in the Hamiltonian represent the electronic kinetic energy, the interaction between the electrons and the nucleus and the interelectronic repulsion (those three terms refer exclusively to group A). On the other hand, the terms containing the S -summation account for the interaction with the frozen groups S . This interaction separates itself in two parts. First, $V_{\text{eff}}^S(i)$ represents the effective potential energy of an electron (of group A) in the mean field of the group S :

$$\begin{aligned} V_{\text{eff}}^S(i) &= -Z^S r_{iS}^{-1} + V_C^S(i) + V_X^S(i) \\ &= V_H^S(i) + V_X^S(i), \end{aligned} \quad (7)$$

where the three terms in V_{eff}^S are the electron-nucleus, the classical electron-electron and the exchange parts of the potential energy (the sum of the first two terms is the Hartree potential V_H^S). Second, the strong orthogonality between the orbitals of the active group A and those of the other groups S is enforced in H_{eff} by means of the projection operator $P^S(i)$. For systems formed by closed shell ions, this operator takes the form [27]

$$P^S(i) = \sum_{g \in S} |\phi_g^S\rangle (-2\epsilon_g^S) \langle \phi_g^S|, \quad (8)$$

where g runs over all occupied one-electron orbitals ϕ_g (with orbital energies ϵ_g^S) of group S .

We now deal with the explicit form of V_{eff}^S [7]. For the closed-shell ions considered here the Hartree part of this potential is given by

$$V_H^S(\vec{r}_1) = -Z^S r_{1S}^{-1} + \int \rho^S(\vec{r}_2) r_{12}^{-1} d\tau_2, \quad (9)$$

where $\rho^S(\vec{r})$ is the electron density of the ion. It is physically and computationally convenient to separate this electrostatic potential into classical and nonclassical (nc) terms such that:

$$V_H^S(\vec{r}_{1S}) = -q^S r_{1S}^{-1} + V_{\text{nc}}^S(\vec{r}_{1S}), \quad (10)$$

where q^S is the net charge of the ion, and V_{nc}^S represents the deviation of V_H^S from a point charge potential due to the finite extension of the electronic density of the ion. This operator can be effectively computed using the Silverstone expansion of a function in a displaced center [28, 29].

The exchange operator V_X^S can be written as the nondiagonal spectral resolution [27]

$$V_X^S(i) = -\sum_l \sum_{m=-l}^l \sum_{a,b} |alm, S\rangle A(l, ab, S) \langle blm, S|. \quad (11)$$

Here $|alm, S\rangle$ are products of spherical harmonics Y_l^m and primitive radial functions for the S ion, a and b run over the Slater-type orbitals (STO) of l symmetry, and $A(l, ab, S)$ are the elements of the matrix

$$A = S^{-1} \mathcal{K} S^{-1} \quad (12)$$

where S and \mathcal{K} are the overlap and the exchange matrices for the S ion in the $\{|alm, S\rangle\}$ basis. Full details can be found in the original paper by Luaña and Pueyo [7].

As indicated above, when the effective Hamiltonian of an active group A is being diagonalized, all the other groups S are considered frozen. Selfconsistency is achieved following an iterative scheme. At each iteration all the inequivalent ions are successively treated as active groups, and the orbital wavefunctions and eigenvalues of the frozen groups are taken from the previous iteration. The iterations are continued until convergence is achieved.

Some features of the PI model are worth mentioning here. In the cluster approaches the solid is partitioned into a "cluster region" and "the rest of the crystal". The physical and mathematical description of both entities should be accurate enough, as well as their interrelations. Frequently, the cluster has been solved using precise quantum-mechanical methods while the environment has been simulated by using point charges [30], but more accurate descriptions of the environment surrounding the active cluster are necessary in order to account properly for cluster-lattice interactions [31]. Besides, the election of the cluster size is also a delicate problem, because surface effects at the cluster boundary may affect the results. In the PI model, the "cluster" is reduced to its minimum size, a single ion, and cluster-lattice interactions are described selfconsistently in the framework of the TES [4, 5]. The cluster approximation can be rigorously formulated within the TES, as cluster-lattice orthogonality is a fundamental requirement of that theory. Another feature of the PI model is that it does not invoke the LCAO approximation. The one-center character of the model leads to a large computational saving with respect to any multi-center cluster approach. The PI model just described has been formulated at the Hartree-Fock level. Now we turn to the introduction of Coulomb correlation.

2.2. Introduction of correlation in the PI model. The Coulomb hole model

The seminal idea of separability is to find electronic groups such that intergroup correlations play a minor role [32]. Intraatomic correlation, on the other hand, contributes significantly to the band gap energy of ionic crystals and has to be included. To take into account intraatomic correlation we have used the Coulomb-Hartree-Fock (CHF) model proposed by Clementi [33, 34]. In the CHF model, the coulomb-repulsion integrals are modified by introducing a spherical hole around each electron in which the other electrons do not penetrate. The radius of this coulomb hole for a particular integral depends on the overlaps between the functions involved, aside from other factors. Two parameters can scale the hole, and their values were chosen to match the empirical correlation energies of He and Ne. Details of the CHF model can be consulted in Clementi's papers [33, 34].

From the point of view of the PI calculations, the CHF model is convenient for several reasons: (a) it is computationally simple; (b) it can be implemented easily in the Roothaan-Bagus SCF (self consistent field) formalism [35]; (c) it reproduces within a few parts per cent the empirical correlation energy for the ground state of free atoms [33, 34]; (d) it is size consistent; and (e) the CHF correlation energy depends on the radial density of the ions, thus incorporating correlation effects upon the formation of the solid.

There are two ways to implement the CHF model. Without going into more detail, we have used the unrelaxed CHF approximation, in which the PI wavefunctions calculated at the HF level are kept fixed and the correlation energy is simply added to the HF energies. Since the coulomb repulsion integrals are reduced by the effect of the hole, the corrected energies of the ions are smaller than their corresponding original PI values. The good performance of the CHF model in accounting for intraatomic correlation can be appreciated in the reviews of refs. [36, 37].

2.3. Basis set

The localized atomic-like orbitals used to describe each ion in the crystal are expanded in a large basis set of STO's [38, 39] because of their superior performance (their precision being near numerical-hartree-fock). An extension of the basis was required for the description of bromides. From an analysis of preliminary calculations we have reasons to think that the basis set used for Br^- may not be the most appropriate to describe this anion in the crystalline environment. Here we have decided to enlarge the basis set for Br^- by adding one $5p$ -polarization function. The exponent of the $5p$ -STO was adjusted by minimizing the total energy of the corresponding crystal. We have found that upon inclusion of the $5p$ -STO, the $4p$ -orbital of Br^- experiences a small contraction with respect to the $4p$ -orbital in the absence of the polarization function. This very small effect is responsible for the improvement of the crystal energy. Within the TES, the portion of the total energy represented by the projection energy is sensitive to the quality of the basis set in the tail region. Further discussion on the influence of basis sets on the results is provided in Sect. 3.

3. Calculation of energy gaps

Following the work of Poole *et al.* [20], the gap is rigorously defined as the difference between the threshold energy E_t and the electronic affinity χ of the crystal:

$$\Delta E_{\text{gap}} = E_t - \chi. \quad (13)$$

The threshold energy is the energy needed to remove an electron from the top of the valence band (VB), whereas the electronic affinity is defined as the energy of an electron at the bottom of the conduction band (CB), referred to the vacuum level. It is important to be aware of this definition, because if

the hole in the VB and the electron in the CB were allowed to interact (electron-hole pair), strictly we would be describing instead an excitonic level.

The problem for a cluster model when trying to obtain band gap energies using Eq. (13) is the calculation of the electronic affinity χ , as it is necessary to deal with an electron in a delocalized state at the bottom of the conduction band [40]. The PI model is not an exception in this respect. Due to the one-center character of the model, we have to center the electron wave function on a lattice site. Besides, the strong ion-lattice orthogonality required by the TES would force the electron to be localized on a given ion, leading to an incorrect representation of a conduction band state. We can, however, give an approximate description of this state by relaxing the orthogonality requirements (see below). For ionic materials the experimental values of χ are small (only a few tenths of eV [20, 41]) compared to E_t and our approximation gives values for χ within the correct order of magnitude. Besides, typical errors in measured gaps are ~ 0.5 eV.

We have calculated the band gap energy in two different ways. The first one identifies the gap with the difference between the energy eigenvalues corresponding to the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) obtained in the PI model at the HF level, that is, we approximate the threshold energy E_t by the HOMO and the electronic affinity χ by the LUMO (with opposite signs):

$$\Delta E_{\text{gap}} = \epsilon(\text{LUMO}) - \epsilon(\text{HOMO}). \quad (14)$$

This energy difference overestimates the gap, as is the case of typical HF band theory calculations [22]. The second way is a Δ SCF calculation.

3.1. LUMO-HOMO difference

The orbital energy of the HOMO level is a quantity readily obtained in the PI model. For a given alkali halide crystal it corresponds to the eigenvalue of the outermost occupied p -orbital of the anion. To obtain the LUMO we can simulate a neutral alkali atom, A^0 , as an impurity in the field created by the pure crystal ($A^0 : A^+ X^-$). Then, the LUMO is identified with the outermost occupied orbital of the neutral alkali impurity. As stated above, when the calculation is performed within the strict framework of the PI model, the localized basis and the condition of strong orthogonalization between the orbitals in neighboring sites would lead to an unphysical localization of this electron on the alkali site. A better description of the LUMO is achieved by freezing the crystal around the A^0 impurity (that is the wave functions of the surrounding ions) and removing the pieces $V_X^S(i)$ and $P^S(i)$ out of the effective Hamiltonian for the impurity. It has to be stressed that our calculation describes the LUMO as an occupied orbital centered on an alkali atom. To allow for the delocalization of this orbital over a substantial region of the crystal, the basis set used for the impurity (taken from Bunge and Barrientos [42] for Li, Na, K, Rb, and from McLean [39] for Cs)

has been enlarged by adding some diffuse *s*-type STO functions, assuming that their exponents form a geometric progression [43]. For the ratio of the geometric progression we took the ratio between the exponents of the two outermost *s*-orbitals of the original basis set, and we enlarged successively the basis set with one, two and three STO's. The calculated LUMO eigenvalue converges fast as the basis set is enlarged. In fact, by adding a fourth diffuse function, the LUMO energy changed by $\sim 10^{-3}$ eV only. With the basis chosen, the electron in the LUMO orbital of alkali halides spreads over a range of about 32 coordination cells from its center. By removing the pieces $V_X^S(i)$ and $P^S(i)$ from the effective hamiltonian for the impurity, our calculation of the LUMO becomes rather similar to the method used in some embedded cluster models, in which the metal impurity, with an extra electron added, is surrounded by a set of point charges chosen and optimized to represent the Madelung potential [44]. The difference between the two procedures is that in our calculation we employ the complete charge distribution of the crystal and not ionic point charges.

The calculation is similar for the oxide crystals. ϵ_{HOMO} is the eigenvalue of the highest occupied anionic orbital in the pure crystal, and ϵ_{LUMO} is obtained by simulating a metal (or silicon) cation with an electron added in its external *s* shell as an impurity in the pure crystal. Unlike the case of alkali halides, in the oxides the metal (or Si) cation remains charged (Be^+ , Mg^+ , Ca^+ , Sr^+ , Ba^+ , Al^{2+} , Si^{3+}) after addition of that electron. The Clementi-Roetti [38] basis for the cations, enlarged by some diffuse functions, were used to simulate the delocalization of the LUMO orbital.

The magnitude of the LUMO eigenvalue is always a small quantity (the largest value is 0.4 eV for $\text{Si}^{3+}:\text{SiO}_2$). Our results concerning the affinity level agree with those obtained for MgO by Bagus *et al.* [40] in the sense that this level bears no simple connection with cationic *s*-orbitals. In all cases it was irrelevant to center the electron wave function on a cationic or an anionic site, the only important issue was to allow for the necessary delocalization of the electron. The number of point-charge shells included in our calculation to converge the Madelung term is about 190, and the picture that arises is that the electron becomes as delocalized as possible, the same conclusion reached by Bagus *et al.* [40].

Results for the calculated band gaps of twenty alkali halide crystals are compared in Table I with experiment [22, 41, 45] and with other calculations. In a similar way, Table II shows the results for seven oxide crystals, also compared with experiment [46–49] and other theoretical results [24, 50]. Typical errors in the experimental gaps are 0.2–0.5 eV [22]. Our calculations were performed using the experimental geometries and lattice constants of the perfect crystals [51, 52]. The calculated (LUMO-HOMO) gaps display the experimental trends: a decrease of the band gap by moving down the periodic table along the cation column when the anion is fixed (the experimental gaps for Br and I-crystals show some exceptions to this trend), and also a decrease by moving down the anion column when the cation is

TABLE I. Band gaps of alkali halide crystals calculated by different theoretical methods, compared to experimental values [22, 41, 45]. $\Delta\epsilon_{\text{HF}}$ (LUMO - HOMO) is a difference of one-particle orbital energy eigenvalues. ΔSCF refers to a difference between the energies of the crystal in appropriate electronic states (see text). Kunz [22] performed band structure calculations for the solid and CI represents a configuration-interaction cluster calculation [53]. All energies are given in eV.

Crystal	$\Delta\epsilon_{\text{HF}}$ (LUMO-HOMO)		ΔSCF			Others		Exp.
	This work	Ref. [53]	HF	CHF	Ref. [53]	Kunz [53]	CI [53]	
LiF	14.9	16.1	12.3	14.1	12.2	14.0		14.2
NaF	13.6	14.7	10.1	12.6	11.6	12.0	11.9	11.5
KF	12.4	13.3	10.5	11.8	10.6	10.9	11.6	10.8
RbF	12.0	12.7	9.3	10.7	10.1	11.0	11.3	10.3
CsF	11.6		8.7	10.5				9.9
LiCl	11.2	13.0	10.15	9.15	10.4	9.7		9.4
NaCl	10.8	12.2	9.6	8.5	9.8	10.0	8.9	9.0
KCl	9.9	11.2	8.7	7.6	9.2	10.0	8.8	8.7
RbCl	9.6	10.8	8.2	7.4	9.0	10.3	8.7	8.5
CsCl	9.0		7.8	6.7				8.3
LiBr	10.9	12.0	10.5	8.2	9.6	8.4		7.6
NaBr	10.5	11.4	9.8	7.0	9.0	10.0	7.9	7.1
KBr	9.7	10.5	9.1	6.5	8.6	8.7	7.9	7.4
RbBr	9.4	10.2	8.8	6.2	8.2	7.1	7.8	7.2
CsBr	8.9		8.3	5.4				7.3
LiI	10.0	11.0	9.5	7.4	8.8			6.4
NaI	9.7	10.5	9.0	6.9	8.4		6.9	6.0
KI	8.9	9.7	8.4	6.3	7.9		7.0	6.1
RbI	8.7	9.4	8.0	5.9	7.7		6.9	5.8
CsI	8.3		7.7	5.6				6.2

fixed. For the alkali halides, we obtain a general overestimation of the gap, with errors which increase with the size of the ions involved. The same trends are observed in a calculation by Berrondo and Rivas-Silva [53] using a model of a cluster embedded in a background of point-like ions. Berrondo's calculation was performed at the HF level and the gap, obtained as the difference of LUMO and HOMO orbital energies, is given in Table I. The error in the present approximate calculation is, however, about 1 eV smaller than in Berrondo's calculation. On the other hand, for oxide crystals, the (LUMO-HOMO) calculation yields excellent agreement with experiment. At this level of theory, correlation and orbital relaxation effects are not yet taken into account, so this exceptional agreement has to be considered as resulting from a subtle cancellation of errors.

TABLE II. Band gaps of seven oxides calculated from several theoretical methods, compared to experimental values. $\Delta\epsilon_{\text{HF}}$ is a (LUMO-HOMO) difference of one-particle orbital energy eigenvalues. ΔSCF refers to a difference between the energies of the crystal in appropriate electronic states (see text). Also included are the *ab initio* band structure calculations of Pandey *et al.* [24] and the *ab initio* valence bond cluster model results of Lorda *et al.* [50]. All energies are given in eV.

Crystal	$\Delta\epsilon_{\text{HF}}$	$\Delta\text{SCF(HF)}$	$\Delta\text{SCF(CHF)}$	Pandey	Lorda	Exp.
BeO	10.29	8.49	10.84			10.6 ^a
MgO	7.91	5.80	7.99	8.21	10.9	7.69 ^b
CaO	7.14	5.08	7.01	7.73	8.0	7.0 ^b
SrO	6.15	3.86	5.77	7.1	6.2	5.7 ^b
BaO	4.92	2.76	4.62		4.8	4.8 ^b
SiO ₂	9.17	6.76	8.67			~ 9 ^c
Al ₂ O ₃	8.96	6.93	9.23			> 9 ^d

^a Ref. 46, ^b Ref. 47, ^c Ref. 48, ^d Ref. 49.

3.2. ΔSCF calculation

The energy gap of an N-electron system is rigorously defined within the ΔSCF method as

$$\Delta E_{\text{gap}} = (E_{N-1} - E_N) - (E_N - E_{N+1}), \quad (15)$$

where E_N is the ground state energy [54]. This is, evidently, equivalent to Eq. (13). For the alkali halide crystals we can write

$$E_t = E_{N-1} - E_N \\ = E_{\text{crystal}}(X^0 : A^+X^-) - E_{\text{crystal}}(A^+X^-), \quad (16)$$

$$\chi = E_N - E_{N+1} \\ = E_{\text{crystal}}(A^+X^-) - E_{\text{crystal}}(A^0 : A^+X^-), \quad (17)$$

associated to the two independent processes of removing an electron from a halogen anion and of placing an electron in a state at the bottom of the conduction band, respectively. $E_{\text{crystal}}(X^0 : A^+X^-)$ represents the energy of the crystal with a single neutral halogen impurity and $E_{\text{crystal}}(A^0 : A^+X^-)$ that of a crystal with a “neutralized” alkali ion (although the neutralizing electron is in a fully delocalized state). Finally $E_{\text{crystal}}(A^+X^-)$ is the energy of the perfect crystal. The geometry of these “doped” crystals is that of the perfect crystal, according to the Franck-Condon principle.

The electronic orbitals of the ions surrounding the neutral impurities (in fact, of all ions in the crystal) were kept frozen in the same electronic states as in the pure crystal. This is not strictly necessary for the case $X^0 : A^+X^-$ but we have found from test calculations that the electronic relaxation of

the cations surrounding the neutral halogen atom is indeed negligible. For the case of $A^0 : A^+X^-$, freezing of the electronic clouds of the surrounding shells of ions is convenient in view of the treatment of the impurity (see below). With these assumptions the energies E_t and χ reduce to a difference of effective energies [55]

$$E_t = E_{\text{eff}}(X^0 : A^+X^-) - E_{\text{eff}}(X^- : A^+X^-) \quad (18)$$

$$\chi = E_{\text{eff}}(A^+ : A^+X^-) - E_{\text{eff}}(A^0 : A^+X^-) \quad (19)$$

where the effective energies of X^- and A^+ refer, evidently, to ions of the perfect crystal. Again, as in the discussion of the HOMO-LUMO gap in Sect. 3.1 above, we have enlarged the basis set to be able to describe an electronic state formally centered on an alkali site although delocalized over a region corresponding to many shells of neighbours. Applying the same argument to alkaline-earth oxides, the equivalent of Eqs. (18) and (19) are

$$E_t = E_{\text{eff}}(\text{O}^- : \text{A}^{2+}\text{O}^{2-}) - E_{\text{eff}}(\text{O}^{2-} : \text{A}^{2+}\text{O}^{2-}) \quad (20)$$

$$\chi = E_{\text{eff}}(\text{A}^{2+} : \text{A}^{2+}\text{O}^{2-}) - E_{\text{eff}}(\text{A}^+ : \text{A}^{2+}\text{O}^{2-}), \quad (21)$$

and related expressions can be easily written for the SiO₂ and Al₂O₃ crystals.

The main contribution to ΔE_{gap} comes from E_t , and χ only provides a small correction. The largest value of χ , which is ~ 0.5 eV is found for SiO₂. This magnitude is consistent with the energy difference between the vacuum level and the lowest conduction band state measured by photoemission spectroscopy [41]. That energy difference is generally smaller than 1 eV, and in most cases much lower.

The gaps obtained by this ΔSCF calculation are given in Tables I and II. Two sets of results are included: the first one corresponds to calculations at the Hartree-Fock level, and the second includes correlation via the CHF model. The gaps obtained for alkali halides are smaller than those calculated by subtracting LUMO and HOMO eigenvalues, a fact that improves the agreement with experiment, in particular for cases involving heavy halogens. The improvement arises from orbital relaxation in response to the removal of one electron from the anion. The relaxation of the orbitals of the halogen atom is included now in the calculation of E_t , but not in the calculation of the HOMO level in Sect. 3.1. This effect of a higher sensitivity of the anions (as compared to cations) to orbital relaxation effects was also found in our previous works on clusters [8, 9]. For oxides, improvement with respect to the LUMO-HOMO difference of Eq. (14) is only found after including correlation.

The electron density of the cations is very localized and practically does not change when the delocalized electron is centered on those cations. Furthermore, the delocalized electron does not interact with itself. This means that correlation gives a negligible contribution to χ , so one can concentrate on the contribution of correlation to E_t . The difference between $\Delta\text{SCF(HF)}$ and $\Delta\text{SCF(CHF)}$ in Tables I and II comes

from this source. We can appreciate in Table I that the correlation correction improves the gap for most alkali halides, with KF, KCl, RbCl and CsCl as the only exceptions. Furthermore, it is worth noting that this correction changes the magnitude of the gaps in the correct direction, namely, increasing the gap energy for fluorides, which have HF gaps below the experimental values, and decreasing the gap for the rest of the crystals, which show (except KCl, RbCl and CsCl) HF gaps larger than the experimental ones. In summary, the global trends remain the same as in the HF calculations, but the quantitative agreement improves with the inclusion of correlation effects. The same can be said of the oxide crystals, where inclusion of correlation reinstates the initial agreement found in the (LUMO-HOMO) calculation. These results lead us to conclude that correlation corrections are important for a quantitative comparison with experiment, although the general trends are reproduced at the HF level.

The band gaps obtained by Kunz [22] for twelve alkali halide crystals and by Pandey *et al.* [24] for three oxides from band structure calculations are given for comparison in Tables I and II. Energy band calculations at the HF level overestimate the band gap with errors of a few eV (see Ref. 22); notice that this is a LUMO-HOMO-type of estimation. Kunz [22, 24] then introduced coulomb correlation by updating a method described by Pantelides *et al.* [56]. Correlation effects lowered the magnitude of the gap, bringing the results (included in Tables I and II) in good agreement with experiment. Comparing with the results obtained by Kunz, we can see that our CHF results are slightly better, except for a few crystals (NaF, KF, RbBr), and that Kunz calculations are less successful in reproducing the general trends. We have just mentioned that HF band structure calculations overestimate the gap by a sizable amount. On the other hand our Δ SCF calculations at the HF level do not seem to be much affected by this problem. We ascribe this to electronic relaxation effects.

In Table I, we also include the results of Berrondo and Rivas-Silva [53], obtained as the difference between the total energies of the lowest electronic excited state and the ground state of a cluster simulating a piece of the ionic crystal, embedded in a system of point charges. These calculations were performed at the HF level and, evidently, include electronic relaxation, so in Table I the corresponding results have been classified under the Δ SCF category. Berrondo's calculations include in addition relativistic effects. A comparison with the present Δ SCF(HF) results shows rather similar gaps. In the same paper Berrondo and Rivas-Silva have obtained the gap by identifying this one with the excitation energy obtained in a Configuration Interaction (CI) calculation, again within a cluster model, in this case a bare cluster without surrounding point charges. As a consequence of the introduction of correlation, the CI calculations give an improvement of the calculated gaps for chlorides, bromides and iodides. In the case of fluorides, where some of the Δ SCF(HF) gaps obtained by Berrondo are below the experimental values, the CI calculation leads to an increase of the gaps. So turning from Δ SCF

to CI seems to work in the right direction, although for fluorides this results in a worsening of the magnitude of the gap. The errors in the CI gaps are not larger than 1 eV. This is also the case for our Δ SCF calculations including correlation, except for NaF, KCl and RbCl, for which the error is 1.1 eV, and for CsCl and CsBr, where the errors are 1.6 eV and 1.9 eV respectively. The computer time required by our calculations is, however, much smaller.

Included in Table II are the theoretical results obtained by Lorda *et al.* [50] for alkaline-earth oxides. They used a model of a linear triatomic M-O-M cluster (M = metal, O = oxygen) embedded in a Madelung field representing the crystal. The *ab initio* wavefunction was written as a linear combination of Slater determinants, each one corresponding to a resonating valence bond structure. In that way a valence bond wave function is obtained which is explicitly correlated from the outset, in the sense that it is not an eigenfunction of a hamiltonian which can be written as a sum of mono-electronic operators (for details, consult chapter 7 of Ref. 32). In order to include external correlation effects they used standard second-order perturbation techniques. This external correlation is defined as the energy contribution of those Slater determinants not explicitly included in the valence bond model space. The gap was then calculated as an energy difference between appropriate resonating valence bond components. Our results are also in better agreement with experiment in this case. Actually, the first excitation energies calculated by Lorda *et al.* should not be identified with the band gap energies, but with localized excitations. This point was emphasized when we gave the definition of the band gap energy above.

Density functional theory (DFT) [57] has also been used to calculate band gaps in ionic crystals. The DFT one-particle eigenvalues have no formal justification as quasi-particle energies although in practice these eigenvalues have been used to discuss the spectra of solids. The DFT band gaps (usually calculated employing the local density approximation for exchange and correlation effects) give values typically 30–50 % less than the gaps observed in the optical spectra. A rigorous formulation requires the calculation of the quasi-particle band structure. This has been done by Hybertsen and Louie [58] by using the so-called GW approximation to the self-energy [59]. These authors have obtained a gap of 9.1 eV for LiCl.

4. Conclusions

A preliminary requirement for the treatment of luminescent impurities in ionic crystals is an accurate description of the band gap. Consequently, we have carried out a series of approximate calculations of the band gap for twenty alkali halide and seven oxide crystals. Two different prescriptions have been used: the first one is a difference between the energies of the LUMO and HOMO orbitals of the crystal, and the second is a Δ SCF calculation based on subtracting total energies. For this purpose the Perturbed Ion (PI) model has been used, supplemented with some additional assumptions

to deal with the state corresponding to one electron at the bottom of the conduction band. Correlation effects have been taken into account by a model introduced by Clementi.

Overall we have obtained a good description of the energy gaps with a very modest computational effort. The gaps show a reasonable agreement with experiment, and also compare well (in many cases favorably) with previous theoretical works. The results support the validity of the PI model and the additional assumptions employed to simulate the physical situation. Further improvement of some particular points (as the modelling of the delocalized electron at the bottom of the conduction band, the treatment of electronic correlation,

and the introduction of relativistic effects for heavy atoms) are expected to improve further the results.

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