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ABSTRACT

The energy separation of the higher lying cation XPS binding energies, BEs, for MgO is examined. It is shown that the Hartree–Fock BEs overestimate the separation of the Mg BE(2s) and BE(2p), because an important many-body effect is neglected in the determination of the Hartree–Fock BEs. Once the many-body effect is taken into account, there is good agreement between theory and the XPS measurement. The character of this atomic many-body effect is established in terms of a nearly degenerate configuration that is needed to describe the wavefunction when an Mg 2s electron is ionized. The results provide additional evidence of the ionic character of the MgO crystal. Given the atomic character of the many-body effect, it is likely to apply also to the BE separations of other closed shell oxides.

I. INTRODUCTION

Many-body effects are known to make significant contributions to the x-ray photoelectron spectroscopy, XPS, of ionic compounds, especially transition metal oxides; see, for example, the review of Ref. 1. Dave Shirley and his colleagues were among the early leaders in establishing important aspects of the physics of these many-body effects. For example, in 1969, he was among the authors to establish the importance of multiplet splitting for the 3s XPS of MnO.[2] This work established that the open Mn 3s shell, which was coupled to a ^{2}S multiplet, would combine with the open Mn $3d^5$ shell, which was coupled to a high spin ^{6}S multiplet, to yield two multiplets ^{7}S and ^{5}S both with significant intensities. This pioneering work demonstrated the importance of taking account of the angular momentum coupling of the open shell electrons to understand the XPS of transition metal oxides. However, there were concerns about the limitations of the quantitative agreement of the multiplet theory and the energy splittings and relative XPS intensities that were measured. Indeed, a few years later, another many-body effect beyond that considered in the original work on the Mn 3s of MnO[2] was shown to lead to a significant improvement between the theoretical predictions and the measurements on the Mn 3s XPS of MnO.[3] This new many-body effect involved a redistribution of the 12 electrons in the n = 3 shells of the Mn 3s ion and not forcing them to be constrained to have the occupation of $3s^13p^63d^5$. In particular, the configuration $3s^23p^43d^6$, where two 3p electrons were moved and placed one into the 3s shell and the other into the 3d shell, was found to be quite important for the 3s ion. Including this configuration in the WF of the 3s ion had a dramatic effect on the energy splitting of the most intense ^{5}S and ^{7}S peaks, and it also led to rather intense satellites. The physical reason for this is that the ^{5}S coupling of the $3s^23p^43d^6$ configuration was nearly degenerate with ^{5}S coupling of the "normal" $3s^13p^63d^5$ configuration. To have near degeneracy, it is not necessary that the difference of the diagonal matrix elements themselves must be a small quantity. The condition for near degeneracy is that the difference of the diagonal matrix elements and the off-diagonal matrix element connecting these configurations should have comparable magnitudes; see the discussion in Ref. 4. The key concept for the 3s XPS of Mn^{2+} is that one obtains near degeneracy by dropping one 3p electron to fill the 3s shell and one promotes another 3p electron into the partly occupied 3d shell. This type of change in the 3s, 3p, and 3d occupations could also be made for other 3d transition metal cations provided that the 3d shell is not filled. Thus, it would seem reasonable that this kind of near degeneracy should be reasonably general for the XPS of other transition metal ionic compounds. Indeed, this generality was demonstrated by Viinikka and Öhrn[5] who examined the 3s XPS of several cations from Cr^{3+} to Ni^{2+}.

More recently, it was shown that a similar near degeneracy effect modified the binding energies, BEs, of the lowest ^2P and ^2S ionizations of Ne and Ar.[6] When the near degeneracy many-body effect was not considered and only Hartree–Fock, HF, and BEs were calculated, the Ne BE(2p) and Ar BE(3p) were found to be smaller than experiments. This is the error of HF ionization potentials or low lying BEs that is to be expected[7] since the ion has one fewer electron than the neutral atom and the errors of the HF energies depend on the number of electron pairs that is smaller for the ion. However, for the Ne BE(2s) and the Ar BE(3s), the HF BEs were larger than experiments, which means that the HF error for the energy of the ion is larger than for the energy of the neutral atom even though there are fewer electron pairs in the ion. This situation arises because a nearly degenerate configuration like the one described above where two np electrons are moved, one dropping into a lower energy ns orbital and one being promoted into a higher energy 3d orbital, is involved. This configuration is possible for the lowest energy ^2S ions of Ne and Ar but it is not possible for the lowest ^2P ions since the 2s shell is filled. Since Mg^{2+} is isoelectronic with Ne, one would expect that the near degenerate configuration would also be important for the Mg^{2+} cation and would be needed to correctly describe the BE difference between the ^2S and ^2P multiplets of Mg^{3+}. However, it is not at all clear that this same near degeneracy effect would be relevant for the BEs in an MgO crystal. This is because the Mg 3d orbital is much more extended than the Mg 2p orbital. One way of estimating the size of an orbital is from the average value of r, the distance from the nuclear center of Mg, for the orbital; this is the expectation value of r, denoted by $\langle r\rangle$. Clearly, orbitals with a larger $\langle r\rangle$ extend further and will be modified more when the atom or ion is in a compound than will orbitals with a smaller $\langle r\rangle$. In particular, $\langle r\rangle$ for the 3d orbital in an excited state of Mg^{3+}, where the configuration is $1s^2 2s^2 2p^4 3d^1$, is more than three times larger than $\langle r\rangle$ for the 2p orbital of the ground state of Mg^{3+}. Thus, the large Mg 3d orbital is too large to fit into the MgO lattice and it would have a strong overlap with the occupied O(2p) orbitals. In effect, it might be expected that the Mg 3d orbital would be quenched in the MgO lattice, and the near degeneracy effect would not be possible for Mg^{2+} cations in MgO. It is the major objective of this paper to show that, in fact, the near-degeneracy that lowers the Mg BE(2s) for the Mg^{2+} cation is also important for MgO. It is essentially as important for MgO as it is for the free Mg^{2+} ion. Dave Shirley pioneered our understanding that many-electron effects must be taken into account to properly understand the significance of XPS BEs. In our present work, we are able to demonstrate an important extension to the many-body effects that need to be considered even for a relatively simple, essentially ideal, ionic compound like MgO.

The outline of the paper is as follows: In Sec. II, the theoretical approaches taken for the calculation of the Mg BE(2s) and BE(2p) and the measurement of the MgO XPS are described. In Sec. III, the properties of the ground state, GS, and the ionic ^2S and ^2P multiplets are presented. This includes characterization of the importance of near degeneracy on the wavefunctions, WFs, of the ^2S multiplet as well as its importance for the BE(2s). In Sec. IV, parallel properties for MgO are described. Here, estimates are also made of the magnitudes of corrections to the calculated BEs that might result from improved calculations including changes due to relativistic effects. In Sec. V, our conclusions are summarized.

II. THEORETICAL AND EXPERIMENTAL DETAILS

A. Cluster models and theoretical methods

Two different material models for MgO are used. One is simply an isolated Mg^{2+} cation and the second is an embedded MgO_6 cluster. This cluster contains a central Mg^{2+} cation surrounded by its six nearest O^{2-} neighbors embedded in point charges to represent the Madelung potential of the octahedral MgO crystal. The point charges assume that the ionic charges are ±2 and are based on an Evjen algorithm for the charges in the bulk, surface, and edges of the cubic model.[8,9] Our studies have indicated that such small embedded clusters will give reliable BE shifts; see, for example, Refs. 10 and 11. Comparison of results from the embedded MgO_6 cluster and from the isolated cation will provide information on the importance of differences between the extended MgO crystal and the atomic Mg^{2+} cation. We recall that there is a very large difference between the BEs of the isolated Mg^{2+} ion and Mg^{2+} in the MgO crystal of 31 eV for both the 2s and 2p BEs, where the experimental MgO BEs are taken from our measurements described below and the isolated ion BEs from Moore's tables.[12] The BEs of the isolated ions are larger than those of the MgO crystal. A large part of this difference arises from the Madelung potential existing in MgO although there is also a difference of ∼5 eV because the BEs of the isolated ion are referenced to vacuum as zero while the MgO BEs are referenced to an E_F as zero. These differences are discussed in detail by Broughton and Bagus.[13] There is also a limitation of the embedded MgO_6 cluster calculation in that it does not include the compressional effect of the Mg^{2+} cations that surround the O^{2-} anions. This compressional effect has been considered in Refs. 10 and 13. The important conclusion is that while the compression lowers the cation BEs, the lowering is essentially constant for all cation levels and, hence, will not affect the ΔBE of the 2s and 2p BEs, which are the essential concern of this paper.

For these models, Hartree–Fock, HF, and multiconfiguration HF, MCHF wavefunctions, WFs, have been computed. The HF WFs are for the GS and 2p and 2s ions of Mg^{2+} and of the embedded MgO_6 cluster; the MCHF WFs are only for the 2s ions. The MCHF is used to take account of a near degeneracy effect which is possible only for the 2s ion; this effect is a static correlation effect,[14,15] which can account for major departures from a one configuration model for states where near degeneracy is present. For the Mg^{2+} ion, the MCHF allows for a "promotion" of two 2p electrons with one filling the 2s shell and the other placed into a 3d shell; this is denoted as $2p^2 \rightarrow 2s3d$. The Mg^{2+} MCHF WF for these two configurations is

$$\Psi(2s\text{ ion};\,^2S) = C_1\left[1s^2 2s^1 2p^6\right] + C_2\left[1s^2 2s^2 2p^4(^1D)3d^1\right], \qquad (1)$$

and the configuration mixing coefficients, C_i, as well as the orbitals are optimized solutions of the variational equations; see, for example, Ref. 16. The MgO_6 MCHF WF is defined in a completely analogous way. In order to prevent a variational collapse, a constraint was imposed on the orbital variation for the 2s ion, which is described in the supplementary material.[28] The BEs are defined as the differences of the energies of GS Mg^{2+} and the energy of the ions where either a 2s or 2p electron has been removed. They are described as ΔSCF BEs; see, for example, Ref. 4 and references therein. For the most part, the calculations are nonrelativistic but a few are relativistic, including both scalar effects and spin–orbit splitting, to determine the extent of relativistic effects on the BEs and ΔBEs. For the atomic calculations, the HF and MCHF WFs are obtained from numerical solutions of the appropriate Hamiltonians and are described with the acronym, NHF. The atomic WFs are also obtained with basis set expansions of the orbitals; see, for example, Ref. 17 for a discussion of the basis set expansions. These basis sets are used to facilitate comparison of the WFs for Mg^{2+} to those for the MgO_6 embedded cluster since for the clusters WFs can only be obtained with basis set expansions. The same basis set, including the functions centered on the O atoms, is used for both the atomic and cluster calculations. This is done in order to avoid artifacts in the comparison of atomic and cluster model results. As a measure of the reliability of the BEs obtained with the embedded MgO_6 cluster, the Mg 2p BE for this cluster is 57.8 eV, which is 6.1 eV larger than the measured (charge corrected) XPS BE of 51.7 eV, see below. This difference arises from the different zeros of BE for the measurement and the calculation and also from the neglect, with the embedded MgO_6 cluster, of the compression due to the environmental Mg cations represented as point charges. The difference of the zero of BE is constant for all Mg cation BEs. There is also strong evidence[10,13] that the compressional effect on the BE is very nearly constant for all cation levels so that it is proper to compare the ΔBE obtained with the cluster to the XPS ΔBE.

These are all nonrelativistic WF calculations. In order to estimate the importance of relativistic effects on ΔBE, relativistic Dirac HF, DHF, WFs[18] were computed for the GS of Mg^{2+} and the orbital energies, ε, of the relativistic, DHF, and nonrelativistic HF WFs of the Mg^{2+} WF were compared. For this purpose, only the Mg centered basis functions were used for these calculations. The important thing is that the same basis sets were used for both the relativistic and nonrelativistic calculations.

The numerical HF and MCHF calculations were performed with programs developed by Fischer.[16] For the basis set expansion calculations, the nonrelativistic HF calculations were performed with the CLIPS programs system[19] and the nonrelativistic MCHF calculations were performed with the CASSCF program developed by Roos *et al.*[20] The relativistic DHF calculations for Mg^{2+} used the DIRAC program system.[21] Details of the calculations, including the geometries and the basis sets, used are given in the supplementary material.[28]

B. Experimental XPS measurements

The experimental Mg 2s to Mg 2p XPS BE difference for MgO is taken from the same sets of data as used in our recent paper on shake loss intensities in MgO, measured in a Thermo K-Alpha instrument.[22] The single crystal sample was cleaved in air immediately prior to insertion. Residual hydrocarbon contamination was very small and there was no evidence of any chemically shifted Mg 2p component. Charge control was adjusted to give the narrowest peaks and showed no evidence of any nonuniform charging. The BEs, as recorded (50 eV pass energy), with no charge correction, were Mg 2p: 49.22 ± 0.05 eV, and Mg 2s: 88.06 ± 0.05 eV (measuring to the peak maxima), resulting in an Mg 2s-2p separation of 38.84 ± 0.1 eV. Charge referenced to C1s of the hydrocarbon present, assigned as 284.8 eV BE (recommended by PHI, Thermo, and NIST), the absolute Mg 2p BE would be 51.7 eV, but for the purposes of this paper we are not concerned with the absolute accuracy, only the Mg 2s-2p separation.

III. ATOMIC RESULTS

We begin by describing and contrasting the results for the BE (2s) and BE(2p) for Ne and Mg^{2+} that have been obtained with numerical HF and MCHF wavefunctions where BEs are not affected by the choice of basis sets. In effect, these results are at the complete basis set limit.[23] The results for the Ne BE's are taken

TABLE I. Experimental and theoretical BE(2s), BE(2p), and ΔBE = BE(2s) − BE(2p) values, in eV, for Ne and isoelectronic Mg^{2+}; the differences of theory with experiment are given as ΔExp. The theoretical values are from HF WFs and, for the 2s ion, from MCHF, WFs. The Na and Mg^{2+} BEs are for numerical, NHF, HF, and MCHF energies. For Mg^{2+} BEs are also given using the same basis set as for the MgO WFs. All BEs are nonrelativistic.

		Exp[a]	HF (ΔExp)	MCHF (ΔExp)
Ne—NHF[b]	BE(2p)	21.53	19.85 (−1.68)	—
	BE(2s)	48.41	49.32 (+0.91)	46.67 (−1.71)
	BE(2s) − BE(2p)	26.88	29.47 (+2.59)	26.82 (−0.06)
Mg^{2+}—NHF	BE(2p)	80.24[c]	78.65 (−1.59)	—
	BE(2s)	118.77	119.31 (+0.55)	116.95 (−1.82)
	BE(2s) − BE(2p)	38.53	40.66 (+2.13)	38.30 (−0.23)
Mg^{2+}—basis set	BE(2p)	80.24[c]	78.73 (−1.50)	—
	BE(2s)	118.77	119.38 (+0.61)	117.08 (−1.69)
	BE(2s) − BE(2p)	38.53	40.65 (+2.11)	38.35 (−0.19)

[a]See Ref. 12.
[b]From Ref. 6.
[c]Weighted average of $^2P_{3/2}$ and $^2P_{1/2}$ the spin–orbit splitting is 0.28 eV (Ref. 12).

from our earlier publication.[6] We also include results for the Mg^{2+} BEs obtained with the basis sets that are used for the calculations of the MgO BEs. All these results are nonrelativistic. The Mg basis sets have also been used to obtain relativistic Bes, which are compared to the nonrelativistic BEs.

In Table I, experimental values[12] for BE(2p) and BE(2s) and the difference, $\Delta BE = BE(2s) - BE(2p)$, for neutral Ne and Mg^{2+} are compared to the results of theoretical calculations. The calculations include the NHF BEs and, for Mg^{2+}, the BEs using basis sets as described in Sec. II. To determine the importance of relativistic contributions to the BEs, the 2s and 2p orbital energies from relativistic and nonrelativistic calculations using only the Mg basis sets are given in Table II. The NHF results in Table I are considered first. It is clear that, as expected from the discussion in Sec. I, the HF BE(2p) is smaller than the experimental BE; the errors of BE (2p) for both Ne and Mg^{2+} are ~1.5 eV. On the other hand, the HF BE(2s) is larger than experiment by either 0.9 eV (Ne) or 0.6 eV (Mg^{2+}). This is because the HF WF for the 2s ion with configuration $1s^2 2s^1 2p^6$ does not include the nearly degenerate configuration $1s^2 2s^2 2p^4 3d^1$. When this configuration is included in the MCHF WFs, the BE(2s) becomes smaller than experiment with an error similar to the error of the HF BE(2p). For Mg^{2+}, the error of the MCHF BE(2s) is 0.2 eV larger than the error of the HF BE(2p). As we discuss below this is due, in part, because of a somewhat larger relativistic contribution to the BE(2s) than to the BE(2p). Before we turn to relativistic corrections, we first consider whether our use of the basis set for the calculations to determine the BEs for MgO, discussed in Sec. IV, might introduce uncertainties in the BE shifts calculated for the crystal. This is done by comparing the results for the Mg^{2+} BEs calculated using the same basis set as for the MgO_6 cluster model to calculate the BEs and BE shifts; these are given in Table I as Mg^{2+}—Basis Set. These basis set results are quite similar to the NHF, which are basis set limit, results; the differences are generally less than 0.1 eV with the largest difference between the NHF and basis set results for the MCHF BE(2s) of 0.13 eV. This difference is the largest because our basis set to describe the 3d orbital uses only two functions. However, all the differences between the basis set limit NHF BEs and ΔBEs are sufficiently small to show that our calculations for the BE shifts of MgO with the embedded cluster model are reliable.

In order to estimate relativistic contributions to the BEs, we compare in Table II the orbital energies calculated for the isolated Mg^{2+} cation for nonrelativistic HF solutions of the Schrödinger equation and relativistic Dirac Hartree–Fock, DHF, solutions of the

TABLE II. Orbital energies, in eV, of the 2s and 2p orbitals for nonrelativistic HF and relativistic DHF solutions for Mg^{2+}; the relativistic ε(2p) is the weighted average of $\varepsilon(2p_{1/2})$ and $\varepsilon(2p_{3/2})$. Differences of the orbital energies, $\Delta\varepsilon = \varepsilon(2p) - \varepsilon(2s)$, and differences between relativistic and nonrelativistic ε, Δ(R-NR) = ε(rel) − ε(non-rel), are also given.

	ε(2p)	ε(2s)	Δε
Non_Relativistic, HF	−81.84	−121.76	39.92
Relativistic, DHF	−81.81	−122.17	40.36
Δ(R-NR)	−0.03	+0.41	0.44

TABLE III. Properties of the 2s, 2p, and 3d orbitals for several states of Mg^{2+} and Mg^{3+} cations from nonrelativistic HF and MCHF calculations. The properties are r_{eff} in Å, see Eq. (2), and occupation numbers, Occ. See the text for details.

	$r_{eff}(2s)$	$r_{eff}(2p)$	$r_{eff}(3d)$	Occ (2s)	Occ (2p)	Occ (3d)
GS	0.40	0.41	—	2.000	6.000	0.000
2p ion (HF)	0.39	0.38	—	2.000	5.000	0.000
2s ion (HF)	0.38	0.38	—	1.000	6.000	0.000
2s ion (MCHF)	0.38	0.38	0.54	1.022	5.956	0.022
Optical	0.37	0.36	1.39	2.000	4.000	1.000

Dirac-Coulomb Hamiltonian.[24] The relativistic correction to the 2p orbital energy is rather small but the relativistic increase in the magnitude of ε(2s) is modest. The differences in the HF orbital energies, Δε, are close to the HF BE(2s) − BE(2p) in Table I indicating that the major origin for the BE shift is an initial state effect and that the 0.4 eV change between the relativistic and nonrelativistic Δε is a good guide to the relativistic contribution to the BE shifts. We assume also that the estimate of the relativistic correction for the BEs of Mg^{2+} will also hold for these BEs in MgO.

Properties of the orbitals and of the WFs for the numerical HF and MCHF calculations on Mg^{2+} are given in Table III to help to explain the role of the 3d orbital in the 2s ionic state calculations. In addition to the GS, 2p and 2s ionic states, the properties are also given for an excited configuration to show the character of a 3d orbital appropriate for excited states. The configuration for this excited state of Mg^{3+} is $1s^2 2s^2 2p^4 3d^1$ coupled to a ^2S multiplet;[25] the configuration and the 3d orbital for this configuration are described as "optical" since it represents an excited state that is observed in the optical spectra of Mg^{3+}.[12] The properties that are given are $r_{eff}(n\ell)$, in Å, for the 3s, 2p, and 3d orbitals to indicate the spatial extent of the orbitals and the occupation numbers of the orbitals, Occ($n\ell$). $r_{eff}(n\ell)$ are defined as

$$r_{eff}(n\ell) = [\langle r^2_{n\ell} \rangle]^{1/2}, \tag{2}$$

where this choice is made so that a direct comparison can be made for the same property calculated for the embedded MgO_6 cluster models of MgO described in Sec. IV. Occ($n\ell$) for the HF WFs are simply the occupations of the $n\ell$ shell; for the MCHF WF, they follow directly from the weights of the HF $1s^2 2s^1 2p^6$ and the nearly degenerate $1s^2 2s^2 2p^4 3d^1$ configurations.[26] GS $r_{eff}(2s)$ and GS $r_{eff}(2p)$ are 0.4 Å and represent the size of the Mg^{2+} cation that fits in the Mg–O distance of 2.1 Å in the MgO crystal.[27] $r_{eff}(2s)$ and $r_{eff}(2p)$ for the HF 2p and 2s ions have similar although slightly smaller values; the smaller values are simply because there are fewer 2s and 2p electrons in the ions, 7, instead of 8 in the GS. For the MCHF 2s ion, $r_{eff}(2s)$ and $r_{eff}(2p)$ are the same as for the HF ion and $r_{eff}(3d) = 0.54$ Å, which is somewhat larger than for the 2s and 2p orbitals. However, it is not so large that it cannot fit into the MgO crystal without exceptionally large overlap and steric repulsion with the O(2p) charge density as will be shown in Sec. IV. The relatively small value of $r_{eff}(3d)$ for the MCHF

TABLE IV. Properties of orbitals and WFs for the HF 2p and 2s ions and the MCHF 2s ion of the embedded MgO_6 cluster model of MgO. The properties are $\Delta BE = BE(2s) - BE(2p)$, in eV, as well as r_{eff}, in Å, and Occ for the Mg 2s, 2p, and 3d orbitals for the HF WFs of the 2s and 2p ions and the 2s ion MCHF WF. See the text and captions to Tables I and III.

	ΔBE	$r_{eff}(2s)$	$r_{eff}(2p)$	$r_{eff}(e_g)$	$r_{eff}(t_{2g})$	Occ(2s)	Occ(2p)	Occ(3d)
2p-Ion HF	—	0.39	0.41	—	—	2.000	5.000	—
2s-Ion HF	40.63	0.39	0.39	—	—	1.000	6.000	—
2s-Ion MCHF	38.34	0.39	0.40	0.58	0.55	1.021	5.958	0.021

correlating 3d orbital is in strong contrast to the much larger size of the optical 3d orbital for an excited state of Mg^{3+} where $r_{eff}(3d) = 1.4$ Å or 2.5 times larger than for the correlating 3d orbital. An orbital of this size is so large that it would not be able to fit into the MgO lattice because of a very large overlap with the O(2p) charge density. The fact that the correlating 3d orbital is so much more compact is why it is possible for this atomic many-body effect to also be important for MgO. The values of the Occ($n\ell$) for the 2s MCHF WF show the extent of the mixing of the second configuration in the WF. They show that 0.044 2p electrons are transferred with 0.022 electrons moving into the 2s and 3d shells, respectively. While this is not large, it is sufficient to reduce the BE (2s) so that it is below the experimental BE(2s) by about the same amount as the BE(2p). Thus, it leads to a BE difference, BE(2s) − BE(2p), that is reasonably close to the measured value. Without taking relativistic effects into account, the theoretical BE(2s) − BE (2p) is smaller than the measured difference of 38.5 eV by 0.2 eV; if we add a correction of 0.4 eV for relativistic effects, the theoretical BE difference would be 0.2 eV larger than the measured value, still a good agreement between theory and experiment.

IV. RESULTS FOR MgO

The same theoretical method used to study the BEs of the isolated Mg^{2+} cation is applied to the BEs for MgO, as represented with the MgO_6 cluster, where the concern is for the Mg $\Delta BE = BE(2s) - BE(2p)$. For MgO, we examine ΔBE rather than BE to avoid the need to adjust our calculated BEs where the zero of energy is vacuum to measured XPS BEs which are relative to E_F for the spectrometer. However, in Sec. II A, we briefly discussed the HF BEs for the embedded MgO_6 cluster compared to experiments. In Table IV, we give the HF and MCHF $\Delta BE = BE(2s) - BE(2p)$ and the orbital properties of r_{eff} and occupations, Occ, as given in Table III for the WFs and orbitals of the isolated Mg^{2+} cation. Although the MgO_6 cluster has the lower cubic symmetry, we still use the designations of 2s and 2p for these orbitals since they retain their atomic character in MgO. For the 3d orbitals, we separate r_{eff} for t_{2g} and e_g components since they are slightly different. Occ(3d) are not separated but summed over the five 3d orbitals since the individual t_{2g} and e_g orbitals have the same occupations of 0.0042. All the values in Table IV have very small differences from the equivalent values for the Mg^{2+} cation in Tables I and III. The largest difference for the orbital properties, r_{eff} and Occ, is for $r_{eff}(e_g)$ of the 2s Ion MCHF WF, which is 0.04 Å larger than $r_{eff}(3d)$ for the equivalent WF of Mg^{2+}. This small difference shows that there is a minor effect on the Mg 3d orbitals from their overlap with the O(2p) charge density. Indeed, the HF and MCHF ΔBE for MgO are different from the equivalent ΔBE for Mg^{2+} by only 0.02 and 0.01 eV, respectively. The difference between the HF and MCHF ΔBE is 2.3 eV for both Mg^{2+} and MgO showing very clearly that this many-electron effect is of comparable importance for both cation and oxide. The ΔBE from the XPS measurement is 38.8 ± 0.1 eV, which is larger by 0.5 eV than the MCHF theoretical value. If we add 0.44 eV as an estimate for the relativistic contribution to ΔBE, see Table II, we will have a theoretical ΔBE of 38.8 eV, which is completely consistent with the measurement. However, we should not rely too strongly on the quantitative accuracy of this agreement. The main point is that the many-body correction arising from including the $2p^2 \rightarrow 2s3d$ near degeneracy is essential to correctly describe the energy separation of the Mg BE(2s) and BE(2p) in MgO. The HF error for the ΔBE is nearly 2 eV larger than the XPS measured ΔBE and would become even larger when corrections for relativistic effects are included. However, the directly calculated ΔBE, when the MCHF near degeneracy effect is included for the Mg 2s BE is included, is smaller than the measured ΔBE by only 0.5 eV and this small error is further reduced when corrections for relativistic effects are taken into account.

V. CONCLUSIONS

There are two important conclusions from our comparison of theoretical predictions for the BE separation of the Mg BE(2s) and BE(2p) with XPS measurements for MgO. First, it is essential to take account of a many-body effect that arises because there is a near degeneracy involving redistribution of electrons between the 2s, 2p, and a d orbital. We have referred to this orbital as 3d although it is quite different from the optical 3d orbital that would be occupied in excited states of the Mg cations. As measured by the effective mean radius, r_{eff}, this optical 3d orbital is over three times larger than the correlating 3d orbital used in the MCHF WF of the embedded MgO_6 cluster model of MgO. The reason for the strong reduction in the size of the correlating 3d orbital from the optical 3d orbital is that this increases the off-diagonal matrix element of the nearly degenerate $1s^2 2s^2 2p^4 3d^1$ configuration with the main 2s-hole configuration, $1s^2 2s^1 2p^6$. The increase in the off-diagonal matrix element increases the energy lowering due to a greater mixing of the nearly degenerate configuration with the main 2s-hole configuration. The near degeneracy effect is also described as a static correlation effect to distinguish it from the dynamic correlation effects that are needed to obtain high accuracy for relative energies; see, for example, Refs. 14 and 15.

Another way of comparing theory with experiments is to consider the sign of the error of the HF ΔBE. When the HF BE($n\ell_1$) − BE($n\ell_2$) is larger than experiments, as is the case with the Mg BE(2s) − BE(2p), this is a strong indication that there will be an important correlation effect for the $n\ell_1$ ion that is not possible for the $n\ell_2$ ion. Thus, without calculations that include many-body effects, it is possible to identify that such effects are likely to be important.

The second conclusion follows from the similarity of the predictions of ΔBE and the similarity of the WF properties between the isolated Mg^{2+} cation and MgO oxide. These close similarities are a further strong indication that MgO is very nearly a perfect ionic crystal composed of Mg^{2+} cations and O^{2-} anions.

In closing, we would like to add that this work is an extension of the way of understanding how XPS measurements provide insight into the electronic structure and chemistry of different compounds that Dave Shirley and his collaborators pioneered. It shows that even though XPS is a mature discipline, there are still new things to learn in how we can understand and extract chemistry from these measurements.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.[28]

REFERENCES

[1]P. S. Bagus, E. Ilton, and C. J. Nelin, Catal. Lett. **148**, 1785 (2018).
[2]C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, Phys. Rev. Lett. **23**, 1397 (1969).
[3]P. S. Bagus, A. J. Freeman, and F. Sasaki, Phys. Rev. Lett. **30**, 850 (1973).
[4]P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. **68**, 273 (2013).
[5]E.-K. Viinikka and Y. Öhrn, Phys. Rev. B **11**, 4168 (1975).
[6]P. S. Bagus, R. Broer, and F. Parmigiani, Chem. Phys. Lett. **421**, 148 (2006).
[7]R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).
[8]H. M. Evjen, Phys. Rev. **39**, 675 (1932).
[9]S. E. Derenzo, M. K. Klintenberg, and M. J. Weber, J. Chem. Phys. **112**, 2074 (2000).
[10]P. S. Bagus, M. J. Sassi, and K. M. Rosso, J. Chem. Phys. **151**, 044107 (2019).
[11]C. J. Nelin, F. Uhl, V. Staemmler, P. S. Bagus, Y. Fujimori, M. Sterrer, H. Kuhlenbeck, and H.-J. Freund, Phys. Chem. Chem. Phys. **16**, 21953 (2014).
[12]C. E. Moore, *Atomic Energy Levels, National Bureau of Standards No. 467* (U.S. GPO, Washington, DC, 1952), see also http://physics.nist.gov/cgi-bin/AtData/main_asd.
[13]J. Q. Broughton and P. S. Bagus, Phys. Rev. B **36**, 2813 (1987).
[14]J. Cioslowski, Phys. Rev. A **43**, 1223 (1991).
[15]E. Valderrama, E. V. Ludena, and J. Hinze, J. Chem. Phys. **110**, 2343 (1999).
[16]C. F. Fischer, Comput. Phys. Commun. **128**, 635 (2000).
[17]I. N. Levine, *Quantum Chemistry* (Prentice-Hall, Upper Saddle River, NJ, 2000).
[18]T. Saue *et al.*, J. Chem. Phys. **152**, 204104 (2020).
[19]CLIPS is a program system to compute *ab initio* SCF and correlated wavefunctions for polyatomic systems. It has been developed based on the publicly available programs in the ALCHEMY package from the IBM San Jose Research Laboratory by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine.
[20]B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. **48**, 157 (1980).
[21]DIRAC, a relativistic *ab initio* electronic structure program, Release DIRAC14 (2014), written by T. Saue, L. Visscher, H. J. Aa. Jensen, and R. Bast, with contributions from V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, C. V. Larsen, J. K. Lærdahl, Y. S. Lee, H. S. Nataraj, P. Norman, G. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. di Remigio, K. Ruud, P. Sałek, B. Schimmelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto, see http://www.diracprogram.org.
[22]P. S. Bagus, C. R. Brundle, and B. V. Crist, J. Vac. Sci. Technol. A **39**, 063206 (2021).
[23]D. Feller, J. Comput. Chem. **17**, 1571 (1996).
[24]L. Visscher, O. Visser, P. J. C. Aerts, H. Merenga, and W. C. Nieuwpoort, Comput. Phys. Commun. **81**, 120 (1994).
[25]J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vols. I and II.
[26]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley, Reading, 1958).
[27]R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963).
[28]See supplementary material at https://www.scitation.org/doi/suppl/10.1116/6.0001655 for information describing computational details.