

# Approaching Multiplet Splitting in X-Ray Photoelectron Spectra by Density Functional Theory Methods: NO and O<sub>2</sub> molecules as examples

Carmen Sousa,<sup>a,\*</sup> Paul S. Bagus,<sup>b</sup> and Francesc Illas<sup>a</sup>

<sup>a</sup>*Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Catalonia, Spain*

<sup>b</sup>*Department of Chemistry, University of North Texas, Denton, TX 76203-5017, USA*

## Abstract

The ability of density functional theory (DFT) based methods to predict the multiplet splitting arising from the core hole ionization of molecules such as NO and O<sub>2</sub>, exhibiting an open shell ground state, is explored. In the NO molecule, N(1s) or O(1s) ionization leads to <sup>3</sup>Π and <sup>1</sup>Π multiplets whereas for O<sub>2</sub>, the presence of an O(1s) core hole leads to doublet and quartet multiplets with distinct BEs. Multiplet splittings obtained using different exchange-correlation functionals show an overall good agreement with experiment and minor variations within the functionals studied when spin contamination resulting from unrestricted DFT calculations is accounted for.

**Keywords:** Core Levels, Binding Energies, Multiplet Splitting, Broken Symmetry Approach, Density Functional Theory

\*corresponding author: [c.sousa@ub.edu](mailto:c.sousa@ub.edu) (C. Sousa)

## I. Introduction

Prediction of electron binding energies (BEs) by means of *ab initio* computational methods has been shown to be a useful tool to help in the interpretation of X-Ray photoelectron spectra, XPS, in a wide range of materials, from gas phase molecules, nanomaterials, to condensed phase systems, like surfaces and bulk solids [1,2]. The well-known *ab initio* Hartree-Fock (HF) method has been extensively used to compute core hole BEs [1,2]. In this approach, the BE of interest, defined as  $BE = E^{N-1}(\text{final}) - E^N(\text{initial})$ , is obtained by computing the energy difference of the initial  $N$ -electron state and the final  $N-1$  electron ionized state with orbitals that have been variationally optimized through a self-consistent field (SCF) procedure. This approximation is usually referred to as  $\Delta$ SCF and accounts for the average relaxation effects of the electronic structure of the system in response to the presence of the core hole. Note also that within the HF method and for closed shell systems, the Koopmans' theorem allows one to obtain a frozen orbital (FO) BE by taking  $BE = -\epsilon$ , where  $\epsilon$  is the corresponding orbital energy of the neutral molecule; this FO BE does not take into account the relaxation, or response, of the valence electrons to the core-hole. For core levels, the FO BE is a poor approximation to the  $\Delta$ SCF BE but, however, it does provide unique information which makes it possible to distinguish initial state, chemical bonding, from final state, screening, effects on the BE [3]. The relationship given above is exact for systems with a closed shell ground state; for systems with an open shell ground state, such as NO ( $^2\Pi$ ) and O<sub>2</sub>( $^3\Sigma$ ),  $BE(\text{FO}) = -\epsilon$  is the weighted average of the FO BEs to the different final state multiplets; see Ref. [1] and references therein. To avoid the confusion about the final state multiplicity, which arises if one attempts to use KT for open shell systems, we have computed the energy of the ionized state with the orbitals/density of the neutral system, but with one core electron less.

The BEs computed by means of the HF ( $\Delta$ SCF) approach include all possible effects that are taken into account at this level of theory; i.e. neglecting electron correlation. While relativistic

effects can be taken into account with Dirac Fock and Dirac DFT methods [4], we have chosen to use non-relativistic since our concern is for the light atoms N and O. It is important to note that HF methods, since they take into account the combination of determinants needed to describe the orbital and spin angular momentum coupling of open shell electrons, allow directly for the calculation of the multiplet splittings. This is not the case for DFT methods, which are inherently based on the use of a single Kohn-Sham determinant. Indeed, the point of this paper is to show the use of a methodology to work around this limitation of DFT.

It is common to use  $\Delta$ SCF values to obtain accurate values of BEs since they include final state effects, as opposite to those obtained through the FO, which by neglecting electronic relaxation in response to the presence of the core hole include initial state effects only [1]. However, the distinction of initial state and final state effects is extremely important since it provides a detailed, fundamental understanding of the physical and chemical origins of changes in the BEs between different elements. In this context, it is worth recalling the study of BE shifts between pyridine and pyrrole [5] where the comparison of FO and  $\Delta$ SCF BEs made it possible to understand the correct origin of the BE shifts between these molecules. Within the HF method, calculated  $\Delta$ SCF BEs are quite accurate but, as mentioned above, while relativistic effects can be included at this level of theory, electron correlation is still lacking. The latter can be accurately accounted for by means of Configuration Interaction, CI, wave functions. In particular, with CI methods it is possible to make a distinction between static and dynamic correlation effects; with this distinction, it is quite possible that the critical electron correlation effects for the calculation of accurate BEs will be included with the relatively small CI descriptions that treat only static correlation [6,7]. While for large systems, CI calculations may become demanding, there are other ab initio methods such as Quantum Monte Carlo that are able to handle rather large systems [8,,10] and that could be adapted to study core-level ionization and excitation.

An alternative approach is provided by Density Functional Theory (DFT) based methods, as long as the exchange-correlation functional chosen is a sufficiently good approximation to the exact, unknown, one. Indeed, recent studies showed the ability of DFT based methods to predict core level BEs of closed shell molecules containing light atoms with an acceptable accuracy [11,,14]. It is the concern of this paper to examine the extension of DFT methods for core-level BEs to open shell molecules. Specifically, we are interested in the capability of DFT methods to properly describe the core hole BEs of molecules featuring an open shell ground state and, more specifically, the corresponding splitting between the different spin-states arising from the ionization process. To this end, we have chosen to study the NO and O<sub>2</sub> diatomic molecules featuring doublet and triplet ground state, respectively. In a first step, we focused on the N and O 1s core level BEs of the NO molecule. Since the NO ground state is a doublet state arising from the  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1$  electronic configuration, ionization of either N(1s) or O(1s) gives rise to two different electronic states with singlet (<sup>1</sup>Π) or triplet (<sup>3</sup>Π) spin coupling between the core hole state and the valence  $2\pi$  antibonding singly occupied orbital, respectively. Likewise, the ground state of the oxygen molecule is a triplet coming from the double occupation of the  $2\pi^*$  valence orbital and ionization of the O(1s) electron from either the O(1s)  $\sigma_g$  or the O(1s)  $\sigma_u$  orbitals leads to two different electronic states, a doublet (<sup>2</sup>Σ) and a quartet (<sup>4</sup>Σ).

Approaching multiplet splitting in DFT based calculations is possible by properly averaging the energy of different Kohn-Sham determinants as shown in the earlier work of Bagus and Bennett [15] for the SCF- $X\alpha$  and popularized through the so-called sum rule of Ziegler, Rauk and Baerends [16]. The latter has been used to estimate the energy of atomic multiplets, which is a necessary ingredient, not always taken into account, to properly compute atomization energies. A similar strategy, often denoted as the broken symmetry approach, has been broadly used to estimate singlet-triplet splitting in organic radicals [17,18], inorganic dinuclear complexes [19,20] and is the basis for

the DFT study of magnetic coupling in solids [21]. Not surprisingly, calculated values strongly depend on the employed DFT method and special care is needed to deduce the singlet-triplet splitting from the energies corresponding to the (approximate) triplet and the broken-symmetry Kohn-Sham determinants [22]. The performance of this computational approach to the singlet-triplet splitting in multiplets related to core level ionization is so far unknown and shedding light on this aspect is the main goal of the present work. To this end, the energy of the  $^1\Pi$  and  $^3\Pi$  multiplets for the N(1s) and O(1s) ionized NO molecule and the  $^2\Sigma$  and  $^4\Sigma$  multiplets originated from the O(1s) ionized O<sub>2</sub> molecule, have been calculated by means of DFT based methods with HF calculations added for comparison; in both cases a  $\Delta$ SCF formalism is used. Results show that, while the resulting BEs depend on the chosen DFT method, in line with previous work, the calculated multiplet splittings show a satisfactory agreement with experiment and are less dependent on the DFT method, as long as the low spin state energies are corrected so as to properly represent singlet and doublet states by removing the spin contamination from unrestricted DFT.

## II. Computational Information

The N(1s) and O(1s) core level BEs of the NO molecule were obtained from spin and symmetry restricted HF calculations (ROHF) in the framework of the  $\Delta$ SCF approach; this is by computing the energy difference between the ionized core-hole, either  $^3\Pi$  or  $^1\Pi$  state, and that of the ground state of  $^2\Pi$  symmetry. Similarly, for the oxygen molecule, the O(1s) core-hole gives rise to two ionized states,  $^4\Sigma$  or  $^2\Sigma$ , and the corresponding BEs are computed with respect to the  $^3\Sigma$  ground state. Here, both, ROHF and UHF formalisms have been used to provide a more direct link to the DFT based calculations where the high (HS) and low (LS) spin unrestricted states are used to approach the corresponding multiplets with the necessary caution to restore the spin symmetry [23], as described more in detail below. One must also note that, depending on whether the core electron

is removed from the  $1\sigma_g$  or  $1\sigma_u$  molecular orbital, final  $^4\Sigma$  or  $^2\Sigma$  states with “g” or “u” symmetry emerge. However, the energy difference between “g” or “u” states is 0.05 eV for the quartet and 0.01 eV for the doublet [24]. In the view of the very small splitting, the “g” or “u” symmetry of the final state will not be further considered. In effect, the spatially localized solutions that we use for  $O_2$  can be viewed as being a suitable sum of the g and u multiplets or alternatively one can form the g or u multiplets by taking sums of the localized solutions [25].

All calculations were carried out in a non-relativistic framework. Both HF and DFT calculations were carried out using the near-HF uncontracted (14s,9p) primitive Gaussian Type Orbitals (GTO) basis set reported by Partridge [26] augmented by a single polarization d function with exponents of 1.0 and 1.2 for N and O, respectively. This large basis set assures the required flexibility to properly describe both the initial state and the final core ionized system. To allow for better comparison, all calculations were performed at the experimental equilibrium distance, 1.151 Å for NO and 1.207 Å for  $O_2$ .

Following previous work for the CO molecule [14], ten different exchange-correlation functionals representative of the various families were selected. The GGA functionals chosen are PBE [27] and BLYP [28,29], the meta-GGA ones are TPSS [30] and RevTPSS [31], whereas the hybrid GGA functionals selected are B3LYP [29,32], PBE0 [33] and SOGGA11-X [34] with 20, 25 and 35.42% of exact Fock exchange, respectively. Two hybrid meta-GGA functionals were also taken into consideration these are the TPSSh [35] and M06 [36] including 10 and 27% of Fock exchange. Finally, we consider the M11 range-separated hybrid functional [37], with exact exchange varying from 42.8% in the short-range to 100% in the long-range interelectronic separation.

In the DFT based calculations for NO, the triplet state is represented by a Kohn-Sham determinant with two unpaired electrons with parallel oriented spin (*i.e.* the HS state) and the

energy of the open shell singlet (*i.e.* the LS state) is derived from a broken symmetry (BS) solution. For O<sub>2</sub>, the quartet state correspond to a single Kohn-Sham determinant with three unpaired parallel oriented electrons coming from a  $1\sigma^1 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 (2\pi_x)^1 (2\pi_y)^1$  electron configuration while the doublet state results from the coupling of two spin parallel oriented electrons in the  $2\pi^*$  orbitals with an electron in the core  $1\sigma$  orbital. Neither of these spin unrestricted Kohn-Sham determinants corresponds to a spin eigenfunction [21,22,23,38] even if, for the highest spin component of the triplet and quartet states, the corresponding configuration state function (CSF) can be described by a single Slater determinant. Consequently, for these HS states, spin contamination is usually small (see Tables S1 and S2 in the Supporting Information) and the energies obtained by these solutions are commonly accepted to be sufficiently accurate although a rigorous proof is lacking. Likewise, the effect that the small spin contamination on the HS state may have in the resulting multiplet splitting is unknown; in the following, it is assumed to be negligible. On the other hand, the Kohn-Sham determinants aimed at describing the open shell singlet and doublet electronic states, which strictly speaking require a CSF involving various Slater determinants, show a large spin contamination by higher spin states. The open shell singlet in NO is mainly contaminated by the triplet state and the doublet state in O<sub>2</sub> by the quartet state. Although the energies obtained by the broken symmetry approach are often used to describe different spin states, a more reliable estimation of the energy can be obtained by applying the formula proposed by Yamaguchi [39,40,41], a variant of the Noodleman [42] approach aimed to remove spin contamination and thus to restore spin symmetry [23,38]. Following this procedure, the corrected energy of the singlet state can be obtained from Eq. (1)

$$E_S = \frac{2(E_{BS} - E_T)}{\langle S_T^2 \rangle - \langle S_{BS}^2 \rangle} + E_T \quad (1)$$

where  $E_S$ ,  $E_T$  and  $E_{BS}$  are the energy of the singlet, triplet and BS solution, respectively, as shown for the case of organic diradicals [43]. The denominator contains the difference between the expectation value of the square of the total spin operator for the triplet and the BS solutions as obtained in the corresponding DFT calculation. In a similar way, the decontaminated energy for the doublet can be expressed as follows:

$$E_D = \frac{\langle S_{BS}^2 \rangle - 0.75}{\langle S_Q^2 \rangle - \langle S_{BS}^2 \rangle} (E_{BS} - E_Q) + E_{BS} \quad (2)$$

Here  $E_D$ ,  $E_Q$  and  $E_{BS}$  are the energy of the doublet, quartet and BS solution for the doublet state, respectively, and  $\langle S^2 \rangle$  correspond to the expectation value of the square of the total spin operator for each of these states.

Most of the HF and all DFT calculations were carried out with the GAMESS-06 program [44]. The ROHF calculations for the O(1s) core hole in O<sub>2</sub> have been carried out using the MOLCAS code [45].

### III. Results and discussion

A summary of N(1s) and O(1s) core level BEs for the two possible final states,  $^3\Pi$  and  $^1\Pi$ , as predicted by  $\Delta$ SCF calculations applied to either HF or DFT based methods are reported in Tables I and II and compared to experiment. For the  $^1\Pi$  state, the BE is computed through the BS approach and making use of Eq. 1 to decontaminate the BS solution. Indeed, the expectation value of the square of the total spin operator for the BS open-shell singlet is far from the expected value of 0, being slightly larger than 1.0, which is an indication that the BS solution has an important contribution of the low-lying triplet state. Instead, the doublet ground state and the triplet ionized state exhibit expectations values of the spin operator very close to the theoretical expected values of 0.75 and 2.0, respectively.



For the BEs, an accurate comparison to experiment requires including the contribution of relativistic effects, even when these effects are not especially large in light elements. These can be estimated by means of 4-component Dirac-Hartree-Fock calculations, which allows for scalar and spin-orbit relativistic effects. Hence, the N(1s) and O(1s) BEs in the NO molecule are computed for the average of configurations of the initial  $^2\Pi$  and final ionized states, neglecting the relativistic contribution to the multiplet splitting, which is very small. For the N(1s) core hole in NO, relativistic effects increase the HF  $\Delta$ SCF BEs by 0.25 eV. For the O(1s) core hole in the NO molecule, the BE is estimated to increase by 0.47 eV. This value is similar to that computed previously for the O(1s) BE in an isolated O atom, 0.45 eV. This atomic relativistic correction for the O(1s) has been used in a previous study of the CO molecule [6] and has also been applied to the O(1s) BE of the oxygen molecule in the present work. The fact that the relativistic contribution to the O(1s) BE in NO and atomic O almost coincide is consistent with the physical fact that this effect is essentially atomic in nature. These corrections, although obtained from relativistic Dirac-HF calculations, have also been applied to the BEs obtained by DFT methods.

Tables I and II report non-relativistic  $\Delta$ SCF BEs obtained by either HF and DFT for the N(1s) and O(1s) core holes, respectively. The values in parentheses correspond to the error with respect to experiment including the relativistic corrections commented above. A close inspection of these tables shows that the ROHF BEs for the O(1s) core hole in NO are around 0.5 eV below the corresponding experimental values of 543.1 and 543.6 for the  $^3\Pi$  and  $^1\Pi$  states [46]. This is to be expected since the contribution of electron correlation to the total energy has to be larger for the initial N electron state than for the final N-1 electron ionized state, therefore HF BE( $\Delta$ SCF) values are expected to be smaller than those provided by XPS experiments. However, for the N(1s) the HF BEs of the  $^3\Pi$  and  $^1\Pi$  hole states are around 1.4 eV larger than experiment. In a previous work [7], this effect has been definitively ascribed to the lack of many-body effects involving near-

degeneracies of various orbitals that can contribute appreciably to the BE. These electron correlation effects, described as non-dynamic (static) or molecular correlation effects, can be taken into account by multireference wave functions, for instance within the Complete Active Space SCF (CASSCF) approach. Indeed, including these many body effects leads to N(1s) BEs in NO slightly below the experimental values [7].

Concerning the values of the N(1s) and O(1s) BEs within the functionals analyzed in this work, one can observe that, in general, although the values are qualitatively correct, the error with respect to experiment fluctuates depending on the particular functional chosen, *i.e.* there is no common trend within a given family of exchange-correlation functionals. Notice that correcting the BS open-shell singlet state by the decontamination procedure (Eq. 1) improves the BEs values of the  $^1\Pi$  states in NO by 0.5-0.8 eV for the N(1s) ionization, depending on the specific functional, and by 0.2-0.3 eV for the O(1s) core hole. This contribution has an important effect on the multiplet splittings as will be discussed later.

The experimental multiplet splitting between the  $^3\Pi$  and  $^1\Pi$  core hole states in NO is 1.4 eV for the N(1s) core hole and 0.5 for the O(1s) core hole states [46,47]. The larger splitting for N(1s) can be understood from the interaction between the N(1s) core hole with the  $2\pi^*$  orbital, which being mainly centered on the N atom is larger than in the case of the O(1s) core hole. Note also that both multiplet splittings are well reproduced in the HF calculations, which comes from the fact that electron correlation effects in the  $^3\Pi$  and  $^1\Pi$  are essentially the same [1,3]. Hence, a prediction of very accurate values of the singlet-triplet splitting does not necessarily imply an equally accurate estimate of the individual  $^3\Pi$  and  $^1\Pi$  BEs.

For the N(1s) core hole, the values of the singlet-triplet splitting computed by various exchange-correlation functionals show a remarkable dispersion, with values between 1.0 and 1.6 eV (experimental value 1.4 eV). For the O(1s) core hole, the computed  $\Delta(^1\Pi-^3\Pi)$  values are in good

agreement with experiment, with errors within  $\pm 0.1$  eV. Note, however, that these values correspond to the spin-corrected energies for the  $^1\Pi$  state, the BS solution leading to multiplet splittings much too low compared to experiment. Hence, decontamination of the BS solutions in unrestricted DFT methods turns out to be essential to properly account for multiplet splittings derived from XPS experiments.

In Tables S3 and S4 of the Supporting Information, results from HF frozen orbital, predicted BEs are included for comparison. The FO BEs, together with the  $\Delta$ SCF BEs, calculated by each of the density functionals are compiled in Tables S3 and S4, for N(1s) and O(1s), respectively. The difference between the HF BEs computed by FO and by  $\Delta$ SCF calculations provides the relaxation energy due to the molecular orbital relaxation in response to the creation of a 1s core hole. The relaxation energy is 16.40 and 16.29 eV for the  $^3\Pi$  and  $^1\Pi$  N(1s) states, respectively, and 20.91 and 21.16 eV for the O(1s)  $^3\Pi$  and  $^1\Pi$  ones. However, in DFT, the difference between the  $\Delta$ SCF and FO BEs does not only account for molecular orbital relaxation due to the ionization, but also includes the differential contribution of exchange and electron correlation in both states as approximately included by each functional. In any case, the difference between the  $\Delta$ SCF and FO BEs slightly varies depending on the particular functional, with mean values of 16.8 and 16.6 eV for the  $^3\Pi$  and  $^1\Pi$  N(1s) core hole states, respectively, and of 20.8 and 21.0 eV for the  $^3\Pi$  and  $^1\Pi$  states of the O(1s) ones. By comparing the relaxation energy obtained by HF and DFT calculations, it can be noticed that the difference in the relaxation energy for the N(1s) hole states is larger than for the O(1s) ones providing a crude indication that some of the exchange-correlations functionals seem to include some non-dynamic electron correlation. Nevertheless, both HF and DFT relaxation energies show comparable magnitudes denoting that the main final state contribution is due to orbital relaxation and not to the differential electron correlation effects that are implicitly (and uncontrollably) taken into account by the exchange-correlation functional.

Table III summarizes the results for the O(1s) core hole ROHF, UHF and DFT  $\Delta$ SCF BEs for the O<sub>2</sub> molecule. As described before, ionization of a 1s core electron in molecular oxygen gives rise to two different hole states,  $^2\Sigma$  and  $^4\Sigma$ . Here, it is important to remark that the BEs reported on Table III have been calculated in a localized molecular orbital representation, i.e., the core hole is localized in one of the two oxygen atoms [47]. The relation between localized and delocalized single core holes in homonuclear diatomic molecules has been studied previously and generated some controversy [48,50]. Nevertheless, it is clear that, in the Born-Oppenheimer approximation, all electronic states of any molecule must fulfill the symmetry requirements; i.e. the exact wavefunction will exhibit the proper symmetry. In this sense, the localized solution just provides a reasonable approximation and the full symmetry can be restored by means of a non-orthogonal configuration interaction mixing the two localized solutions as discussed by Broer and Nieuwpoort [25]. For the purpose of the present work, the localized solution is appropriate enough.

For comparison purposes, the HF calculations for the O<sub>2</sub> molecule have been performed within the restricted (ROHF) and unrestricted (UHF) approximations. For the  $^4\Sigma$  state, the value of the ROHF BE is around 0.15 eV larger than the UHF BE obtained from the HS state. This difference can be ascribed to the inclusion of some electron correlation through the spin polarization in the unrestricted calculations albeit at the price of introducing spin contamination as well. For the UHF BS state, correcting for the spin contamination so as to approach the proper  $^2\Sigma$  solution, increases the BE by 0.34 eV, from 542.60 to 542.94 eV. The corresponding BE computed by ROHF calculations lies at 542.70 eV, in between the two values, indicating that the expression applied to correct the spin contamination is appropriate. Again, one must recall that UHF introduces some electron correlation so that ROHF and spin projected UHF are not totally comparable.

The results obtained by DFT methods for the O<sub>2</sub> molecule mainly corroborate the trend found for the O(1s) core hole in the NO molecule. The  $^4\Sigma$  hole state is described by the BS

approach as a single determinant with three unpaired electrons with an expectation value of the square of the total spin operator slightly higher than the assumed value of 3.75 as shown in Table S2 for each of the functionals explored. The resulting BEs are lower than experiment, with deviations ranging from 0.1 eV to more than 1 eV depending on the specific functional. When the 1s core hole couples to the triplet coupled valence  $2\pi^2$  electrons, giving rise to an open-shell doublet state,  $^2\Sigma$ , the BS solution turn out to be contaminated by quartet states with expectation values of the square of the total spin operator larger than 1.75 instead of the expected 0.75 value. In Table III, the BEs obtained directly by the BS approach or by applying the Yamaguchi correction (Eq. 2) are displayed. As it was found for the NO molecule, the values of the BE become closer to experiment when the energy of the BS solution is only partly corrected by the approximate way to (partially) remove spin contamination. The differences in the  $^2\Sigma$  BEs between these two approaches are 0.3-0.4 eV, depending on the functional. The BEs computed using the decontaminated energy for the doublet state show a variable precision relying on the functional. However, for most of the functionals, the errors in the  $^4\Sigma$  and  $^2\Sigma$  BEs cancel out and the final  $^2\Sigma - ^4\Sigma$  splitting is in general within 0.2 eV accuracy.

#### IV. Conclusions

The ability of various computational DFT based methods to properly describe the N(1s) and O(1s) BEs and multiplet splittings in the NO and O<sub>2</sub> open shell molecules has been assessed.

Ionization of both N(1s) and O(1s) core levels in NO results in  $^3\Pi$  and  $^1\Pi$  final multiplets with a given multiplet splitting whereas for the oxygen molecule, O(1s) ionization leads to two different multiplets,  $^2\Sigma$  and  $^4\Sigma$ . The HF method provides a rigorous representation of the symmetry

of the multiplets resulting from each core ionization, and a good description of the energy separation corresponding to these multiplet splittings.

The DFT based methods explored do not provide a rigorous representation of the final states as they need to rely on spin unrestricted approaches and broken symmetry solutions. In spite of the lack of theoretical rigor, the broken symmetry approach applied to DFT based methods provides a fairly accurate estimate of the multiplet splittings provided the approximate energy of the open-shell singlet and doublet multiplets is obtained by removing spin contamination. Despite the rather accurate estimate of each multiplet splitting, the behavior of the different groups of functionals in approaching core hole BEs is unpredictable and exhibits an erratic behavior, in the line of previous findings.<sup>14</sup>

The present study shows that the energy splitting of multiplets emerging in XPS experiments can be approached by DFT methods based on broken symmetry solutions, on the condition that corrections to avoid spin contamination in unrestricted DFT calculations are made.

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**Table I.** N(1s) core level binding energies (BE) for the NO molecule as obtained from  $\Delta$ SCF calculations using ROHF and various DFT based methods. Note that for the HF calculations the final state has the appropriate symmetry whereas in the DFT based calculations the HS and BS solutions have been used to approach each multiplet. In the case of the BS, the BEs are obtained from the broken symmetry solution and applying the correction of Eq. 1 (see text). In parentheses, the difference with respect to experiment including the Dirac HF relativistic correction of 0.25 eV in the BEs (see text). All energy values are in eV.

| Final State             | $^3\Pi$        | $^1\Pi$       |                | $\Delta(^1\Pi - ^3\Pi)$ |       |
|-------------------------|----------------|---------------|----------------|-------------------------|-------|
| Experiment <sup>a</sup> | 410.1          | 411.5         |                | 1.4                     |       |
| ROHF                    | 411.26 (1.41)  | 412.60 (1.35) |                | 1.34                    |       |
| DFT                     | HS             | BS            | Eq. 1          | BS                      | Eq. 1 |
| PBE                     | 409.34 (-0.51) | 409.92        | 410.50 (-0.75) | 0.58                    | 1.16  |
| BLYP                    | 410.21 (0.36)  | 410.71        | 411.21 (-0.04) | 0.50                    | 1.00  |
| TPSS                    | 410.19 (0.34)  | 410.84        | 411.48 (0.23)  | 0.65                    | 1.29  |
| RevTPSS                 | 410.37 (0.52)  | 411.09        | 411.80 (0.55)  | 0.72                    | 1.43  |
| PBE0                    | 409.88 (0.03)  | 410.52        | 411.17 (-0.08) | 0.65                    | 1.29  |
| B3LYP                   | 410.43 (0.58)  | 411.00        | 411.57 (0.32)  | 0.57                    | 1.14  |
| SOGGA11-X               | 410.27 (0.42)  | 411.07        | 411.86 (0.61)  | 0.80                    | 1.58  |
| TPSSh                   | 410.32 (0.47)  | 410.99        | 411.65 (0.40)  | 0.67                    | 1.33  |
| M06                     | 409.84 (-0.01) | 410.58        | 411.36 (0.11)  | 0.74                    | 1.52  |
| M11                     | 410.96 (1.11)  | 411.60        | 412.23 (0.98)  | 0.64                    | 1.27  |

<sup>a</sup>Ref. 46

**Table II.** O(1s) core level binding energies (BE) for the NO molecule as obtained from  $\Delta$ SCF calculations using ROHF and various DFT based methods. Note that for the HF calculations the final state has the appropriate symmetry whereas in the DFT based calculations the HS and BS solutions have been used to approach each multiplet. In the case of the BS, the BEs are obtained from the broken symmetry solution and applying the correction of Eq. 1 (see text). In parentheses, the difference with respect to experiment including the Dirac HF relativistic correction of 0.47 eV in the BEs (see text). All energy values are in eV.

| Final State             | $^3\Pi$        | $^1\Pi$        |                | $\Delta(^1\Pi - ^3\Pi)$ |       |
|-------------------------|----------------|----------------|----------------|-------------------------|-------|
| Experiment <sup>a</sup> | 543.1          | 543.6          |                | 0.5                     |       |
| ROHF                    | 542.10 (-0.53) | 542.58 (-0.55) |                | 0.48                    |       |
| DFT                     | HS             | BS             | Eq. 1          | BS                      | Eq. 1 |
| PBE                     | 541.92 (-0.71) | 542.14         | 542.37 (-0.76) | 0.22                    | 0.45  |
| BLYP                    | 542.73 (0.10)  | 542.94         | 543.15 (0.02)  | 0.21                    | 0.42  |
| TPSS                    | 542.73 (0.10)  | 542.97         | 543.22 (0.09)  | 0.25                    | 0.50  |
| RevTPSS                 | 542.99 (0.36)  | 543.26         | 543.54 (0.41)  | 0.27                    | 0.55  |
| PBE0                    | 542.14 (-0.49) | 542.37         | 542.61 (-0.52) | 0.24                    | 0.47  |
| B3LYP                   | 542.64 (0.01)  | 542.86         | 543.09 (-0.04) | 0.23                    | 0.45  |
| SOGGA11-X               | 542.42 (-0.21) | 542.71         | 543.01 (-0.12) | 0.29                    | 0.59  |
| TPSSh                   | 542.73 (0.10)  | 542.98         | 543.23 (0.10)  | 0.25                    | 0.50  |
| M06                     | 542.23 (-0.40) | 542.47         | 542.72 (-0.41) | 0.24                    | 0.49  |
| M11                     | 543.28 (0.65)  | 543.49         | 543.70 (0.57)  | 0.21                    | 0.42  |

<sup>a</sup>Ref 46



**Table III.** O(1s) core level binding energies (BE) for the O<sub>2</sub> molecule as obtained from  $\Delta$ SCF calculations using ROHF, UHF and various DFT based methods. Note that for the ROHF calculations the final state has the appropriate symmetry whereas in the UHF and DFT based calculations the HS and BS solutions have been used to approach each multiplet. In the case of the BS, the BEs are obtained from the broken symmetry solution and applying the correction of Eq. 2 (see text). In parentheses, the difference with respect to experiment including the Dirac HF relativistic correction of 0.45 eV in the BEs (see text). All energy values are in eV.

| Final state             | $^4\Sigma$     | $^2\Sigma$     |                | $\Delta(^2\Sigma - ^4\Sigma)$ |       |
|-------------------------|----------------|----------------|----------------|-------------------------------|-------|
| Experiment <sup>a</sup> | 543.55         | 544.47         |                | 0.92                          |       |
| ROHF                    | 542.09 (-1.01) | 542.70 (-1.32) |                | 0.61                          |       |
| UHF/DFT                 | HS             | BS             | Eq. 2          | BS                            | Eq. 2 |
| UHF                     | 541.93 (-1.17) | 542.60         | 542.94 (-1.08) | 0.67                          | 1.01  |
| PBE                     | 541.89 (-1.21) | 542.59         | 542.95 (-1.07) | 0.70                          | 1.06  |
| BLYP                    | 542.76 (-0.34) | 543.40         | 543.72 (-0.30) | 0.64                          | 0.97  |
| TPSS                    | 542.73 (-0.37) | 543.48         | 543.86 (-0.16) | 0.75                          | 1.13  |
| RevTPSS                 | 542.97 (-0.13) | 543.81         | 544.23 (0.21)  | 0.84                          | 1.26  |
| PBE0                    | 542.18 (-0.92) | 542.91         | 543.28 (-0.74) | 0.73                          | 1.10  |
| B3LYP                   | 542.72 (-0.38) | 543.41         | 543.76 (-0.26) | 0.69                          | 1.04  |
| SOGGA11-X               | 542.53 (-0.57) | 543.36         | 543.77 (-0.25) | 0.82                          | 1.24  |
| TPSSh                   | 542.76 (-0.34) | 543.52         | 543.90 (-0.12) | 0.76                          | 1.14  |

<sup>a</sup>Ref. 46

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