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ELECTRONIC STRUCTURE OF MAGNESIUM OXIDE

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ABSTRACT

MgO is a very interesting material and it has been extensively analysed both; experimentally and theoretically. The electronic structure of the MgO crystal has been calculated with the perturbed – ion (PI) method. The PI atomic like orbitals are eigen functions of Fock operators that contain nuclear coulombic and exchange lattice potentials plus lattice projection operators enforcing the ion-lattice orthogonality. These lattice-consistent ionic orbitals from crystalline basis set that may be useful in a number of applications. The PI bonding picture of MgO consists of lattice stabilized Mg^{2+} and O^{2-} ions described with well separated wave functions. The PI electron density of Mg^{2+} is very close to the free-ion function, but that of the oxide is more concentrated than the density of O^{2-} in vacuo. The PI densities are tested and compared with others by computing diamagnetic susceptibilities, form factor and the change of electronic kinetic energy upon the crystal formation. Also it shows important applications as a catalyst and it is frequently used as a host lattice for transition-metal impurities in a large variety of optical and magnetic studies.

Key words: Electronic structure, Perturbed-ion method, Crystalline basis set, Chemical bonding.

INTRODUCTION

Magnesium oxide is a very interesting material and it has been extensively analyzed both; experimentally and theoretically. Besides the intrinsic interest of its optical properties and lattice dynamics, it shows important applications as a catalyst and it is frequently used as a host lattice for transition-metal impurities in a large variety of optical and magnetic studies.

The ionicity of MgO, as determined from electronegativity differences, is large. Consequently, this crystal has been described in terms of simple ionic models. On the other hand, its wide valence band, large electric constant and small exciton binding energy differ from typical insulator values and permit us to consider the MgO as a semiconductor.[1]

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The electronic structure of MgO has been computed several times by means of different approaches. Relevant exceptions being the pseudopotential plane-wave calculation by Chang and Cohen[2] and the crystalline Hartree-Fock (HF) calculation by Causa et al.[3]

The ionic picture of MgO is based on the existence of Mg^{2+} and O^{2-} ions. Thus, the first basic problem with the ionic picture of the MgO and other oxides is the correct description of the O^{2-} wave function.

The PI method gives the total energy per molecule and the effective and net energies for each different ion in the crystal. Using these quantities, the chemical bonding may be analyzed in terms of independent ionic contributions. Elastic constants and thermodynamic properties are obtained from the total energy in the usual manner. Furthermore, the PI model works as a basis-set generator : it gives HF one-center wave functions for each different ion in the crystal, which are consistent, in the self-consistent-field (SCF) sense, with the lattice potential. This basis set is much more appropriate than the free-ion basis for describing the electron distribution in ionic crystals.

Since the PI method is a HF scheme, it includes the electron correlation error. To deal with it, we have considered the Coulomb-Hartree-Fock (CHF) approach of Clementi.[4,5] The PI-CHF results show that the correlation energy changes with the interionic distance quite remarkably.

The ionic picture of MgO emerging from the PI calculation consists of Mg^{2+} ions very similar to the free-ion species, and O^{2-} ions with a valence electron density largely contracted with respect to the free-ion function.[6] The PI O^{2-} 2p function is also more contracted than the local orbital of Pantelides et al.[1] and the Watson functions, but very similar to the local description given by Pandey and Vail.[7] Our O^{2-} wave function gives a diamagnetic susceptibility and a change of electron kinetic energy upon crystal formation in agreement with the experiment. Thus, we conclude that the PI method gives a simple but rigorous procedure for stabilizing the oxide ion in the lattice by invoking two basic quantum mechanical idea required by the Pauli principle : the nonlocal exchange interaction and the wave-function orthogonality.

In this paper, we present a non-empirical description of the Mg^{2+} and O^{2-} ions in MgO. Such a description is a prerequisite for the *ab initio* calculation of local properties of impurities systems. Moreover, this ionic description is useful in various magnetic resonance experiments.

COMPUTATION

THE WAVE FUNCTION OF O^{2-} IN MgO

In Table 1, we present the 5s, 5p PI solutions for O^{2-} obtained at the experimental geometry of the NaCl phase of MgO.

Table 1: PI solutions for Mg^{2+} and O^{2-} in MgO computed at the experimental distance R = 3.97882 Bohrs.

			1s	2s			2p
Mg^{2+}	1s	17.00270	0.07631591	–0.01997279	2p	12.58860	0.01037091
	1s	11.44730	0.89825895	–0.22577423	2p	6.05091	0.28254864
	2s	10.70430	0.03260429	–0.10829400	2p	3.40554	0.55798544
	2s	4.97455	0.00678032	0.43984801	2p	2.44651	0.21372924
	2s	3.30779	–0.00143951	0.66886705			
	Orbital energy		–48.92617	–3.64228			–2.16459
O^{2-}	1s	13.42550	0.03833729	–0.00030074	2p	7.82044	0.0277053
	1s	7.61467	0.93731264	–0.21162552	2p	3.42975	0.1909289
	2s	6.31491	0.03523405	–0.07930387	2p	1.74399	0.7387200
	2s	3.21269	0.00295046	0.38679022	2p	0.86393	0.1781234
	2s	1.75076	0.00047938	0.72604702	2p	0.40831	–0.1023350
	Orbital energy		–20.22785	–1.04806			–0.32229

In Fig. 1, the total radial density of the Mg^{2+} and O^{2-} ions is plotted at the observed crystal geometry as well as the free-ion densities. The lattice interactions do not produce observable effects on the Mg^{2+} density. The model predicts that this cation behaves as a hard sphere in passing from free space to the lattice. The core density of the oxide also remains unchanged, and a charge transfer from the outer-valence to the inner-valence density of this anion is clearly visible in the figure. As expected, the anion is much more sensitive to the lattice interactions. The orbital contraction of the oxide in the lattice can be related to the good convergence of the PI SCF process, in contrast with the situation encountered in the in vacuo calculation of the O^{2-} ion.[6,8]

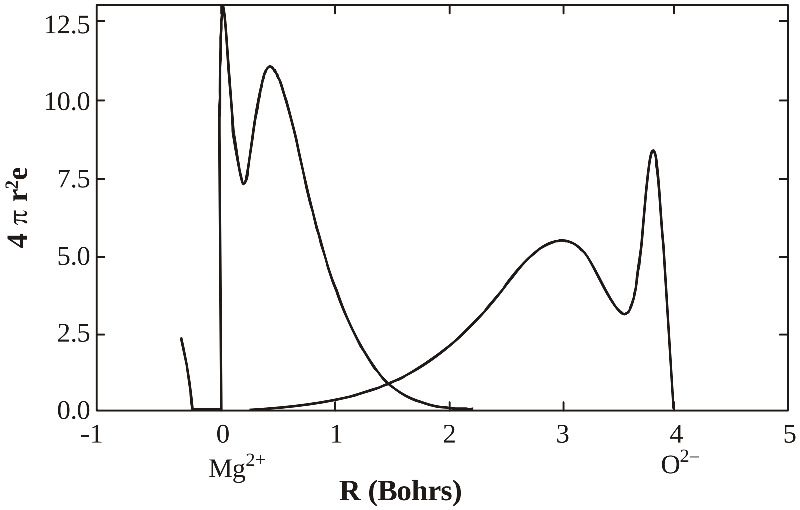


Fig. 1

The orbital analysis of the electron density reveals that the differences between the free-ion and PI O^{2-} densities are essentially due to the different description of the 2p atomic orbital (AO).

In Fig. 2, the 2p PI AO of the O^{2-} ion in MgO, the free ion AO (HH)[6] and other solutions have been collected from the literature. We have limited the comparison in this figure to some particularly interesting cases. The Watson orbital with q (sphere) = 2 a.u. (W_2), because it is very frequently used, the AO[1] because it was obtained by a method, which is conceptually very close to the *ab initio* PI method, and the Pandey-Vail AO (PV)[7], because it is derived from a high-quality, all-electron [O^{2-} $(Mg^{2+})_6$] cluster calculation interfaced to a well-tested lattice model.

The PI method produces a clear contraction of the 2p AO in the direction pointed out by the Watson potential. In the region, where the bonding interactions are important, the PI function is remarkably smaller than the free ion AO. The tails of the PI and PV functions are very close but the PMK function differs from our PI orbital for distances larger than 0.5 Bohrs. The analysis of the PI results reveals that the orbital contraction is mainly due to the action of the lattice-projection operators; thus, being a direct consequence of the orthogonality between the O^{2-} wave function and the quantum lattice.

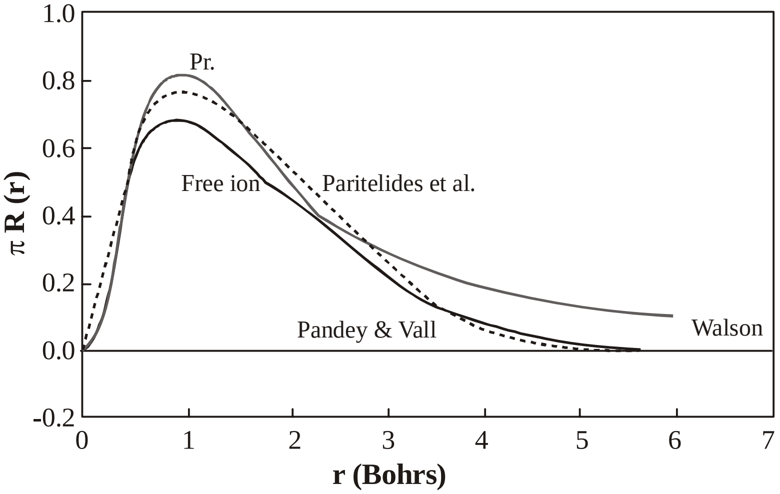
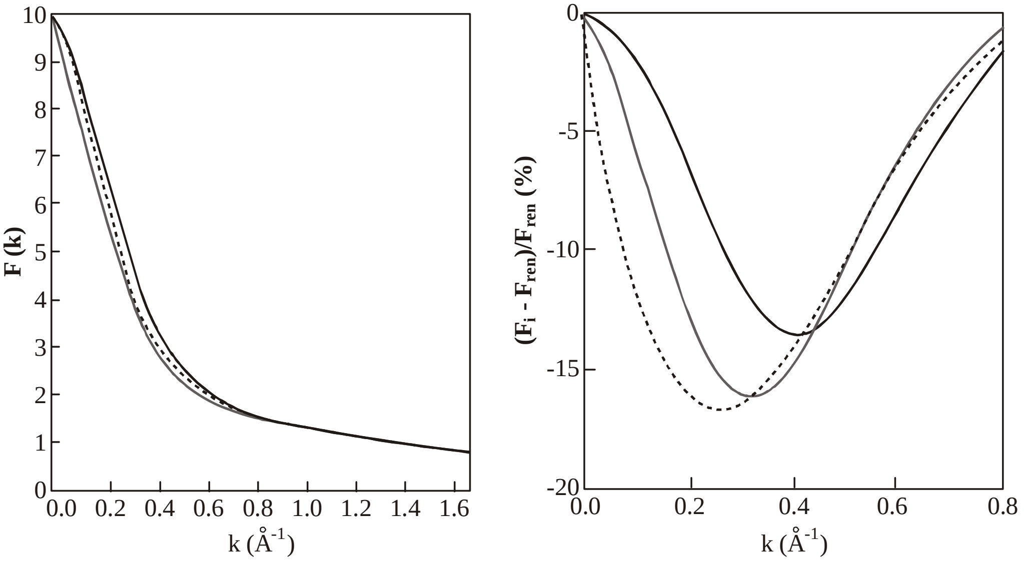


Fig. 2

In Fig. 3, the k dependence of the form factor for O^{2-} computed with PI, Watson's[9] and free-ion HH basis sets has been presented.[6] The renormalized form factor F_{ren} is defined in terms of atomic orbital contributions and ionic-orbital occupation numbers :

$$F_{ren} = \sum_{nl} N_{nl}^{ion} f_{nl}^{atom} \quad \ldots(1)$$



(a) **(b)**

Fig. 3

Since the falling of the form factor with increasing k is sharper for more diffuse wave functions, F_{ren} gives the more external form factor and the free-ion basis the more internal one. Our PI basis gives a form factor close to F_{ren}. The small differences in Fig. 3(a) are due to differences in the 2p AO and they disappear for $k > 1$ Å^{-1}. The differential form factors is -

$$100\,(F_1 - F_{ren}) / F_{ren} \qquad \ldots(2)$$

It supplies a better way to detect these differences among basis sets, as revealed in the plot Fig. 3(b). The PI solution gives the form factor closest to the renormalized value, which in the case represents the larger deviation from the free-space AO, in agreement with Fig. 2. The Watson orbital gives an intermediate result between the free-ion and PI wave functions.

The orbital contraction implies an increment of electronic kinetic energy relative to free neutral atoms. This increment is a severe test for the curvature of the wave function because it involves a second-order derivative.

The free-ion O^{2-} description largely deviates from the empirical $\Delta T[O]$, showing once more that the real oxide ion has a very different electron density in the crystal. Watson functions produce $\Delta T[O]$ between 0 and – 4 eV, with a small effect associated with the selected charge for the Watson sphere. These values are still largely different from the empirical estimate. PMK oxide function produces $\Delta T[O] \sim -12$ eV, corresponding to an O^{2-} (s) wave function less contracted than that of 0^0(g). PV and PI functions give the correct sign for $\Delta T[O]$. The PI value of +28.76 eV is actually in remarkable agreement with the empirical figure. Thus, this is an independent and very severe measure of their reliability.

Fig. 4 shows the PI radial density of the O^{2-} ion as computed at several values of the NaCl-phase lattice constant. The sensitivity of this function against changes in the cell size is evident in contrast with the result found in alkali halides. These variations are also detected in the k dependence of the form factors and may help to understand the modification of the latter quantities with the external pressure. They are essentially the same as the following overlap integrals show : $\langle 1s(O^{2-}, CaO)|1s\ (O^{2-}, MgO)\rangle = 1.00000$, $\langle 2s(O^{2-}, CaO)|2s\ (O^{2-}, MgO)\rangle = 0.99999$, and $\langle 2p(O^{2-}, CaO)|2p\ (O^{2-}, MgO)\rangle = 0.99961$. This result suggests an interesting conservation of the ionic size in these two crystals.

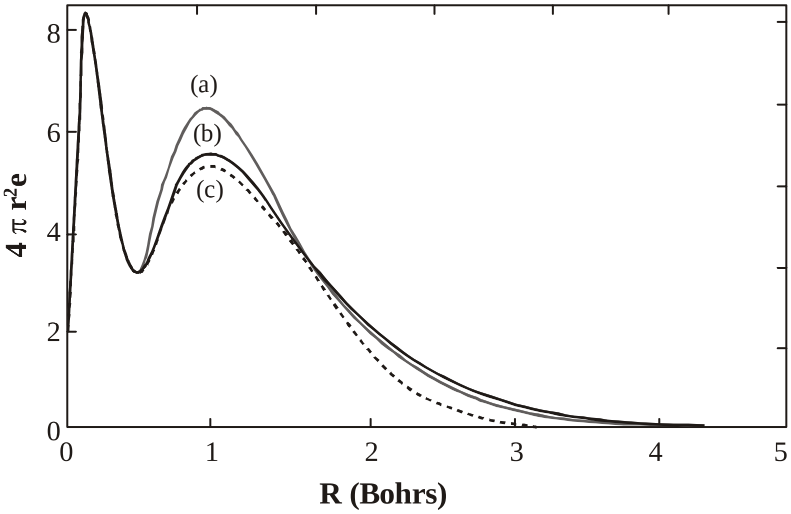


Fig. 4

CONCLUSION

In this paper, the main results have been reported of an investigation on the electronic structure of MgO performed with the *ab initio* perturbed ion model. This is an atomic like Hartree-Fock model that supplies a global description of the crystal from the one-center ionic wave functions generated by ion-in-the-lattice calculations. These lattice-consistent crystal AO's reproduce very well the observed increment of the kinetic energy of the electrons relative to the neutral atoms. Thus, the PI basis reported here may be a good choice for further applications. Of particular significance may be the capability of the PI method to give theoretical crystal wave functions at very high pressures.

The PI method gives the total energy of the crystal and reveals that the linear combination of atomic orbitals (LCAO) approximation may not be essential to describe the electronic structure of the MgO. This could be due to the high ionicity of this crystal. Our results are consistent with the ionic description of the crystal in terms of Mg^{2+} and O^{2-} ions. The cation is essentially identical to the ion in free space but the oxide shows a very large radial contraction. This deformation contributes to the crystal binding as a repulsion that is compensated with the large and negative ion-lattice interaction.

The PI AO's can be a very useful tool in further theoretical analyses of ionic crystals, particularly in those involving high pressures or impurities.

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