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Functional dependence of core-excitation energies

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We examine in depth the functional dependence of computed core-electron binding and excitation energies based on a total-energy difference approach within Kohn-Sham density functional theory. Twenty-seven functional combinations were studied using a database of reliable experimental data on 18 molecules. The computed core-electron binding energies are largely dependent on the choice of exchange functional. The term value of the first resonant excited state and energy differences between the lowest core-excited states are, however, quite insensitive to the choice of functionals since the errors due to the core-region cancel out. Using these results we define a different exchange functional, which mixes two functionals designed by Perdew and Wang (PD86 and PD91), with the best results for both excitation and binding energies obtained for a mixing ratio 60:40 between these. We also reexamine the relativistic corrections for inner-shell excitations. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1809610]

I. INTRODUCTION

Recent progress in spectroscopic techniques for the soft x-ray region using synchrotron radiation enables us to examine in detail the electronic structure of molecules as well as the chemical reactions induced by inner-shell excitations.[1–5] Combining spectroscopic techniques such as x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy (XPS), x-ray emission spectroscopy, and Auger electron spectroscopy, we can experimentally through core excitation obtain the electronic structure as well as dynamical information for molecules in the gas phase, surface adsorbed systems,[4] and in the liquid phase.[6] Especially, the core-electron binding energy (CEBE) is an important physical quantity and the chemical shift of core ionization potentials formed the basis for the notion of ESCA, electron spectroscopy for chemical analysis.[7,8]

For the last decade, theoretical techniques to calculate core-electron binding energies have been developed by several groups.[9–18] Especially methods based on density functional theory (DFT) provide sufficient accuracy in spite of the simplicity of the computational method and are thus used widely in chemical applications. Two kinds of methods have been proposed previously. One is the so-called DFT/uGTS method by Chong and co-workers,[9–11] which makes use of the transition potential model.[19] The other is the ΔKohn-Sham (ΔKS) method proposed by Triguero and co-workers,[14,15,20] where the CEBE is calculated as the energy difference between the total Kohn-Sham energies of the core-ionized cation and of the neutral parent molecule. Recent progress has enabled the CEBE to be calculated within the DFT framework to within 0.2 eV of the experimental values for various molecules.[12]

The CEBE provides important information on the chemical environment at the core-ionization site, but techniques to obtain the full XA spectrum, where the CEBE provides a reference point, are desirable. This requires optimizing highly excited electronic states, which furthermore lie embedded in the continuum based on valence-ionized states. By imposing the requirement of a $1s^1$ core occupation the core-excited states computationally form a sequence with no lower-lying states that fulfill this requirement.[21] Experimentally the discrete states below the core-ionization edge are lifetime broadened through the various decay channels, as well as vibrationally broadened; these effects are modeled in calculations by a Gaussian broadening of the oscillator strengths. Typically a larger broadening is applied to continuum states above the edge to compensate for the discrete sampling of the kinetic energies inherent with the use of a local Gaussian type basis. We have developed and implemented efficient techniques to generate XAS spectra using the transition potential method[19] within the STOBE-DEMON DFT code.[22] These have been tested and applied in a series of papers where also the energy positions of low-lying excited states were examined.[14,15,23,24] We have furthermore extended this method to obtain variationally a sequence of core-excited states in a state-by-state procedure with very good results for small molecules, e.g., gas phase pyridine.[20]

Many exchange and correlation functionals have been proposed in the literature and it is necessary to determine the sensitivity of the results to the various combinations of exchange and correlation functionals. Although investigations of the functional dependence of computed CEBEs have appeared,[11,12,14] no corresponding systematic study has been performed with respect to the core-excitation energies. The functional dependence was investigated briefly in the early work by Triguero *et al.*,[14,15] but only for a very limited set of functionals and molecules.

Furthermore, in order to compare computed CEBEs with experimental measurements, some small corrections need to be introduced, i.e., relativistic terms, and vibronic and zero-point vibrational corrections. Vibronic coupling can generate

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significant effects on intensities in XAS through symmetry breaking, which makes, e.g., the $1a_1$ to $4a_1$ transition weakly allowed in gas phase methane, or generate overlapping Franck-Condon profiles which affects, e.g., the intensity ratio between the two lowest states in gas phase pyridine.[20] For CEBEs, on the other hand, these effects show up mainly as a Franck-Condon profile and are not so significant as has already been discussed in the literature.[1,14] The relativistic effect is relatively small but significant for core-excited states of the first-row atoms, such that it is a good approximation to add this effect as a perturbation based on atomic calculations. Unfortunately there is confusion in the literature as to the magnitude of the relativistic correction on the CEBEs for many-electron atoms. Historically, Pekeris estimated the relativistic corrections for two-electron atoms and ions by solving the nonrelativistic Schrödinger equation numerically and computing the mass-velocity and Darwin terms using first-order perturbation theory.[25] For molecules, two different sets of corrections have been proposed. Chong[10] estimated the relativistic correction in molecules by linear extrapolation based on the two-electron atomic systems. His values were close to half of those of Pekeris, and he argued that the estimation by Pekeris was larger than those in neutral molecules due to the absence of valence electrons. On the other hand, one of the authors and co-workers[15] have proposed another set of values obtained from calculations on the respective atoms, where the differential relativistic effect between a neutral and core-ionized atom was computed as the first-order perturbation theory estimate of the mass-velocity and Darwin terms. Contrary to the extrapolated values obtained by Chong this set of values agreed well with those of Pekeris.

In the present study, the functional dependence is studied systematically for not only the CEBE but also the term value of the first-excited state as well as for the energy differences between core-excited states for a representative set of first-row molecules in the gas phase. We use the term value in order to separate effects of the functionals in the core region and the valence or Rydberg spatial regions. The CEBE will measure the behavior of the functionals in the core spatial region while the term values constitute the difference between core-excited states, thus largely eliminating possible discrepancies of the functionals in the region of the core. The term values, apart from providing a direct measure of the performance of the functionals further from the nucleus, are furthermore of interest since these are what is usually measured experimentally. Finally, we reexamine the relativistic corrections on core electron binding energies in the present work.

II. CALCULATIONAL PROCEDURE

A total of 18 molecules with well established experimental data for both CEBE and term values were selected for the present investigation. The geometries for the 14 molecules (CH_4, CO, C_2H_2, C_2H_4, C_2H_6, HCN, H_2CO, CH_3OH, CO_2, CF_4, N_2, NH_3, H_2O, and HF) were taken as the experimental gas phase geometries, while for BF_3, BCl_3, HFCO, and CH_3F, geometry optimizations were performed using GAUSSIAN98 (Ref. 26) at the MP2/cc-pVDZ level of approximation.

The detailed computational procedure has already been described elsewhere.[14,20] In short, in order to determine the absolute energy position of the excited states, ΔKS calculations, i.e., allowing full relaxation of the fully ionized core hole state, were performed to compute the relaxed ionization energy (IP). The core-excited states were variationally determined with maintained orthogonality between the excited states through the following procedure: The first excited state was obtained by fixing the occupation of the core spin orbital to zero and placing the excited electron in the first unoccupied orbital. A full relaxation with this constraint leads to a state that is near orthogonal to the ground state due to the $1s^{-1}$ configuration. The next state was then obtained by removing the variationally determined excited orbital from the variational space and occupying the next level. This procedure gives a variational lower bound to the energy and guarantees orthogonality between the excited states since all remaining orbitals now have to be orthogonal to the successively defined and eliminated levels.[20]

Relativistic effects on the IP were obtained for the atoms in this study using the same procedure as Triguero *et al.*,[15] and added to produce the overall shift of the energy position; the corrections were obtained from calculations on the respective atoms using uncontracted basis sets and including correlation through the modified coupled pair functional[27] approach. The differential relativistic effect was obtained as the first-order perturbation theory estimate of the mass-velocity and Darwin terms. These calculations were carried out with the STOCKHOLM package.[28] In the ΔKS-calculations on molecules with more than one atom of the same element as the core-excited atom the non-core-excited atoms were described by effective core potentials (ECP).[29] This simplifies the definition of the core hole state, since the use of an ECP description eliminates the $1s$ level of the atoms to which it is applied. This procedure is helpful in core-hole calculations for an atom, which is not the only one of its kind in the studied molecule. The ECPs introduce insignificant effects on the computed excited states.

In order to obtain an improved representation of relaxation effects in the inner orbitals, the ionized center was described by the IGLO-III basis of Kutzelnigg *et al.*,[30] and (6311/311/1) basis sets were used for the other heavy atoms, while a (311/1) basis set was used for the hydrogen atom. The auxiliary basis sets were (3,1;3,1) for hydrogen and (5,2;5,2) for the other atoms, where the nomenclature $[N_C(s),N_C(spd);N_{XC}(s),N_{XC}(spd)]$ indicates the number of s- and spd-type functions used to fit the Coulomb and exchange correlation potentials, respectively. This selection is suitable to avoid linear dependence in the auxiliary basis set. Nine gradient-corrected exchange functionals named PD86,[31] PD91,[32] DEPK,[33] BE86,[34] BA86,[35] BE88,[36] PBE,[37] PBE2,[38] and RPBE[39] and three correlation functionals named PD86,[31] PD91,[32] and PBE[37] were applied in all possible combinations in the present study. Thus a total of 27 combinations of functionals were examined. The calculations have been performed using the STOBE-DEMON program.[22]

TABLE I. Energy difference (in eV) between calculated and experimental CEBEs for the PD86-PD86 (*f*1), PD86-PD91 (*f*2), and PD86-PBE (*f*3) functional combinations. AD, MAD, AAD, and MAX-MIN denote the average deviation of the calculated value from experiment, the maximum absolute deviation, the average absolute deviation, and the difference between maximum and minimum deviations (including sign) for the different functional combinations, respectively.

Exch[a] Corr[b] Functional number	PD86 PD86 *f*1	PD86 PD91 *f*2	PD86 PBE *f*3
BF_3 B(*K*)	−0.255	−0.450	−0.652
BCl_3 B(*K*)	0.227	0.029	−0.151
CH_4 C(*K*)	0.508	0.330	0.136
CO C(*K*)	0.530	0.299	0.099
C_2H_2 C(*K*)	0.571	0.371	0.184
C_2H_4 C(*K*)	0.584	0.385	0.197
C_2H_6 C(*K*)	0.458	0.271	0.076
HCN C(*K*)	0.480	0.271	0.076
H_2CO C(*K*)	0.376	0.173	−0.024
CO_2 C(*K*)	0.083	−0.137	−0.341
CH_3OH C(*K*)	0.374	0.184	−0.011
CH_3F C(*K*)	0.399	0.217	0.019
HFCO C(*K*)	0.022	−0.190	−0.392
CF_4 C(*K*)	−0.232	−0.438	−0.647
N_2 N(*K*)	0.292	0.051	−0.151
NH_3 N(*K*)	0.489	0.266	0.063
HCN N(*K*)	0.460	0.220	0.020
CO O(*K*)	0.749	0.482	0.268
H_2O O(*K*)	0.709	0.445	0.231
H_2CO O(*K*)	0.541	0.267	0.058
CO_2 O(*K*)	1.053	0.735	0.528
CH_3OH O(*K*)	1.003	0.735	0.528
HFCO O(*K*)	0.474	0.198	−0.015
HF F(*K*)	0.700	0.399	0.167
CH_3F F(*K*)	0.567	0.257	0.034
HFCO F(*K*)	0.027	−0.292	−0.518
CF_4 F(*K*)	0.243	−0.080	−0.308
AD	0.42	0.19	−0.02
MAD	1.05	0.78	0.65
AAD	0.46	0.30	0.22
MAX-MIN	1.31	1.23	1.22

[a] Exchange functionals.
[b] Correlation functionals.

III. RESULTS AND DISCUSSION

As typical examples, we present the computed CEBEs using the PD86 exchange functional[31] in combination with, respectively, the PD86,[31] PD91,[32] and PBE[37] correlation functionals in Table I. Relativistic corrections have been included in all the values in the table. From the table, it is clear that the CEBEs strongly depend on the combination of functionals. Note that the average deviation (AD) of the calculated value from experiment becomes lower in the sequence with PD86, PD91, and PBE as correlation functionals. Both the maximum absolute deviation (MAD) and the average absolute deviation (AAD) show a similar tendency. However, the difference between maximum and minimum deviation (MAX-MIN) is not sensitive to the choice of correlation functional.

TABLE II. AD, MAD, and AAD of energy difference (in eV) between experimental and theoretical CEBEs and AAD for *T*1, and ΔE for target molecules with different functional combinations. *F* denotes the functional combination enumeration used in the figures.

Exchange functionals	Correlation	*F*	XPS AD	MAD	AAD	*T*1 AAD	ΔE AAD
PD86	PD86	*f*1	0.42	1.05	0.46	0.41	0.17
PD86	PD91	*f*2	0.19	0.78	0.30	0.25	0.18
PD86	PBE	*f*3	−0.02	0.65	0.22	0.24	0.18
PD91	PD86	*f*4	−0.37	0.97	0.39	0.38	0.17
PD91	PD91	*f*5	−0.61	1.29	0.61	0.23	0.18
PD91	PBE	*f*6	−0.82	1.51	0.82	0.22	0.18
DEPK	PD86	*f*7	−0.27	0.80	0.31	0.33	0.17
DEPK	PD91	*f*8	−0.51	1.12	0.51	0.22	0.20
DEPK	PBE	*f*9	−0.71	1.34	0.71	0.21	0.20
BE86	PD86	*f*10	−0.06	0.65	0.21	0.36	0.18
BE86	PD91	*f*11	−0.30	0.95	0.33	0.23	0.20
BE86	PBE	*f*12	−0.50	1.18	0.50	0.22	0.20
BA86	PD86	*f*13	−0.17	0.73	0.24	0.36	0.18
BA86	PD91	*f*14	−0.41	1.04	0.42	0.23	0.20
BA86	PBE	*f*15	−0.61	1.26	0.61	0.22	0.20
BE88	PD86	*f*16	−0.37	0.98	0.38	0.32	0.18
BE88	PD91	*f*17	−0.60	1.30	0.60	0.21	0.20
BE88	PBE	*f*18	−0.81	1.52	0.77	0.20	0.19
PBE	PD86	*f*19	−0.52	1.20	0.53	0.36	0.17
PBE	PD91	*f*20	−0.77	1.52	0.77	0.22	0.18
PBE	PBE	*f*21	−0.98	1.74	0.98	0.21	0.18
PBE2	PD86	*f*22	−0.16	0.84	0.26	0.34	0.18
PBE2	PD91	*f*23	−0.41	1.16	0.42	0.21	0.19
PBE2	PBE	*f*24	−0.61	1.38	0.61	0.21	0.19
RPBE	PD86	*f*25	0.01	0.65	0.25	0.38	0.18
RPBE	PD91	*f*26	−0.23	0.97	0.29	0.22	0.18
RPBE	PBE	*f*27	−0.44	1.19	0.44	0.21	0.19

Other combinations of functionals are also examined. The resulting AD, MAD, and AAD for all 27 combinations of functionals applied to the set of 18 molecules are shown in Table II and illustrated in Figs 1, 2, and 3. In this table and figures, we show the deviations from experiment of the computed CEBEs, the term value of the first resonant excitation energy *T*1 and energy differences between the lowest resonantly excited states ΔE for the series of molecules. Note that for CH_4 and CF_4, the transition to the first resonant

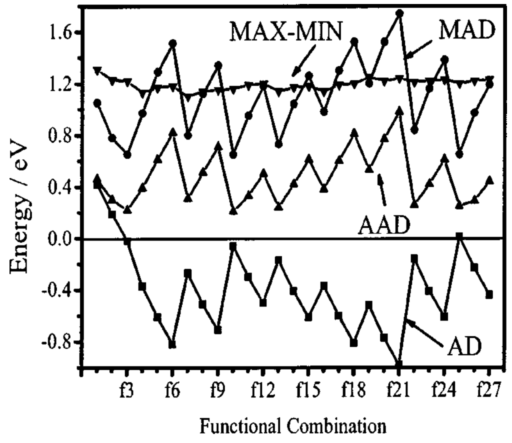

FIG. 1. Functional dependence of AD, MAD, and AAD of the energy difference (in eV) between experimental and theoretical CEBEs for the target molecules using different functional combinations. Notation of functionals given in Table II.

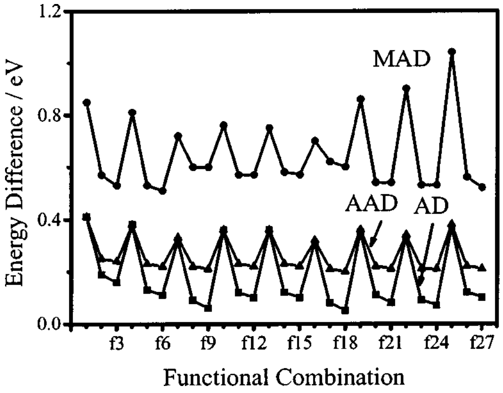

FIG. 2. Functional dependence of AD, MAD, and AAD of the energy difference (in eV) between experimental and theoretical first term values $T1$ for the target molecules using different functional combinations. Notation of functionals given in Table II.

excited state is not a good reference for comparison of calculated values with experiment. The reason for this is that these molecules have T_d symmetry and the orbital symmetry of the lowest unoccupied molecular orbital is of a_1 symmetry, making the transition to this core-excited state at the C and F K-edges forbidden by the dipole selection rule. The intensities of these transitions are thus weak and due to vibronic coupling and, especially for CF_4 at the F K-edge, it is very difficult to determine the peak position precisely from experiment. Actually, absorption spectra for CF_4 at the F K-edge have been reported from high-resolution electron energy loss measurements by Zhang *et al.*[40] and from high-resolution electron yield spectra by Ueda *et al.*[41] Zhang *et al.* determined the peak position for the first excited state, while in the work of Ueda *et al.* it could not be determined in spite of the high-resolution experiment because of its appearance as a broad feature overlapped with fine structure. On the other hand, the transition to the second resonant state is allowed and the intensity is also large. Thus, this transition provides a more reliable reference for comparison of computed and experimental excitation energies.

The computed CEBEs are rather strongly dependent on the choice of functionals, with the MAD varying between 0.65 and 1.54 eV mainly depending on the choice of correlation functional. From Fig. 1 we find a clear oscillatory behavior as the nine exchange functionals are combined with the three correlation functionals with the PD86 correlation functional giving the smallest maximum deviation and PBE the largest. The same trend is followed by the AADs which are of the order 0.5 eV smaller in general. As described in the preceding paragraph, the differences between the maximum and minimum deviations, however, are rather insensitive to the choice of combination of functionals. The nearly invariant spread between these extreme cases (Fig. 1) shows no significant improvement from simply changing the functional combinations. As discussed by Chong and co-workers[11,12] one must go to much larger basis sets in order to improve on the maximum deviations. The functional dependence of $T1$, shown in (Fig. 2), is much weaker. Except for the case of the PD86 correlation functional we find all AADs less than 0.25 eV, indicating that all the exchange functionals used in the present study can describe the excitation energy correctly, and that the PD91 and PBE correlation functionals constitute equally good choices for the calculation of $T1$. For both CEBE and $T1$, we find systematic oscillations with respect to the three correlation functionals included in the study, indicating that the influence of the correlation functional is always similar and independent of the selection of the exchange functional. The deviation from experiment thus largely depends on the selection of the exchange functional. The deviations from experiment of the computed ΔE's are shown in Fig. 3 and are found to be insensitive to the functional combinations, indicating that the errors of the functional combination have been canceled out by taking the difference between the two states involved. The AAD is quite low, below 0.2 eV, for all combinations of functionals. This is quite rewarding when it is recalled that this is formed through the successive differences between the three lowest core-excited states of the full set of 18 molecules. The sensitivity to the form of the functionals is thus mostly connected with the description of the high-density core region and much less to the outer valence and Rydberg regions probed by the excited electron. For a computed XAS spectrum we can in consequence expect that the errors due to the functional will lead to an overall shift of the spectrum, but not affect significantly the relative energy positions of the peaks.

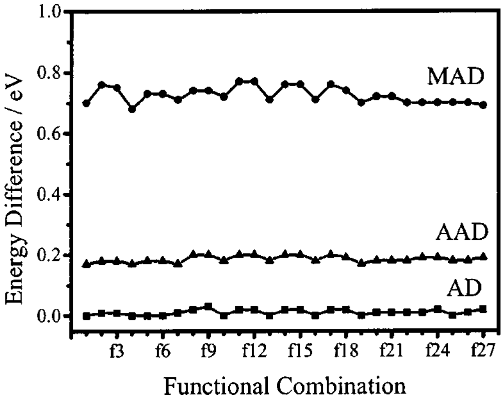

FIG. 3. Functional dependence of AD, MAD, and AAD of the energy difference (in eV) between experimental and theoretical ΔE for the target molecules using different functional combinations. Notation of functionals given in Table II.

From the above tables and figures, features for the selection of the functional combinations can be seen. First, the PD86 exchange functional results in an overall overestimate of the CEBEs compared with experiment, while on the other hand the PD91 exchange functional results in a too low value. Second, the PD86 correlation functional results in a poor estimate of $T1$. ΔE are independent of the selection of functionals. Considering these results, we can propose a different mixed functional designed to minimize the error from experiment for computed CEBEs, $T1$, and ΔE. The new exchange functional is defined by mixing the PD86 and PD91 exchange functionals according to

TABLE III. AD, MAD, and AAD of energy difference (in eV) between experimental and theoretical CEBEs and $T1$. For the CEBEs, the energy difference between maximum and minimum deviation are also shown. Nomenclature "mix(X-Y)" means mixing ratio for the PD86 and PD91 exchange functionals.

	Exchange functional Correlation functional	PD86 PD91	Mix(60-40) PD91	Mix(50-50) PD91	Mix(40-60) PD91	PD91 PD91
CEBE	AD	0.19	−0.14	−0.22	−0.30	−0.61
	MAD	0.78	0.70	0.79	0.89	1.29
	AAD	0.31	0.20	0.23	0.29	0.58
	MAX-MIN	1.23	1.07	1.07	1.07	1.17
$T1$	AD	0.20	0.15	0.17	0.17	0.15
	MAD	0.57	0.55	0.55	0.55	0.53
	AAD	0.27	0.27	0.24	0.25	0.23

$$\mathrm{EXCH(MIX)} = a\,\mathrm{EXCH(PD86)} + b\,\mathrm{EXCH(PD91)},$$

$$a + b = 1.0, \tag{1}$$

where EXCH means the exchange functional and the mixing ratio is $a:b$. The mixing ratio is determined to minimize the deviations AD, MAD, and AAD from experiment. PD91 was used as correlation functional for the fit. The results are shown in Table III. By mixing the exchange functional PD86 with PD91, AD is strongly refined, and the best estimation is obtained for a 60:40 mixing ratio. The $T1$ and ΔE (not shown) are insensitive to the value of the mixing ratio.

The core-excitation energies of carbon monoxide at the C and O K-edges require some special consideration. In the previous study,[15] the estimation of $T1$ at the C K-edge was not good with an error from the experimental value of about 1 eV. In the light of the overall substantially higher accuracy obtained for the other molecules this large deviation is surprising. The origin of this discrepancy lies in the single-determinant character of the wave function used to obtain the density from the Kohn-Sham orbitals in the DFT formalism. This results in a contamination of the desired open-shell singlet state by the triplet state of the same orbital occupation, something that has not been discussed in this context before. Thus the excited state in the ΔKS method is in general obtained with some admixture of higher multiplicity components; the error introduced by this will depend on the exchange-splitting between the two components. Since, for a closed shell molecule such as CO, this involves the coupling between the remaining 1s core-electron and the excited electron, the effect is normally small. However, in the case of CO it is large and significant.

In the resonant excited state, that is the open-shell singlet state, the spin-contamination is due to admixture of the triplet state. In order to exclude the triplet component, the scheme proposed by Daul[42] can be applied,

$$E(\text{singlet}) = 2E(\text{singlet}') - E(\text{triplet}), \tag{2}$$

where, "singlet′" means the singlet state from the single-determinant calculation for the two-electron open-shell system. As a typical example we show the results for the PD86-PD91 functional in Table IV. The energy splitting between the singlet and triplet states $\Delta(S\text{-}T)$ is approximately the exchange integral between the core and excited electron orbitals, which corresponds to the localization of the excited electron, i.e., if this value becomes large, the excited electron is localized on the core-excited atom. Experimentally, this energy splitting has been observed through the energy difference between an electron impact energy-loss spectrum[43] and

TABLE IV. CEBEs, the term value of the first, second, and third resonant excited states $T1$, $T2$, and $T3$ (in eV) using the PD86-PD91 functional. These are examined using two basis sets BS1 and BS2. For BS1, the energy difference, $\Delta(S\text{-}T)$, between the singlet and triplet states are also shown.

	Expt. Energy	BS1[a] Energy	Difference	$\Delta(S\text{-}T)$	BS2[b] Energy	Difference
CO C K-edge						
CEBE	296.08	296.38	0.30		296.35	0.27
$T1$	8.68	9.25	0.57	1.21	9.27	0.59
$T2$	3.71	2.66	−1.05	0.04	4.06	0.35
$T3$	2.75	2.19	−0.56	0.18	3.41	0.66
$\Delta(T2\text{-}T1)$	4.97	6.58			5.21	
$\Delta(T3\text{-}T2)$	0.96	0.47			0.65	
CO O K-edge						
CEBE	542.40	542.88	0.48		542.96	0.56
$T1$	8.29	8.56	0.27	0.35	8.56	0.27
$T2$	3.60	3.81	0.21	0.08	3.99	0.39
$T3$	2.62	2.78	0.16	0.04	3.39	0.77
$\Delta(T2\text{-}T1)$	4.69	4.74			4.57	
$\Delta(T3\text{-}T2)$	0.98	1.03			0.61	

[a] IGLO-III basis set.

[b] (61111111/41111/111) basis sets with two s, p, and d types of diffuse functions.

TABLE V. Relativistic corrections for the first-row atoms in eV.

	Two-electron atom		Neutral atom			
Atom	Pekeris[a]	This work	Chong[b]	Triguero[c]	This work	Scaled
B	0.05	0.09	0.02		0.06	0.03
C	0.11	0.18	0.05	0.2	0.14	0.08
N	0.24	0.35	0.11	0.3	0.26	0.18
O	0.44	0.62	0.20	0.4	0.47	0.33
F	0.75	1.01	0.34	0.7	0.77	0.57

[a] From Table X in Ref. 25.
[b] References 10 and 12.
[c] Reference 15.

XAS.[44] As seen from the table, only $\Delta(S\text{-}T)$ for the first resonant excited state at the C K-edge is large, 1.21 eV, indicating that the excited state assigned to $\pi^*(\mathrm{CO})$ is localized mainly on the carbon in the core-excited molecule. For higher states, the $\Delta(S\text{-}T)$ is very small due to the Rydberg character of the excited orbital. Our computed value of 1.21 eV for the $\Delta(S\text{-}T)$ compares well to the experimental observation of a 1.3 eV splitting between the singlet and triplet coupled $1s \rightarrow \pi^*$ excitations in CO at the C K-edge.[43–46]

In a similar fashion, $\Delta(S\text{-}T)$ for the first resonant excited state is also larger for CO_2 at the C K-edge and for BF_3 and BCl_3 at the B K-edge. In the same table, results using substantially larger basis sets are also shown. The computed values for CEBEs and $T1$ are similar for these two basis sets, indicating that the use of IGLO-III basis sets for a core-hole are appropriate for the estimation of these states. For $T2$ of the CO C K-edge, however, the character of the excitation is $C(1s) \rightarrow 3s$ Rydberg state and the basis set must be augmented by Rydberg type functions. With this extended basis the second and third excited states at the C K-edge are calculated correctly. For the CO O K-edge, good estimations for $T1$, $T2$, and $T3$ are achieved even for the IGLO-III basis set indicating much less Rydberg character of the excited states at the O K-edge. The above procedure has been followed for CO, CO_2, BF_3, and BCl_3 to generate the values presented in Tables I and II.

We now turn to a discussion of the relativistic corrections to the core excitation or ionization energies for atoms and molecules. Our computed values are compared to earlier results in Table V. Our estimated values for the two-electron system are larger than those of Pekeris, which most likely is due to the precision of the wave function. Pekeris solved the Schrödinger equation for the two-electron atom explicitly, while in the present case standard molecular orbital basis set techniques were used with a relatively large uncontracted basis set. For the neutral atoms we observe a reduction of the differential relativistic effect due to the presence of the valence electrons as discussed by Chong; our reestimated values are comparable with the previous ones, while on the other hand, Chong's values are close to half or one third of our values. His estimated corrections for the many-electron atoms were based on a reduction of the order of 50% rather than the 25% obtained from our calculations. It is clear from the direct comparison with the reference values for the two-electron atoms that our computational approach overestimates the relativistic effect upon core ionization. We can, however, use our directly computed values for the two-electron atoms to obtain the scaling factor needed to correct for this computational deficiency and apply that to the computed values for the many-electron atoms. The resulting improved corrections are consistently higher than those proposed by Chong but lower than the previous estimate by Triguero *et al.*; the revised values are given in the final column of the table and have been applied throughout this work.

IV. SUMMARY

In the present paper, the functional dependence of CEBEs, the term value of the first resonant excited state $T1$, and the energy differences between the three lowest resonantly excited states ΔE have been examined. The CEBEs mainly depend on the core electron and the resulting computed values are largely dependent on the exchange functional. On the other hand, the term value of the first resonant excited state $T1$, mainly depends on the excited electron since it involves the difference between the core-ionized and first core-excited state. As a result we find that the $T1$ values are insensitive to the choice of exchange functional. The effects of the selection of correlation functional is similar for both CEBEs and $T1$s and we find that the PD86 correlation functional is not suitable for the evaluation of $T1$. The energy differences ΔE, between the lowest core-excited states are also insensitive to the combination of functionals because of the cancellation of errors for the difference between two states. To decrease the error in the functional combination, a different functional is proposed, which is the mixed exchange functional between PD86 and PD91 and the best estimation is a 60:40 mixing ratio in our study. Although we have not specifically addressed issues as, e.g., effects on the computed CEBEs from going to larger basis sets, we nevertheless find that the CEBEs are reliably predicted with an accuracy of 0.2 eV. As discussed by Takahata and Chong,[12] this quantity does not lead to serious problems in practical applications.

Furthermore, for the term values or differential excitation energies we find that the choice of functionals does not affect the results due to most of the errors being determined by the core region. For a computed XAS spectrum we can thus expect that errors in the functionals will lead to an overall shift of the spectrum, while the relative energy positions will be significantly less affected.

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[1] J. Stöhr, *NEXAFS Spectroscopy* (Springer, New York, 1992).
[2] D. M. Hanson, Adv. Chem. Phys. **77**, 1 (1990).
[3] R. N. Zare, Science **279**, 1875 (1998).
[4] A. Nilsson, J. Electron Spectrosc. Relat. Phenom. **126**, 3 (2002).
[5] K. Mase, M. Nagasono, S. Tanaka, T. Sekitani, and S. Nagaoka, Fiz. Nizk. Temp. **29**, 321 (2003).
[6] Ph. Wernet, D. Nordlund, U. Bergmann *et al.*, Science **304**, 995 (2004).
[7] K. Siegbahn, C. Nordling, A. Fahlman *et al.*, *ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (North-Holland, Amsterdam, 1969).
[8] K. Siegbahn, C. Nordling, G. Johansson *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).
[9] D. P. Chong, Chem. Phys. Lett. **232**, 486 (1994).
[10] D. P. Chong, J. Chem. Phys. **103**, 1842 (1995).
[11] G. Cavigliasso and D. P. Chong, J. Chem. Phys. **111**, 9485 (1999).
[12] Y. Takahata and D. P. Chong, J. Electron Spectrosc. Relat. Phenom. **133**, 69 (2003).
[13] F. Gel'mukhanov and H. Ågren, J. Phys. Chem. **103**, 5848 (1995).
[14] L. Triguero, L. G. M. Pettersson, and H. Ågren, Phys. Rev. B **58**, 8097 (1998).
[15] L. Triguero, O. Plashkevych, L. G. M. Pettersson, and H. Ågren, J. Electron Spectrosc. Relat. Phenom. **104**, 195 (1999).
[16] P. S. Bagus, F. Illas, G. Pacchioni, and F. Parmigiani, J. Electron Spectrosc. Relat. Phenom. **100**, 215 (1999).
[17] S. Hamel, P. Duffy, M. E. Casida, and D. R. Salahub, J. Electron Spectrosc. Relat. Phenom. **123**, 345 (2002).
[18] S. Carniato and P. Millié, J. Phys. Chem. **116**, 3521 (2002).
[19] J. C. Slater, Adv. Quantum Chem. **6**, 1 (1972).
[20] C. Kolczewski, R. Puüttner, O. Plashkevych *et al.*, J. Chem. Phys. **115**, 6426 (2001).
[21] H. Ågren, V. Carravetta, O. Vahtras, and L. G. M. Pettersson, Theor. Chem. Acc. **97**, 14 (1997).
[22] K. Hermann, L. G. M. Pettersson, M. E. Casida *et al.*, STOBE-DEMON, version 1.0.
[23] M. Nyberg, M. Odelius, A. Nilsson, and L. G. M. Pettersson, J. Chem. Phys. **119**, 12577 (2003).
[24] M. Cavalleri, H. Ogasawara, L. G. M. Pettersson, and A. Nilsson, Chem. Phys. Lett. **364**, 363 (2002).
[25] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN98, Revision A.4.
[27] D. P. Chong and S. R. Langhoff, J. Chem. Phys. **84**, 5606 (1986).
[28] P. E. M. Siegbahn, M. R. A. Blomberg, L. G. M. Pettersson, B. O. Roos, and J. Almlöf, STOCKHOLM—A general purpose quantum chemical set of programs.
[29] L. G. M. Pettersson, U. Wahlgren, and O. Gropen, Chem. Phys. **80**, 7 (1983).
[30] W. Kutzelnigg, U. Fleischer, and M. Schindler, *NMR-Basic Principles and Progress* (Springer, Heidelberg, 1990).
[31] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
[32] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[33] A. E. DePristo and J. D. Kress, J. Chem. Phys. **86**, 1425 (1987).
[34] A. D. Becke, J. Chem. Phys. **84**, 4524 (1986).
[35] A. D. Becke, J. Chem. Phys. **85**, 7184 (1986).
[36] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[37] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[38] Y. Zhang and W. Yang, Phys. Rev. Lett. **80**, 890 (1998).
[39] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).
[40] W. Zhang, T. Ibuki, and C. E. Brion, Phys. Chem. **160**, 435 (1992).
[41] K. Ueda, Y. Shimizu, H. Chiba, M. Okunishi, K. Ohmori, Y. Sato, E. Shigemasa, and N. Kosugi, J. Electron Spectrosc. Relat. Phenom. **79**, 441 (1996).
[42] C. Daul, Int. J. Quantum Chem. **52**, 867 (1994).
[43] D. A. Shaw, G. C. King, D. Cvejanović, and F. H. Read, J. Phys. B **17**, 2091 (1984).
[44] T. K. Sham, B. X. Yang, J. Kirz, and J. S. Tse, Phys. Rev. A **40**, 652 (1989).
[45] A. Nilsson, O. Björnebolm, E. O. F. Zdansky, H. Tillborg, N. Mårtensson, J. N. Andersen, and R. Nyholm, Chem. Phys. Lett. **197**, 12 (1992).
[46] O. Björneholm, A. Nilsson, A. Sandell, B. Hernnäs, and N. Mårtensson, Phys. Rev. Lett. **68**, 1892 (1992).