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Consequences of electron correlation for XPS binding energies: Representative case for C(1s) and O(1s) XPS of CO

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In this paper, we present a study of the signs and the magnitudes of the errors of theoretical binding energies, BE's, of the C(1s) and O(1s) core-levels compared to BE's measured in X-Ray photoemission, XPS, experiments. In particular, we explain the unexpected sign of the error of the Hartree-Fock C(1s) BE, which is larger than experiment, in terms of correlation effects due to the near degeneracy of the CO(1π) and CO(2π) levels and show how taking this correlation into account leads to rather accurate predicted BE's. We separate the initial state contributions of this near degeneracy, present for the ground state wavefunction, from the final state near degeneracy effects, present for the hole state wavefunctions. Thus, we are able to establish the importance for the core-level BE's of initial state charge redistribution due to the π near-degeneracy. While the results for CO are interesting in their own right, we also consider whether our conclusions for CO are relevant for the analysis of XPS spectra of a wider range of molecules. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4964320]

I. INTRODUCTION

Wavefunctions, WF's, have been used extensively to understand, predict, and assign the peaks in X-Ray photoelectron spectra, XPS, see Ref. 1 for a review of representative applications of WF theory to XPS and for a discussion of the theoretical formulations. It is possible to obtain reasonably accurate XPS binding energies, BE's, for core levels with the ΔSCF method where the BE's are denoted as BE(ΔSCF). This method involves calculating the WF's and total energies for the initial state configuration and for the final, core-hole, state configuration and taking the BE(ΔSCF) as the difference of the variational total energies of the initial and final states. The very large majority of WF calculations of core-level BE's are done using Hartree-Fock, HF, theory. For compounds containing light atoms, C, N, O, and F, the errors of HF BE(ΔSCF) are typically of order 0.5-1.0 eV.[2–4] Similar accuracy can be obtained with BE(ΔSCF) methods based on density functional theory, DFT;[2–7] indeed with an appropriate choice of density functional, the DFT BE(ΔSCF) are somewhat more accurate than the HF BE(ΔSCF). One expects the HF BE(ΔSCF) to be smaller than the XPS experiment and this is normally the case; see, for example, Refs. 2–4. The expectation that the HF BE(ΔSCF) will be smaller than experiment follows from a logic originally proposed by Mulliken.[8] The final, ionic state has fewer electrons, hence fewer electron pairs, than the initial state and, hence, one expects the correlation energy, that is the error of the HF energies, to be smaller in the final state than in the initial state. It is easy to see, given that the error of the higher energy state, the final state with the core hole, is smaller than the error of the initial state, that the calculated HF BE(ΔSCF) will be smaller than that measured in the XPS experiment.

However, there are exceptions to this simple rule for the order of the error of HF ΔSCF BE's and there are cases where BE(ΔSCF) is larger than experiment. This means that the correlation energy of the hole-state, with one fewer electron, is larger than the correlation error of the initial state. One of the earliest exceptions found where the HF BE(ΔSCF) is greater than experiment was for the lowest ^2S states of Ne^+ and Ar^+ and their isoelectronic ions.[9] For Ar, for example, the lowest ^2S state has the configuration $\ldots 3s^1 3p^6$ and there is a nearly degenerate configuration with a ^2S multiplet that is $\ldots 3s^2 3p^4 3d^1$.[10] Since this configuration involves filling the 3s hole with a 3p electron and promoting another 3p electron to the higher energy, but still bound, 3d level, it has been described as a frustrated Auger configuration, FAC.[11] The static correlation introduced by mixing the two configurations is present only for the 3s-hole configuration but not for the initial configuration. When this static correlation effect is taken into account, the ΔSCF BE is now, correctly, smaller than the XPS experiment.[10] Furthermore, this static correlation is general and it also leads to corrections for the 3s-hole XPS of 3d transition metal cations.[11,12] However, for the special cases of Ne and Ar, the static correlation involves the same shell as the ionized electron. For CO, considered in this paper, the static correlation does not involve the same shell as the shell ionized in the XPS measurement.

For CO, the O(1s) BE(ΔSCF) obtained with HF wavefunctions is, as expected, lower than the XPS BE by ∼1 eV while the C(1s) BE(ΔSCF) is larger than the XPS BE, also by ∼1 eV, opposite to the expected order; see Ref. 13 and results in this paper. For CO, the static correlation does not involve the deep core, C(1s) and O(1s), shells but involves the higher lying valence levels, in particular the 1π and 2π shells where the 1π is fully occupied and the 2π is empty in the HF configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^0. \quad (1)$$

In order to determine these many-body effects, we use Complete Active Space, CAS,[14] WF's where configurations are formed by distributing the 4 CO π electrons over the space of the 1π and 2π orbitals. As for the HF WF's, the CAS orbitals and configuration mixing, CI, coefficients are variationally optimized for each of the states of interest, the ground state, GS, and the C(1s) and O(1s) hole states. One important effect for the mixing of configurations where one or more electrons are moved from the 1π to the 2π shell with respect to the reference $1\pi^4$ configuration is that the charge distribution may be different from that in the reference or HF configuration. This is because the 1π orbital is a bonding orbital dominantly centered on O, while the 2π orbital is an anti-bonding orbital dominantly centered on C; see, for example, Ref. 15 or another standard Quantum Chemistry reference. Thus occupation of the 2π orbital will move the center of CO charge from O toward C and the electrostatic potential at the C and O nuclei may change leading to changes in the C(1s) and O(1s) BE's. This change in the center of charge of the CO ground state wavefunction is an initial state effect. In terms of the language of valence bond, VB, theory, one can view that the effect of the static correlation is to discriminate the contribution of the different resonant valence bond forms (CO $\leftrightarrow$ C^+O^- $\leftrightarrow$ C^-O^+ . . .) which the HF wavefunction includes on the same footing.[16] Furthermore, the use of multi-configuration WF's for the core-hole states may allow a different relaxation, or screening, in the hole state WF's than occurs for the HF wavefunctions and this will lead to different final state contributions to the BE's. In other words, while for the HF WF, the screening must be entirely through changes in the orbital character, for the multi-configuration WF's, there is an additional screening through changes in the mixing in the WF of the configurations where 1π electrons are moved to the 2π shell. Our objectives in this work are twofold. First, we wish to examine whether the inclusion of static, near degeneracy, electron many-body effects leads to having both O(1s) and C(1s) ΔSCF BE's smaller than the measured XPS BE's and that the error of the calculated BE's is reduced and is below 1 eV. The second objective is to determine the origin of the many-body changes in the BE's and to relate them to features of the many-body WF's. This analysis will include separation of the changes in the BE's due to many-body effects into the initial state effects that arise from the changes in the ground state WF and final state effects due to changes in the many-body hole state WF's. To our knowledge, this type of analysis of the many-body contributions to core-level BE's has not been made before. The SCF and CASSCF WF's that we use directly allow the role of static correlation in the CO π space to be investigated; furthermore, they allow the separation of initial and final state contributions.[1]

In our discussion above and in the remainder of the paper, we have used concepts and terminologies that merit further discussion in order to avoid ambiguity or uncertainty concerning our usage of them. In particular we have described a classification of electron correlation effects as being static or dynamic and we have described a division of the contributions to core-level BE's in terms of initial and final state effects. The classification of static as contrasted to dynamic electron correlation[17–21] is commonly used to distinguish the correlation effects that arise from near degeneracy of different configurations from the dynamical correlation effects that are required to obtain very precise energies. Although, there may be an uncertainty in the division of particular terms to be included in each classification,[18,19,21] our usage is very clear in that we are concerned with the correlation that arises from including the 1π and 2π orbitals of CO in the active space and, hence, the included correlation effects are non-dynamical. In particular, we shall examine how this participation is different for the CO GS and for the C(1s) and O(1s) core-hole states. We are not concerned with finer distinctions of the inclusion of σ orbitals in the active spaces. The separation of initial and final state contributions to core-level BE's is standardly used in the interpretation of XPS BE's.[1] However, we want to be explicit about our usage of these distinctions and of the related concept of relaxation energies since they are important to relate the core-level BE's to the electronic structure of the material under study.[1] Initial state effects are those which arise essentially from the electrostatic potential at the ionized atom in the WF of the GS. For closed shell HF WF's, the initial state BE's are rigorously given by Koopmans' theorem,[1–3] KT. However, as we show in Sec. II, the definition of initial state effects has a rigorous generalization beyond HF to correlated WF's. In this generalization, one applies an annihilation operator to the GS WF, to obtain what we will call an FO, or Frozen Orbital, WF where no response to the core-hole is allowed and FO BE's arise entirely from the charge distribution of the GS WF. It is important to remark that while only the orbitals are fixed in the FO single configuration HF WF's, in the CAS CI WF's, both the orbitals and the configuration mixing coefficients are fixed in the FO CAS CI WF's. As we note in a later discussion, our use of FO WF's follows that introduced by Aberg[22] for the analysis of XPS satellites. The relaxation energy, E_R, is also a rigorously defined quantity that is the difference between the energy of the FO and the fully self-consistent SCF WF for the hole states.[1,2] In this sense, E_R is a direct measure of the energetic importance of the response, or relaxation, of the WF orbitals and CI mixing coefficients to the presence of the core-hole; thus, E_R is a pure final state effect.[1] The distinction between initial state and final state effects is especially important when one considers shifts of BE's between inequivalent atoms in a system, as between atoms at the surface and in the bulk of a solid,[1] or between different atoms in different molecules.[2–4] Here, it allows the chemical contributions to the BE shifts to be distinguished from those arising from the response to the presence of the core-hole. In our use in the present paper, we use the FO analysis of initial state effects to decompose the contributions to the changes in the BE's between the HF and the CAS WF's. This decomposition allows us to distinguish the changes in the CAS BE's, which include static correlation effects that arise from the changes in the charge distribution in the initial, GS, state from those that arise from the relaxation. We stress that the final state relaxation changes include changes in the CI mixing of the 2π orbital in the final hole state CAS WF as well as changes in the orbitals. This will be discussed further when we present the results.

In Sec. II, the theoretical methodology and the computational methods used are presented and described in relationship to the scientific issues addressed. In particular, rigorous definitions are given for the separation of initial and final state effects. In Sec. III, the theoretical BEs are presented and compared with the XPS BE's. Properties of the CAS wavefunctions are considered in connection with the shifts of the core-level BE's that arise due to these changes. Finally, in Sec. IV, we summarize our conclusions and stress the magnitude of the changes that may arise from static, near degeneracy, electron correlation effects, and describe the features that indicate that such static correlation effects may be present.

II. THEORETICAL METHODOLOGY AND COMPUTATIONAL DETAILS

The HF and CASSCF wavefunctions use spatial and spin equivalence restrictions and the CO ground state, GS, WF is a pure $^1\Sigma^+$ while the hole-state WF's are pure $^2\Sigma^+$. For the GS CASSCF, the 4 π electrons are active and configurations are included where these electrons are distributed over 4, $1\pi_x$, $1\pi_y$, $2\pi_x$, and $2\pi_y$, active orbitals; this is denoted as CAS(4,4). For the core hole states, either the 1σ, O(1s), or the 2σ, C(1s), orbital is added to the active electron space but it is forced to be singly occupied in all configurations in the CAS wavefunction. Although the active spaces are increased for these hole state CAS WF's, we still refer to them as CAS(4,4) where (4,4) now refer only to the π active spaces. We shall use the 1π and 2π occupation numbers, N(1π) and N(2π), as a measure of the importance, especially the relative importance, of the CAS static correlation effects for the GS and the core-hole states. For the HF WF's these occupation numbers are N(1π) = 4.00 and N(2π) = 0.00 for all states; for the CAS(4,4) WF's, the occupation numbers are the CAS natural orbital occupation numbers.[14] For these wavefunctions, we consider BE's for initial state effects only, denoted BE(FO) for frozen orbital BE's, and BE(ΔSCF) where both initial and final state effects are included.[1] The formal mathematical definition of the FO WF for the core ion[22] is that an annihilation operator for the core orbital is applied to the initial, N electron GS WF, to yield the N − 1 electron FO WF, Ψ(FO), for the core hole

$$\Psi_i(\mathrm{FO}) = a_i \Psi^N(\mathrm{GS}). \tag{2}$$

In Eq. (2), a_i is an annihilation operator for the i-th orbital, where i is either O(1s) or C(1s), and Ψ^N(GS) is the N electron wavefunction for the GS. The physical meaning of Ψ_i(FO) is that, within the sudden approximation, SA, it is the wavefunction that is created at the instant of photoionization.[22] It was introduced to determine losses to satellites in the XPS spectra.[22,23] In the present case, we use Ψ(FO) to permit a decomposition of the BE's into contributions from initial state effects and final state effects. We stress that the Ψ_i(FO) in Eq. (2) does not have to be limited to a single configuration but it can be a fairly general CI wavefunction and, hence, it can include a rather broad range of many electron, or electron correlation effects. The only limitation in the definition of Ψ_i(FO) is that the i-th core electron cannot be correlated in the GS WF; however, this correlation is not included in the CAS(4,4) WF since only the π electron static correlation is treated.

For the energies, the expectation value of the energy of Ψ(FO) gives the FO energy of the core ionized molecule, E(FO) = $\langle\Psi(\mathrm{FO})|H|\Psi(\mathrm{FO})\rangle$ and the SCF energy of the variational solution for the N − 1 electron core ion, either HF or CAS(4,4), is E(SCF) = $\langle\Psi(\mathrm{SCF})|H|\Psi(\mathrm{SCF})\rangle$. The respective BE's, BE(FO) and BE(ΔSCF), are the differences between the appropriate ionic and GS energies. For simplicity, we have dropped the index i, indicating core-hole, in this discussion. The difference between BE(FO) and BE(ΔSCF),

$$E_R = \mathrm{BE(FO)} - \mathrm{BE}(\Delta\mathrm{SCF}), \tag{3}$$

defines the relaxation energy, E_R, where E_R must be ≥0 since it denotes the energy lowering due to the screening of the core-hole.[1] The CO molecule is placed along the z-axis with C at (0,0,0) and O at (0,0,1.128 Å). The experimental equilibrium[24] R(C–O) is used for all SCF and CAS calculations in order to be able to directly compare the SCF and CAS BE's without introducing effects due to using different R(C–O) for these two kinds of WF's.[3] It is appropriate to use the same R(C–O) for the GS and the core-hole states since the XPS process, neglecting vibrational excitations which may introduce a fine structure in the XPS,[25] is a vertical transition.[1] In order to allow a more nearly correct comparison to experiment, we have also estimated relativistic corrections to the directly calculated non-relativistic BE(ΔSCF) following the procedure that we have used earlier for the N(1s) BE's.[3] For the open shell atoms, C, with configuration $2p^2$, and O, with configuration $2p^4$, we have calculated total HF and Dirac-Hartree-Fock, DHF, energies for the average of configurations[26] of these open shell atoms. The relativistic calculations were based on 4 component spinors and included scalar as well as spin-orbit relativistic effects. The average of configuration HF and DHF energies were calculated for the GS and for the hole-states. The relativistic correction is the difference of the HF and DHF BE's. These corrections increase the calculated non-relativistic BE(ΔSCF) by 0.13 eV for C and 0.45 eV for O. The average of the configuration energies are used to avoid having to separate the relativistic corrections for the individual Russell-Saunders multiplets and J levels of the atoms; however, for these light atoms, we find that the corrections are quite similar for these different multiplets. The relativistic corrections obtained reflect only atomic effects but they should give us reliable estimates of the relativistic corrections for the CO BE(ΔSCF). To confirm that this procedure provides a very accurate estimate of the relativistic corrections to the O(1s) and C(1s) BE's, we have also determined BE's from relativistic DHF calculations for the CO molecule and compared them to non-relativistic BE's obtained with the same basis set. The relativistic BE's obtained from this direct procedure were identical, within 0.01 eV, to those obtained, as described above, using relativistic corrections from atomic calculations for C and O 1s ionizations.

The same C and O Cartesian Gaussian basis sets were used for all calculations. The exponents were taken from the 10s and 6p basis sets optimized by Duijneveldt[27] with a single d exponent of 0.8 (C) and 1.25 (O) added. The basis sets were not contracted except for the innermost 3s functions that were contracted to a single function leading to basis sets with 8s and 6p basis functions. The logic of using only minimal contractions was to allow the basis set to represent, with comparable quality, both the ground and the core-hole states.[2,3] To a good approximation, when an electron is removed from a core shell, the electrons see a nucleus with an effective charge that is larger by one; thus C with a 1s electron removed appears to be a N nucleus and O with a 1s electron removed appears to be a F nucleus. This is the equivalent core model proposed by Jolly.[28,29] It is necessary to use uncontracted or minimally contracted basis sets to have the necessary flexibility to accurately represent the orbitals for both the initial and the final, core-hole, configurations.[2,3] The HF WF's, the FO CAS WF's, and the orbital properties were calculated using the CLIPS suite of programs.[30] The CAS(4,4) WF's were computed using the CASSCF programs developed by B. Roos and P. E. M. Siegbahn at Lund and Stockholm.[14] The relativistic atomic and CO calculations were carried with the DIRAC program system.[31]

For the 1s-hole state CAS WF's, we took a precaution to avoid variational collapse to the lowest ionic state rather than to the core-level ionic state. This involved several pairs of steps of fixing, or freezing, a subset of the orbital space while the remaining orbitals were varied. In the first step, the single occupied 1s orbital was frozen as determined for the HF WF and the other orbitals were variationally optimized. In the second step of this pair, the occupied orbitals, both the active, 1π and 2π, and the inactive, doubly occupied σ, were frozen as determined in the first CASSCF step, and the singly occupied 1s orbital was allowed to mix with the virtual space. This pair of steps was repeated until there were no further changes in the CAS energies or orbitals; it was found that three pairs of steps were sufficient to obtain convergence to the full CASSCF solution.

III. RESULTS AND DISCUSSION

In Table I, the C(1s) and O(1s) BE(ΔSCF) for the SCF and CAS(4,4) WF's are compared with experiment. In this table, we also include the BE(ΔSCF) with a relativistic correction added of 0.13 eV for the C(1s) and 0.45 eV for the O(1s) BE's. These relativistic corrections were determined from calculations on the C and O atoms, see Sec. II, and include only atomic effects but they should be reliable estimates for the relativistic corrections for CO. The HF ΔSCF BE, with relativistic corrections, for O(1s) is as expected too small by 0.6 eV but the HF ΔSCF BE for C(1s) is too large by more than 1 eV, which is completely unexpected. This sign of the error for the C(1s) BE means that there is more correlation energy for the C(1s) core ionized state of CO^+ than there is for the neutral CO. As we noted in the Introduction, it is unexpected that a system with fewer electrons will have a larger correlation energy. In the following, we will show how this anomalous sign of the BE error can be explained by an important static correlation effect for the 10 valence electrons in the GS and the core-hole states that we study. Based on the equivalent core model,[28,29] it is an acceptable approximation to view CO^+ with a C 1s-hole as equivalent to NO^+ and to view CO^+ with a O 1s-hole as equivalent to CF^+.[1] An important near degeneracy effect for the 14 electron isoelectronic series is that involving excitations from 1π to 2π. When this near degeneracy is taken into account in a CAS(4,4) WF, we find that the predicted BE's for both C(1s) and O(1s) are both smaller than experiment, exactly as predicted and explained by Mulliken.[8] Also, the magnitudes of the errors of the CAS(4,4) BE's with the relativistic correction are substantially reduced to 0.33 eV for C(1s) and 0.32 eV for O(1s) indicating that we have included the key electron correlation effects with our treatment of the 1π-2π near degeneracy. In particular, once static correlation effects are included the errors of the O(1s) and C(1s) BE's, with a relativistic correction included, are almost identical. Thus, the remaining dynamical correlation effects will not introduce differential changes between the C(1s) and O(1s) BE's. Of course, the remaining error in these BEs should be accounted for by inclusion of dynamical correlation effects, which we do not consider since the static correlation reduces the errors in the BE(ΔSCF) and because the differential dynamical correlation effects between the O(1s) and C(1s) BE's are small. However, it still remains to understand the origin of the changes between the HF and CAS BE's.

TABLE I. Comparison of the ΔSCF C(1s) and O(1s) BE's obtained from HF and CAS wavefunctions with experiment where R(C–O) = 1.128 Å is the experimental r_e.[24] We also include the BE with a correction for relativistic effects, denoted the rows HF-rel and CAS(4,4)-rel; see text. An error with respect to experiment less than zero indicates that the calculated BE is less than the experimental XPS value. All BE's and errors are in eV.

	O(1s) BE - eV	Error	C(1s) BE - eV	Error
Experiment[a]	542.57 ± 0.03	…	296.24 ± 0.03	…
HF	541.55	−1.02	297.18	+0.94
HF-rel	542.00	−0.57	297.31	+1.07
CAS(4,4)	541.80	−0.77	295.78	−0.46
CAS(4,4)-rel	542.25	−0.32	295.91	−0.33

[a] See Ref. 33.

In order to understand the nature of the static correlation for the ground state of CO, we give, in Table II, the properties of the 1π and 2π orbitals and the total dipole moments, μ, for the HF and CAS WF's. The properties in Table II are the occupation number and the ⟨z⟩. Both the HF and CAS 1π orbitals are bonding and strongly polarized toward O, as

TABLE II. For the GS, HF, and CAS 1π and 2π orbital occupation numbers, N, and ⟨z⟩, in Å, with respect to the C atom at z = 0 and the O atom at z = +R(C–O); the difference in the total energy of the HF and CAS WF's is given as ΔE and the dipole moments, μ, are also given.

	1π		2π			
	N	⟨z⟩-Å	N	⟨z⟩-Å	ΔE(eV)	μ(D)[a]
HF	4.00	+0.862	…	…	…	−0.331
CAS(4,4)	3.91	+0.836	0.09	+0.469	2.08	+0.232

[a] Experimental μ(CO) = +0.110 D; see Ref. 24.

expected since O is an electron acceptor. As shown by the ⟨z⟩, the 1π center of charge is 75% of the way from C to O. The HF 1π has an occupation of 4 while the occupation of the CAS(4,4) 1π is reduced to 3.91 with 0.09 electrons occupying the 2π orbital. This orbital is anti-bonding between C and O and lies closer to C than O; the center of charge, ⟨z⟩ = 0.47, for the CAS 2π orbital is only 40% of the way from C to O. This occupation of the 2π orbital in the CAS(4,4) WF means that, in this WF, there is a motion of the center of electronic charge from O toward C. This motion of the center of electronic charge leads to a change in μ from −0.3 D for the HF WF to +0.2 D for the CAS WF. Both the HF and CAS WF's correctly show that μ(CO) is small, nearly zero, which is surprising especially considering the polar character of the CO bond. This polar character is shown, for example, by the derivative of μ at the equilibrium bond distance,[32] r_e which is 0.7 in units of electrons, consistent with a large negative charge on O. However, the sign of the HF dipole moment is incorrect, while the sign of the CAS(4,4) $\mu > 0$ is correct; the remaining small 0.1 D difference with experiment can be recovered when dynamic correlation effects are included. However, the 0.5 D change in the total dipole from the HF to the CAS(4,4) WF shows that there is a motion of charge from O towards C. This is fully consistent with our analysis of the occupation of the 2π orbital, where the ⟨z⟩ shows that it is closer to C than to O, in the CAS(4,4) WF. In order to have an indication of the magnitude of the motion of charge, the 0.5 D change in μ is equivalent to moving 0.1 electrons from the position of the O nucleus to the position of the C nucleus. While this motion is not especially large, it could lead to changes in the core-level XPS BE's.

The direction of the initial state effect of this charge motion can be seen from considerations of the electrostatics involved in moving the charge from O to C. From this motion, the O becomes somewhat less negatively charged and the C somewhat less positively charged. The electrostatic effect of a larger net charge, less negative or more positive, on an atom is to lead to an increase in the core-level BE's while a smaller net charge, less positive or more negative, leads to a decrease in the BE's; see Ref. 1 and references therein. Thus we would expect the motion of charge from the HF to the CAS WF's would decrease the initial state C(1s) BE because C has gained electrons, in the CAS(4,4) WF with respect to the HF WF, through the occupation of the 2π orbital. Furthermore, the motion of charge would increase the initial state O(1s) BE because O has lost electrons through the 2π occupation. The initial state change in the CAS(4,4) C(1s) BE is in the correct direction to change the sign of the error of the CAS(4,4) BE(ΔSCF) from being larger than experiment to smaller than experiment; see Table I. The initial state change in the CAS(4,4) O(1s) BE is in the correct direction to reduce the magnitude of the error of the HF BE(ΔSCF); see Table I.

In order to have a more complete understanding of the separation of the changes in BE's between the HF to CAS(4,4) WF's into contributions from initial and final state effects, we present additional information in Tables III and IV. In Table III, the initial state BE's, labelled BE FO, and the final state relaxation energies, E_R see Eq. (3), for the HF and CAS WF's are given. The changes from HF to CAS values of BE(FO) and E_R are also shown in Table III. For the calculation of the initial state CAS BE(FO), the GS CI expansion coefficients as well as the GS variational orbitals are used in the WF where the 1s electron is annihilated. In order to better understand the changes in E_R, we present in Table IV information on the CAS(4,4) WF's for the O(1s) and C(1s) hole states that parallels the information in Table II for the GS. In particular, we give the N(1π), N(2π), and ΔE for these CAS WF's; the differences in the occupation numbers, N, will help us understand the changes of E_R between the HF and CAS WF's. The data in Table III show that the direction of the changes of the BE(FO) is as expected from the electrostatic considerations discussed above. The CAS(4,4) O(1s) BE(FO) is 0.3 eV larger than the HF BE(FO) while the CAS(4,4) C(1s) BE(FO) is 0.75 eV smaller than the HF BE(FO). The magnitudes are not the same because the 1π and 2π orbitals have different spatial extents which change the potential of electrons in these orbitals at the respective nuclei. However, the changes in the C(1s) and O(1s) BE(FO) are both reasonably large and have exactly the direction expected on simple electrostatic considerations. On the other hand, the changes in the relaxation energy, E_R, between the HF and CAS C(1s) and O(1s) BE's differ by an order of magnitude; large for the C(1s) BE and small for the O(1s) BE. Before we consider these differences in the CAS E_R, we discuss how the initial and final state contributions to BE(ΔSCF) influence the C(1s) and O(1s) BE's. Since the relaxation energy, E_R, lowers the BE, a positive change in E_R for the CAS WF from the HF WF, Δ(CAS-HF) > 0 in Table III, means that the relaxation contributes to a lowering of the CAS BE(ΔSCF) with respect to the HF value. The total change in the CAS BE(ΔSCF) with respect to the HF value is given by

$$\Delta(\text{CAS-HF})[\text{BE}(\Delta\text{SCF})] = \Delta(\text{CAS-HF})[\text{BE(FO)}] - \Delta(\text{CAS-HF})[E_R]. \quad (4)$$

TABLE III. Initial state contributions to the O(1s) and C(1s) BE's of CO, BE(FO), and relaxation energies, E_R, for HF and CAS wavefunctions; all energies are in eV.

	O(1s)		C(1s)	
	BE(FO)	E_R	BE(FO)	E_R
HF	562.34	20.79	309.19	12.01
CAS(4,4)	562.64	20.84	308.44	12.66
Δ(CAS-HF)	+0.30	+0.05	−0.75	+0.55

TABLE IV. For the O(1s) and C(1s) states, HF and CAS 1π and 2π orbital occupation numbers, N, and the difference in the total energy of the HF and CAS WF's, ΔE, are given.

State		N(1π)	N(2π)	ΔE(eV)
O(1s)	HF	4.00	…	…
	CAS(4,4)	3.95	0.05	1.82
C(1s)	HF	4.00	…	…
	CAS(4,4)	3.81	0.19	3.48

This equality can be seen in the data presented in Table I and Table III. Thus for the O(1s) BE, the initial state contribution from Δ(CAS – HF)[BE(FO)], which raises the CAS BE, is slightly offset by the small final state contribution from Δ(CAS – HF)[E_R], which lowers the CAS BE. On the other hand for the C(1s) BE, the initial and final state contributions are additive and both act to lower the CAS BE(ΔSCF). Furthermore, they are of comparable magnitude; the final state contribution is over 70% of the initial state contribution. We may use the information on the CAS WF's in Tables I and IV to understand the large difference in the changes in the Δ (CAS-HF) values for E_R between the O(1s) and C(1s) hole state WF's. As we noted earlier, there are two contributions to E_R for the CAS WF's. One is from the orbital relaxation and the other is from the change in the importance of the configuration mixing of excitations from the HF reference configuration. That this mixing is different for the GS and the hole-states can be seen from the π occupation numbers, N(1π) and N(2π), for the CAS WF; see Tables II and IV. For the O(1s) CAS(4,4) WF the π static correlation is comparable to, but somewhat less important, than for the GS CAS(4,4) WF. The change in energy for the O(1s) CAS WF is 1.8 eV or 10% smaller than the 2.1 eV lowering of the GS total energy. Also the O(1s) CAS N(1π) = 3.95 is a bit closer to the HF value of 4.0 than is the GS CAS N(1π) = 3.91. The similar importance of the static correlation for the GS and the O(1s) CAS WF's suggests that the main relaxation from the FO WF is from the change in the orbital character with only a small contribution from the change in the CAS CI coefficients. This is fully consistent with a small Δ(CAS-HF) value for E_R of +0.05 eV; see Table III. The situation is quite different for the C(1s) CAS(4,4) WF where the π static correlation is significantly more important than for the GS; see Table I and Table IV. The change in energy for the C(1s) CAS WF is 3.5 eV or ∼65% larger than the lowering of the total energy of the GS. Similarly, the O(1s) CAS N(1π) = 3.8 is significantly smaller than the GS value of 3.9, directly showing the larger importance of the mixing of the 2π orbital in the CAS WF. Thus, the contribution of changes in the CI coefficients to the CAS E_R, as well as changes in the orbitals, will be large and it is no surprise that the O(1s) Δ(CAS – HF) value for E_R is an order of magnitude larger than the comparable value for the C(1s) hole state.

IV. CONCLUSIONS

We have investigated a physical mechanism that leads to HF XPS BE's being larger than observed XPS BE's. This direction of error is opposite to the general expectation that HF BE's will be smaller than experiment because the correlation error of HF WF is expected to be smaller for an N – 1 electron ion than for the N electron initial state. We have considered the case of CO where the HF O(1s) BE(ΔSCF), which includes initial state electrostatic and final state relaxation contributions, is as expected larger than the experimental XPS BE but where the HF C(1s) BE(ΔSCF) is ∼1 eV larger the XPS BE. We have shown that there is a static, near degeneracy correlation effect in the π space that changes the order of the error of the theoretical BE's so that both the O(1s) and C(1s) BE's are smaller than experiment. The static correlation involves introducing configurations with occupation $1\pi^{4-n}2\pi^{n}$ in addition to the HF configuration $1\pi^{4}2\pi^{0}$ within a complete active space, CAS, multi-configuration self-consistent field formulation where both the orbitals and the configuration mixing coefficients are variationally optimized. We have shown that, when corrections for relativistic effects are included, the errors of the O(1s) and C(1s) BE's are small, ∼0.3 eV, and almost the same. In addition, we have identified the physical reason for the initial state contribution to the BE's where the 1π and 2π near degeneracy is taken into account as arising from a motion of electronic charge from O to C. From simple electrostatic considerations, this motion of charge with respect to HF wavefunctions leads to an increase of the O(1s) BE and a decrease of the C(1s) BE with respect to the HF values. Furthermore, we have shown that the difference of the E_R for the CAS wavefunctions from the HF wavefunctions depends on whether the C(1s) or the O(1s) BE is considered. We have related this to the different extent of the static correlation for the GS and the O(1s) and C(1s) hole state CAS wave functions. The π correlation is similar for the GS and the O(1s) CAS(4,4) WF's and the CAS and HF E_R are quite similar. On the other hand, the π static correlation is significantly more important for the C(1s) CAS WF than for the GS WF. Thus for the O(1s) hole state, the CAS(4,4) E_R is larger than the HF E_R because, for the CAS case, the relaxation includes changes in the CAS CI coefficients as well as changes in the orbitals.

Although we have specifically investigated CO, our observations may have general validity in that errors of the HF core-level BE's compared with values from XPS measurements could identify cases where static correlation effects are important for the GS WF and properties. A cornerstone of our logic for the core level ionizations of light atoms in molecules is that the GS and the core-hole configurations are iso-electronic in the valence region where the effects of static correlation are treated. Thus if static correlation is important for the core-hole configurations, it will also be important, albeit perhaps with different magnitude, for the ground state configuration. If the HF BE(ΔSCF) is larger than experiment, this shows that correlation effects are larger for the N – 1 electron core-hole state than for the N electron GS. It is possible, perhaps even likely, that this difference of electron correlation will arise from static effects, at least this was the case for CO. On the other hand, if the HF BE(ΔSCF) is smaller than experiment by an amount much larger than average, as was the case for the O(1s) core-hole of CO, this is also an indication of possibly important static electron correlation effects. In this case the correlation effects are much smaller for the N – 1 electron core-hole state than for the N electron GS. Again, in this case, it is reasonable to suggest that the different extent of electron correlation could arise from static effects. An important caveat for the use of errors of the HF BE(ΔSCF) to identify cases where static correlation effects may be important is that suitably large basis sets with minimal contractions of the basis functions used to describe the core region should be used to calculate the WF's and the BE's. These are the basis sets used in the present work and in our prior studies of the 1s BE's of first row atoms in several molecules.[2–4]

In our application to CO, we have shown that the static correlation that makes the CAS BE(ΔSCF) smaller than experiment and reduces the magnitude of the error of the core-level BE's also reduces the error of the CO dipole moment and leads to a $\mu > 0$ in agreement with experiment. Our arguments about using the errors of HF BE(ΔSCF) to identify cases where a treatment of static correlation may be required can also be applied to our earlier analysis[2] of 19 N(1s) BE's in 17 different molecules. The errors of all the HF BE(ΔSCF) were <0 showing that the HF BE's were all less than experiment and, without the relativistic correction that was estimated to be 0.2 eV,[3] they were, in magnitude, ≤ 0.5 eV with only 6 outliers with larger errors.[2] For these outliers, it might be worthwhile to investigate whether static correlation effects might be important. Our arguments about the general utility of the errors of HF BE(ΔSCF) to identify the need to treat static electron correlation are speculative. However, to our knowledge, this is the first time that evidence has been presented to show that the errors of calculated HF core-level BE's may indicate that there are static correlation effects in the ground, initial state wavefunctions that need to be taken into account.

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[1] P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. **68**, 273 (2013).

[2] N. P. Bellafont, F. Illas, and P. S. Bagus, Phys. Chem. Chem. Phys. **17**, 4015 (2015).

[3] N. Pueyo Bellafont, P. S. Bagus, and F. Illas, J. Chem. Phys. **142**, 214102 (2015).

[4] N. Pueyo Bellafont, F. Viñes, and F. Illas, J. Chem. Theory Comput. **12**, 324 (2016).

[5] D. P. Chong, J. Electron Spectrosc. Relat. Phenom. **159**, 94 (2007).

[6] M. Segala, Y. Takahata, and D. P. Chong, J. Electron Spectrosc. Relat. Phenom. **151**, 9 (2006).

[7] D. P. Chong, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **116**, 1760 (2002).

[8] R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).

[9] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

[10] P. S. Bagus, R. Broer, and F. Parmigiani, Chem. Phys. Lett. **421**, 148 (2006).

[11] P. S. Bagus, R. Broer, and E. S. Ilton, Chem. Phys. Lett. **394**, 150 (2004).

[12] P. S. Bagus, R. Broer, and E. S. Ilton, J. Electron Spectrosc. Relat. Phenom. **165**, 46 (2008).

[13] P. S. Bagus, in *Proceedings of the International Symposium on X-Ray Spectra and Electronic Structure of Matter*, edited by A. Faessler and G. Wiech (Fotodruck Frank Ohg, Munich, West Germany, 1973), Vol. 1, p. 256.

[14] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. **48**, 157 (1980).

[15] I. N. Levine, *Quantum Chemistry* (Prentice-Hall, Upper Saddle River, NJ, 2000).

[16] F. Illas *et al.*, Chem. Phys. **107**, 361 (1986).

[17] O. Sinanoglu, Adv. Chem. Phys. **14**, 237 (1968).

[18] P. E. Siegbahn, *Methods in Computational Molecular Physics* (Springer, 1983), p. 189.

[19] J. Cioslowski, Phys. Rev. A **43**, 1223 (1991).

[20] P. Knowles, M. Schuetz, and H.-J. Werner, in *Modern Methods and Algorithms of Quantum Chemistry*, edited by J. Grotendorst (John von Neumann Institute for Computing, Juelich, 2000), Vol. 3, p. 97.

[21] E. Valderrama, E. V. Ludena, and J. Hinze, J. Chem. Phys. **110**, 2343 (1999).

[22] T. Aberg, Phys. Rev. **156**, 35 (1967).

[23] R. Manne and T. Åberg, Chem. Phys. Lett. **7**, 282 (1970).

[24] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules* (Van Nostrand, New York, 1979), Vol. 4.

[25] B. Kempgens *et al.*, J. Phys. B **30**, L741 (1997).

[26] L. Visscher *et al.*, Comput. Phys. Commun. **81**, 120 (1994).

[27] F. B. van Duijneveldt, IBM RJ94, 1971.

[28] W. L. Jolly, in *Proceedings of the International Conference on Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, Netherlands, 1972), p. 629.

[29] W. L. Jolly and D. N. Hendrickson, J. Am. Chem. Soc. **92**, 1863 (1970).

[30] 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.

[31] DIRAC, a relativistic *ab initio* electronic structure program, Release DIRAC08, 2008, written by L. Visscher, H. J. Aa. Jensen, and T. Saue, with new contributions from R. Bast, S. Dubillard, K. G. Dyall, U. Ekström, E. Eliav, T. Fleig, A. S. P. Gomes, T. U. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, P. Sałek, and J. Sikkema, http://dirac.chem.sdu.dk, 2008.

[32] R. A. Toth, R. H. Hunt, and E. K. Plyler, J. Mol. Spectrosc. **32**, 85 (1969).

[33] S. R. Smith and T. Darrah Thomas, J. Electron Spectrosc. Relat. Phenom. **8**, 45 (1976).