Studying a Non-Empirical Description of the Mg²⁺ and O²⁻ Ions in MgO

Dr. Jayant Balwant Patwardhan

Associate Professor, Department of Physics, Pratap College, Amalner, Jalgaon, Maharashtra

Abstract

Electronegativity discrepancies show that MgO has a high ionicity. As a result, basic ionic models have been used to describe this crystal. MgO is an insulator with a wide valence band, but its high electric constant, low exciton binding energy, and big dielectric constant make it a semiconductor. As seen in the PI bonding diagram of magnesium oxide, Mg^{2+} and O^{2-} are stabilised in the lattice by well-defined wave functions. However, Mg2PI $^{+}$'s electron density is extremely close to the free ion function, whereas that of O^{2-} in vacuo is more concentrated. Diamagnetic susceptibilities, form factors, and changes in electronic kinetic energy are used to compare the PI densities to those of other materials. Catalyst applications and host lattice experiments including transition-metal impurities both indicate significant benefits from using it, as do other optical and magnetic research.

Keywords: *Catalyst, Electric, Energy, Electronic, Dielectric.*

I. INTRODUCTION

MgO is a crucial support for thin films and different metal catalysts. It is necessary to comprehend the geometrical and electrical characteristics of the bulk, interface, and both clean and adsorbate-covered surfaces. Defects, dopants, and interfaces may all be important factors. Intriguing comparative materials for transition-metal oxides with the same rock salt crystal structure include magnesium oxide (MgO). It is well known that many-body effects dominate the electronic structure of substances like NiO, Co0, and MnO, making the interpretation of the ARUPS data challenging. On the other hand, a one-particle framework may be used to describe the electrical structure of magnesium oxide. ARUPS data on MgO can therefore be used to estimate the contribution of oxygen states in the spectra of the transition metal oxides in the limiting situation of zero hybridization of the oxygen with the transition-metal 3d states. The valence band is primarily composed of highly dispersive 02p derived states.

It is quite simple to generate a clean and well-ordered MgO (100) surface under ultra-high vacuum conditions, which facilitates surface science study. Under a range of irradiation types, the surface was shown to be very stable. However, the fact that MgO is such an excellent insulator with a band-gap of 7.8 eV hinders surface-sensitive approaches utilizing low energy charged particles.

The surface geometry and its dynamical characteristics have been described using a variety of diffraction and scattering techniques. They are thermal diffraction, high resolution electron energy loss spectroscopy, reflection high energy electron diffraction, low energy electron diffraction (LEED), and high energy electron diffraction (RHEED). He atom diffraction, neutron scattering, and impact collision ion scattering spectroscopy (ICISS). Solving charging issues with low energy electron methods has received a lot of attention (less than 100 eV). Solutions have been devised, including co-irradiation of high energy electrons in HREELS and primary electron energy modulation in LEED. Numerous theoretical studies on structure and dynamics have been done in addition to the experiments.
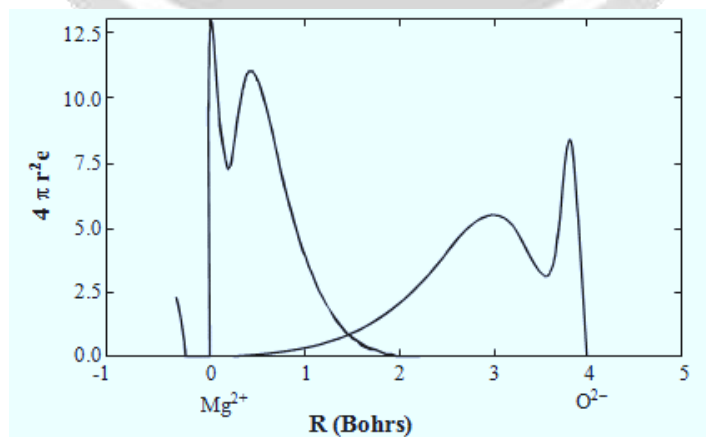
II. CALCULATION OF THE WAVE FUNCTION OF O2− IN MgO

The 5s, 5p PI solutions for O2 found at the experimental geometry of the NaCl phase of MgO are shown in Table 1.

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

			1s	2s			2p
Mg2+	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
O2−	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

Figure 1 shows the free-ion densities as well as the overall radial density of the Mg2+ and O2-ions at the observed crystal geometry. The Mg2+ density is not changed in any discernible ways by the lattice interactions. According to the model, this cation will behave as a hard sphere as it moves from free space to the lattice. A charge transfer from the outer-valence to the inner-valence density of this anion is clearly seen in the image, and the core density of the oxide likewise does not change. The anion is far more susceptible to the lattice interactions, as would be predicted. In contrast to the condition observed in the in vacuo calculation of the O2- ion, the orbital contraction of the oxide in the lattice can be connected to the good convergence of the PI SCF process.

Figure 1: Total Radial Density of the mg2+ and o2− ions

The variations between the free-ion and PI O2-densities are mostly caused by the dissimilar description of the 2p atomic orbital, according to the orbital analysis of the electron density (AO).

The free ion AO (HH)6, the 2p PI AO of the O2- ion in MgO, and other solutions have been gathered from the literature and are shown in Figure 2. In this figure, we have just included a few very intriguing situations for comparison. The Pandey-Vail AO (PV)7 is derived from a high-quality, all-electron [O2-(Mg2+)6] cluster calculation interfaced to a well-tested lattice model. The Watson orbital with q (sphere) = 2 a.u. (W2) was chosen because it is very frequently used, the AO1 was chosen because it was obtained by a method that is conceptually very similar to the ab initio PI

The 2p AO clearly contracts using the PI approach in the direction suggested by the Watson potential. The PI function is substantially lower than the free ion AO in the area where bonding interactions are significant. Even while the PMK function deviates from our PI orbital at distances greater than 0.5 Bohrs, the PI and PV function tails are quite near together. Because the O2-wave function and the quantum lattice are orthogonal, the analysis of the PI findings shows that the orbital contraction is mostly caused by the action of the lattice-projection operators.
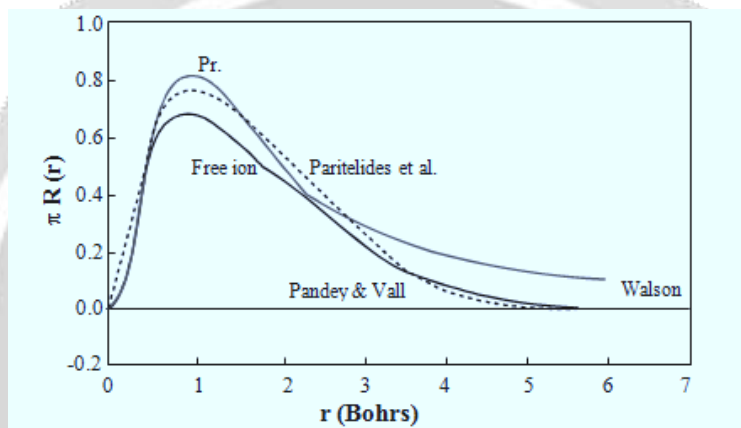

Figure 2: 2p PI AO of the O^{2-} ion in MgO

The form factor for O2 estimated using the PI, Watson's 9, and free-ion HH basis sets is shown in Figure 3. 6 Ionic-orbital occupancy numbers and atomic orbital contributions are used to define the renormalized form factor Fren :
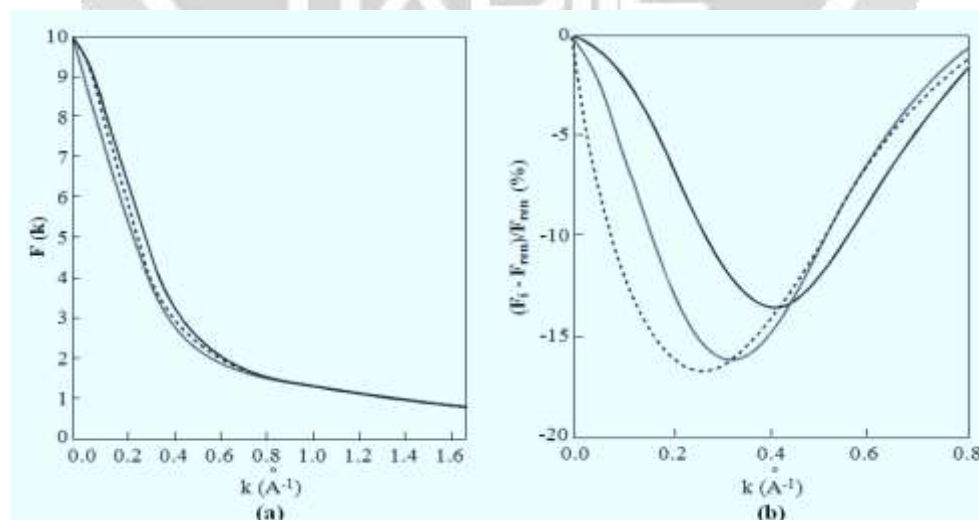

Figure 3: k dependence of the form factor for O^{2-} computed with PI

Fren assigns the more exterior form factor and the free-ion basis the more interior one because the form factor's decline with rising k is greater for more diffuse wave functions. Our PI foundation results in a form factor that is similar to Fren. The slight variations in Figure 3(a) are brought about by variations in the 2p AO, and they vanish for $k > 1$ Å−1. the many form factors are -

100 (F1 – Fren) / Fren

As seen in the graphic in Figure 3, it provides a better means to identify these discrepancies between basis sets (b). According to Figure 2, the PI solution yields the form factor that is most similar to the renormalized value, which in this case reflects the bigger departure from the free-space AO. The Watson orbital produces a result in between the PI wave function and the free-ion function.

III. RESULTS

In comparison to free neutral atoms, the orbital contraction indicates an increase in electronic kinetic energy. This increase requires a second-order derivative, which poses a rigorous test of the wave function's curvature.

The empirical DT[O] and the free-ion O2- description diverge significantly, demonstrating once more that the actual oxide ion has a drastically different electron density in the crystal. The chosen charge for the Watson sphere has a minimal influence on the range of DT[O] that Watson functions generate, which is between 0 and - 4 eV. These numbers continue to diverge significantly from the empirical estimate. The O2-(s) wave function from the PMK oxide function, which is less condensed than the 00 wave function, is represented by DT[O] - 12 eV. (g). The right sign for DT[O] is provided via the PV and PI functions. The empirical figure and the PI value of +28.76 eV accord quite well. This is a very objective and harsh evaluation of their dependability.

The O2- ion's calculated PI radial density is shown in Figure 4 for a range of NaCl-phase lattice constant values. In contrast to the outcome observed in alkali halides, the sensitivity of this function to variations in cell size is obvious. These fluctuations may be seen in the form factors' k dependency as well, which may shed light on how the external pressure affects these latter variables. The overlap integrals below reveal that they are nearly identical: á1s(O2−, CaO)|1s (O2−, MgO)ñ = 1.00000, á2s(O2−, CaO)|2s (O2−, MgO)ñ = 0.99999, and á2p(O2−, CaO)|2p (O2−, MgO)ñ = 0.99961. This finding points to an intriguing ionic size conservation in these two crystals.
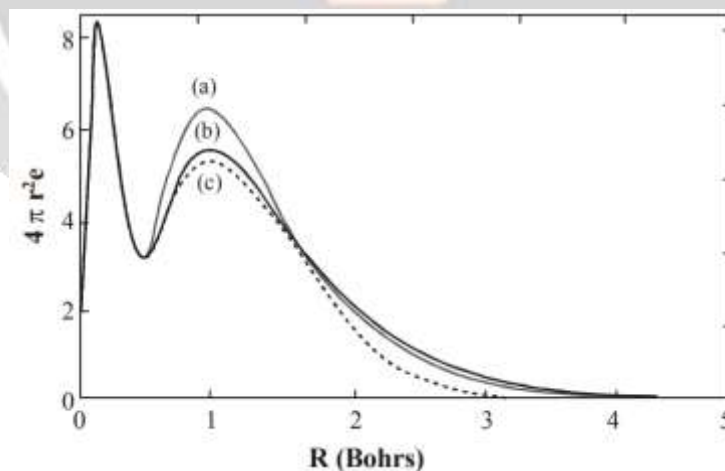

Figure 4: PI radial density of the O^{2-} ion

IV. CONCLUSION

The major findings of an inquiry into the electronic structure of MgO using the ab initio perturbed ion model are presented in this work. Hartree-Fock-like model provides a global description of the crystal from the one-center ionic wave functions generated by the ion in the lattice computations. They accurately mimic the observed increase

in electron energy relative to neutral atoms using these lattice consistent crystals. It is possible that future applications will benefit from the PI basis described in this paper. The PI method's capacity to provide theoretical crystal wave functions at extremely high pressures may be particularly significant. This technique provides the crystal's total energy and shows that the LCAO approximation may not be necessary to describe MgO's electronic structure. This might be because to the crystal's strong ionicity. Using the ionic description of the crystal, we found that our results were in agreement with the ionic description of the crystal. Free space, the cation is nearly identical to the ion in terms of its radial contraction. The substantial and negative ion-lattice interaction compensates for the repulsion caused by this crystal deformation. If you're looking to do deeper theoretical investigations of ionic crystals, the PI AOs can be a great help.

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