

Self-consistent-field calculations of core excited states

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The accuracy of core excitation energies and core electron binding energies computed within a Δ self-consistent-field framework is assessed. The variational collapse of the core excited state is prevented by maintaining a singly occupied core orbital using an overlap criterion called the maximum overlap method. When applied to a wide range of small organic molecules, the resulting core excitation energies are not systematically underestimated as observed in time-dependent density functional theory and agree well with experiment. The accuracy of this approach for core excited states is illustrated by the calculation of the pre-edge features in x-ray absorption spectra of plastocyanin, which shows that accurate results can be achieved with Δ self-consistent-field calculations when used in conjunction with uncontracted basis functions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3092928]

I. INTRODUCTION

In recent years, x-ray spectroscopic techniques, such as near edge x-ray absorption fine structure (NEXAFS), have undergone tremendous advances due to the intensity and high resolution obtainable with synchrotron radiation. This revealed a richness in structure that can match more traditional UV spectroscopy. These methods are now powerful techniques that are used to study a wide range of systems.¹ Despite this progress in experimental measurements, the calculation of core excited states received much less attention than the calculation of valence excited states.

There exist a number of approaches to computing NEXAFS spectra. Earlier work used multiple scattering X_α methods,² static exchange,³ and transition potential calculations,⁴ and these methods have been used to study a wide range of systems. More recently, NEXAFS spectra have been computed using time-dependent density functional theory (TDDFT).^{5–8} Within TDDFT core excited states can be computed efficiently by restricting the single excitation space to include only excitations from a subset of (core) orbitals.^{5,9} Also within TDDFT, Norman and co-workers used a resonant converged complex polarization propagator to study NEXAFS.^{10,11} In general, these methods provide a spectral profile that agrees well with experimental measurements. However, the core excitation energies are underestimated and it is necessary to apply a shift to the computed spectrum to obtain agreement with the experiment. The amount by which the excitation energies are underestimated increases with the nuclear charge of the atomic centers on which the core orbitals are localized. This error stems from the approximate exchange within the exchange-correlation functionals. To correct for this error, exchange correlation functionals with varying fractions of Hartree–Fock (HF) exchange,^{12,13} a self-interaction correction,^{14,15} and a combination of exchange functionals¹⁶ have been introduced. Re-

cently, a “short range” corrected exchange-correlation functional has been introduced that provides accurate core excitation energies with TDDFT.¹⁷ This is in contrast with long range corrected exchange-correlation functionals that can describe charge transfer excitations accurately.¹⁸ Alternatively, excited state methods that use exact exchange, such as CIS(D), can be used.¹⁹

The underestimation of the core excitation energy is avoided by a Δ self-consistent-field (SCF) or Δ Kohn–Sham approach, wherein the excitation energy is simply the difference in energy between the ground- and excited-state HF or Kohn–Sham calculation. Obtaining a core-excited state within this approach is not straightforward, and usually some constraints, overlap criterion, or intermediate optimization with a frozen core hole is used to prevent the collapse of the core hole during the SCF procedure.^{20–22} In this contribution, the accuracy of a Δ SCF method to study core excited states and core electron binding energies (CEBEs) is assessed and it is shown that these approaches provide an efficient and accurate approach for computing these properties. Finally, the pre-edge features observed in the x-ray absorption spectra of plastocyanin are computed.

II. COMPUTATIONAL METHODS

The most common approach to solving the time-independent Schrödinger wave equation for an n -electron system,

$$\hat{H}\Psi_k = E_k\Psi_k, \quad (1)$$

is to treat \hat{H} as a sum of one-electron operators. The resulting eigenfunctions are single determinants,

$$\Psi_k^{\text{SCF}} = \det[\chi_i(\mathbf{r}_j, s_j)], \quad (2)$$

where the $\chi_i(\mathbf{r}, s) = \psi_i(\mathbf{r})\sigma(s)$ are spin orbitals and each molecular orbital (MO),

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$$\psi_i(\mathbf{r}) = \sum_{\mu}^N C_{\mu i} \phi_{\mu}(\mathbf{r}), \quad (3)$$

is expanded in a finite basis $\{\phi_{\mu}\}$. The MO coefficients $C_{\mu i}$ are usually determined by minimizing the energy in a SCF procedure. In general, this yields the ground state solution. Within a SCF framework, core-excited states can be obtained by maintaining the core hole to prevent the variational collapse. An original approach was reported by Bagus.²⁰ The wave function is constrained to have a singly occupied core orbital, with the core orbital identified as the one which most closely resembles the corresponding eigenvector used to construct the HF operator. Such an overlap approach has been used to study the Auger and $1s$ shake up spectra of H_2O (Refs. 23 and 24) and is available in the DIRAC program.²⁵ In the approach of McWeeny,²⁶ the optimum orbitals for an excited state are obtained by minimizing the energy of the configuration defined by averaging over all states arising from variable occupation of the spin orbitals within each shell, without transfer of electrons between the shells.

Recently, we extended the overlap approach to finding excited state solutions of the SCF equations.²⁷ For each iteration within a SCF procedure the Fock (or Kohn–Sham) matrix is formed from the current MOs. Solving the generalized eigenvalue problem,

$$\mathbf{FC}^{\text{new}} = \mathbf{SC}^{\text{new}} \boldsymbol{\varepsilon} \quad (4)$$

(where \mathbf{S} is the basis function overlap matrix) gives the new MO coefficient matrix \mathbf{C}^{new} and orbital energies $\boldsymbol{\varepsilon}$. In conventional SCF approaches, the n orbitals with the lowest orbital energies are then occupied. However, excited state solutions can be obtained by defining an alternative set of occupied orbitals. For example, for core-excited states a single occupancy for a core orbital can be maintained throughout the SCF process and the relevant core orbital can be identified by the overlap between the new and old set of orbitals.²⁰ In our approach, which is called the maximum overlap method (MOM), the orbitals that are occupied are chosen to be those that overlap most with the *span* of the old occupied orbitals. The new occupied orbitals are identified by defining an orbital overlap matrix,

$$\mathbf{O} = (\mathbf{C}^{\text{old}})^{\dagger} \mathbf{SC}^{\text{new}}. \quad (5)$$

O_{ij} gives the overlap between the i th old orbital and the j th new orbital and the projection of the j th new orbital onto the old occupied space is

$$p_j = \sum_i^n O_{ij} = \sum_v^N \left[\sum_{\mu}^N \left(\sum_i^n C_{i\mu}^{\text{old}} \right) S_{\mu v} \right] C_{vj}^{\text{new}}. \quad (6)$$

The n occupied orbitals are chosen to be the ones with the largest projections p_j . This approach is applicable in non-symmetric systems in which there is a significant difference between the old and new set of orbitals. Excitation energies computed with this approach at the HF, MP2, and B3LYP levels of theory were shown²⁷ to be competitive with their

conventional analogs CIS, CIS(D), and TD-B3LYP. Furthermore, charge transfer states can be computed accurately with DFT.

The procedure for computing core excited states with the MOM is as follows. Initially, a set of orbitals is required. For the majority of the calculations shown here, the ground state orbitals of the molecule were used. For core excitations from core orbitals that are not symmetrically unique, using the ground state orbitals will result in a core excited state with a delocalized core hole. In order to obtain a localized core hole, the symmetry of the wave function needs to be broken. An effective way to achieve this is to use orbitals from the isoelectronic ion in which the nuclear charge of the atom on which the local core hole localized is increased to $Z+1$. All core-excited state calculations were performed with the Q-CHEM software package²⁸ and used an unrestricted HF or Kohn–Sham formalism.

An additional complication with the computation of core excited states is that relativistic effects cannot be ignored. Relativistic effects lead to a significant lowering of the energy of core orbitals, while the energies of the valence orbitals remain roughly constant. Since in creating a core excited state an electron is removed from a core orbital, the extent to which the core orbital is lowered due to relativity can provide an approximate relativistic correction to the core-excitation energy. In this work, the effect of relativity was estimated from the lowering of the core orbital energy between nonrelativistic and relativistic HF/cc-pCVTZ calculations. For calculations with an uncontracted basis set, the relativistic correction was computed at the HF level with the 6-31G* basis set with all the basis functions uncontracted. This lowering in energy is insensitive to the molecular environment of the core orbital and the corrections used in this work were derived from atomic calculations since this avoids the need for relativistic calculations on large systems. The relativistic energy was computed with the Douglas–Kroll–Hess Hamiltonian²⁹ with the MOLPRO software package.³⁰ Ekström *et al.*³¹ have shown that such scalar relativistic corrections are sufficient for K -edge spectra. For the L -edge spectra, spin-orbit coupling was shown to be significant and resulted in a splitting of 1.2 eV for H_2S . However, for the L -edge spectra considered here, the experimental spectra are not of sufficiently high resolution to resolve the different spin orbit components reliably. Consequently, in our primary analysis spin orbit coupling has not been accounted for, and the results have been corrected for scalar relativistic effects as described above.

III. RESULTS AND DISCUSSION

A. Core electron binding energies

Before focusing on the calculation of core excitation energies, we will discuss the related property of CEBEs. CEBEs can reveal information about chemical interactions and chemical bonding in both gas and condensed phases.³² There are two main approaches to the computation of CEBEs. The unrestricted generalized transition state method^{33,34} has been applied to study a range of molecules and achieves an accuracy of about 0.2 eV compared to

TABLE I. Deviations of calculated CEBEs (in eV) and computed B3LYP oscillator strengths (f). Bold type denotes the atom at which the $1s$ electron is ionized.

Molecule	Exp. ^a	6-311G**			cc-pCVQZ			u6-311G**		
		HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
C ₂ H ₂	290.82	+0.72	+0.95	+0.60	+0.29	+0.62	+0.65	+0.66	+0.66	+0.64
CH ₄	290.91	+0.24	+0.44	+0.20	-0.19	+0.06	-0.24	-0.16	+0.10	+0.16
CH ₃ OH	292.42	+0.37	+0.45	+0.32	-0.05	+0.12	+0.19	+0.10	+0.10	+0.27
CH ₃ CN	292.45	+0.79	+0.76	+0.53	+0.31	+0.41	+0.43	+0.42	+0.42	+0.49
CH ₃ CN	292.98	+0.21	+0.29	0.00	-0.09	-0.09	+0.01	-0.03	-0.03	-0.06
HCN	293.40	+0.48	+0.63	+0.23	+0.08	+0.26	+0.28	+0.31	+0.31	+0.20
H ₂ CO	294.47	+0.86	+0.57	+0.94	+0.27	+0.21	+0.33	+0.22	+0.22	+0.76
CO	296.21	+1.59	+0.97	+0.16	+0.79	+0.44	+0.14	+0.53	+0.53	-0.08
CO ₂	297.69	+2.05	+0.60	-0.28	+1.55	+0.23	-0.16	+0.28	+0.28	-0.30
NH ₃	405.56	+0.22	+0.39	+0.40	-0.27	+0.02	+0.99	-0.29	-0.05	+0.22
CH ₃ CN	405.64	+0.04	+0.34	+0.79	-0.61	-0.19	+0.63	-0.12	-0.12	+0.60
HCN	406.78	+0.04	+0.54	+1.01	-0.60	+0.02	+0.99	+0.08	+0.07	+0.81
NNO	408.71	+1.23	+0.64	+0.26	+0.46	+0.08	+0.30	+0.58	+0.16	+0.13
N ₂	409.98	+0.65	+0.61	+0.41	-0.46	+0.03	+1.18	-0.30	+0.14	+1.16
NNO	412.59	+2.03	+0.60	+0.22	+1.07	+0.11	-0.22	+1.39	+0.22	+0.06
CH ₃ OH	539.11	-0.22	+0.19	+0.54	-0.82	-0.27	+0.50	-0.36	-0.36	+0.16
H ₂ CO	539.48	-0.56	+0.22	+0.64	-1.22	-0.33	+0.11	-0.34	-0.34	+0.26
H ₂ O	539.90	-0.10	+0.14	+0.67	-0.66	-0.24	+0.37	-0.72	-0.41	+0.04
CO ₂	541.28	+0.20	+0.44	+0.56	-0.50	-0.15	-0.28	-0.13	-0.13	+0.19
NNO	541.42	-0.11	+0.54	+0.86	-0.79	-0.05	+0.83	-0.75	-0.03	+0.46
CO	542.55	-0.26	+0.44	+0.93	-1.01	-0.21	+0.89	-0.13	-0.12	+0.52
HF	694.23	-0.17	+0.13	+0.65	-0.90	-0.37	+0.56	-0.86	-0.50	+0.09
F ₂	696.69	-0.68	+0.26	+1.19	-1.64	-0.51	+1.07	-1.39	-0.38	+0.54
MAD ^b	...	0.60	0.48	0.54	0.64	0.22	0.49	0.44	0.25	0.36

^aReference 36 and references therein.^bMean absolute deviation.

experiment.³⁵ However, later work reported this method to rely on a fortuitous cancellation of errors.³⁶ Δ SCF methods provide a more intuitive approach to compute CEBEs,^{20,37,38} in which the CEBE is computed as the energy difference between the neutral parent molecule and the core-ionized cation. More recently CEBEs have been computed within a multireference perturbation treatment.³⁹ Within a multiconfigurational treatment, the core-ionized state is directly optimized as an excited state and the variational collapse is avoided. For the CH₄, NH₃, H₂O, and HF molecules, an average error of 0.11 eV with the VTZ basis set of Ahlrichs was reported. A symmetry adapted cluster-configuration interaction general- R method has also been applied to the problem of CEBEs, and predicted the CEBEs of C, N, O, and F in a total of 22 molecules with an average error of 0.11 eV.⁴⁰ Table I shows CEBEs computed using HF, B3LYP, and MP2 with the 6-311G** and cc-pCVQZ (Refs. 41 and 42) basis sets. The experimental data are from a previous study³⁶ and comprise synchrotron and x-ray measurements. All calculations report vertical excitation energies computed at the structure of the parent molecule optimized at the B3LYP/6-311G* level of theory.

The aim of these calculations is to demonstrate the accuracy that is obtained using standard techniques. Clearly, a high level of accuracy can be achieved using specifically tailored methods optimized for the computation of CEBEs.³⁶ For calculations of CEBEs of first row atoms, it is common not to incorporate an explicit correction for relativistic ef-

fects. However, we estimate the relativistic correction to be +0.1, +0.21, +0.36, and +0.63 eV for the $1s$ orbitals of C, N, O, and F, respectively. Consequently, even for first row atoms this is significant and all the results presented have been corrected to include this effect. With the 6-311G** basis set, mean absolute deviations (MADs) of 0.60, 0.48, and 0.54 eV with largest errors of +2.05, +0.97, and +1.19 eV are obtained at the HF, B3LYP, and MP2 levels of theory, respectively. This represents a reasonable agreement with experiment, but is not as accurate as previous studies.^{36,39} In general, for the 6-311G** basis set the CEBEs are overestimated indicating that the energy of the core-ionized cation is too high relative to the ground state.

Previous work has shown that increasing the quality of the basis set leads to more accurate results,^{36,39} in particular, the presence of basis functions to describe the core region is important. The 6-311G** basis set has only one contracted basis function to describe the core $1s$ orbital. The cc-pCVQZ has a much better description of the core region and when used in conjunction with B3LYP and MP2 the MADs are reduced. MADs of 0.64, 0.22, and 0.49 eV for HF, B3LYP, and MP2, with largest errors of -1.64, -0.51, and +1.18 eV are obtained. B3LYP gives the most accurate predictions and a MAD of 0.22 eV represents a high level of accuracy that is close to the most accurate methods reported in the literature.^{39,40} However, the cc-pCVQZ basis set is very large and cannot be used to study large systems. An

TABLE II. Deviations of computed excitation energies (in eV) and computed B3LYP oscillator strengths (f) for the first row atoms with the u6-311(2+,2+)G** basis set.

Excitation	Exp. ^a	TD-B3LYP	MP2	B3LYP	f
CO C(1s) \rightarrow π^*	287.4	-11.1	0.0	-0.8	0.55
CO C(1s) \rightarrow 3s	292.4	-12.8	+0.2	+0.5	0.13
CO C(1s) \rightarrow 3p $_{\pi}$	293.3	-13.0	+0.3	+0.5	0.13
CO C(1s) \rightarrow 3p $_{\sigma}$	293.5	-13.3	+0.2	+0.4	0.06
H ₂ CO C(1s) \rightarrow π^*	286.0	-10.3	+0.9	-0.1	0.48
H ₂ CO C(1s) \rightarrow 3s a_1	290.2	-11.7	+0.9	0.0	0.17
H ₂ CO C(1s) \rightarrow 3p b_2	291.3	-12.0	+1.1	-0.2	0.34
H ₂ CO C(1s) \rightarrow 3p b_1	291.7	-12.1	+1.0	+0.1	0.15
CO ₂ C(1s) \rightarrow π^*	290.8	-10.9	+0.2	-1.0	0.57
CO ₂ C(1s) \rightarrow 3s	292.7	-12.5	-0.5	-0.3	0.04
CO ₂ C(1s) \rightarrow 3p	295.0	-12.8	-0.1	+0.9	0.09
CH ₄ C(1s) \rightarrow 3s	287.1	-11.8	0.0	-0.5	0.00
CH ₄ C(1s) \rightarrow 3p	288.0	-11.9	+0.4	+0.5	0.06
N ₂ O N _f (1s) \rightarrow π^*	401.1	-12.1	+1.1	-0.8	0.48
N ₂ O N _f (1s) \rightarrow 3s	404.0	-12.7	+1.0	-0.7	0.24
N ₂ O N _f (1s) \rightarrow 3p	405.9	-13.3	+1.6	0.0	0.10
N ₂ O N _c (1s) \rightarrow π^*	404.8	-12.4	+1.2	-1.0	0.55
N ₂ O N _c (1s) \rightarrow 3s	407.5	-12.9	+0.5	+0.4	0.10
N ₂ O N _c (1s) \rightarrow 3p	407.8	-13.3	+2.4	+2.2	0.06
CO O(1s) \rightarrow π^*	534.2	-14.1	+0.7	-0.7	0.47
CO O(1s) \rightarrow 3s	538.9	-15.8	+0.7	-0.3	0.07
CO O(1s) \rightarrow 3p $_{\pi}$	539.9	-16.1	+0.7	-0.4	0.08
H ₂ CO O(1s) \rightarrow π^*	530.8	-13.8	+0.7	-0.4	0.52
H ₂ CO O(1s) \rightarrow 3s a_1	535.4	-15.0	+0.8	-0.2	0.08
MAD ^b	...	12.7	0.7	0.5	...

^aReference 19 and references therein.^bMean absolute deviation.

alternative way of improving the description of the core region with the 6-311G** basis set is to uncontract the basis functions. This gives the basis set greater flexibility to describe the core region. Table I also shows computed CEBEs for the 6-311G** basis set with all the basis functions uncontracted. This basis set is denoted as u6-311G**. For this basis set, MADs of 0.44, 0.25, and 0.36 eV with largest errors of 1.39, +0.66, and +1.16 eV are obtained for HF, B3LYP, and MP2. With the u6-311G** basis set, the results are comparable to or better than those for the much larger cc-pCVQZ basis set. Furthermore, with uncontracted basis functions even smaller basis sets give comparable agreement with experiment. For B3LYP with the u6-311G* and u6-31G* basis sets, MADs of 0.25 and 0.30 eV are obtained. If the correction for relativity is not included the MADs for HF and B3LYP rise to 0.60 and 0.39, while the MAD for MP2 is reduced to 0.29 eV, which shows that this correction does have a significant effect on the results. We have chosen to uncontract all basis functions in the basis set because it is beneficial to study excitations from the 2p orbitals of heavier atoms. For excitations from the 1s orbital of first row atoms, it would be sufficient to just uncontract the core 1s orbital. For the 6-311G** basis set, this gives results that are very similar to the fully uncontracted basis set with MADs of 0.60, 0.27, and 0.26 eV for HF, B3LYP, and MP2, respectively. Since the calculation of the core-ionized state has the same computational cost as the ground state calculation, it

provides a low cost and accurate approach to computing CEBEs, particularly when used in conjunction with modest basis sets with uncontracted basis functions.

B. Core excited states

Tables II and III show the deviation from experiment of the computed vertical core excitation energies for the singlet excited states at the MP2/cc-pVTZ ground state structures for a range of molecules using TDDFT and the MOM with the u6-311(2+,2+)G** basis set. The experimental values are taken from previous studies.^{12,13,19} One of the striking features of the results is the poor performance of TD-B3LYP, which underestimates all excitation energies, in some cases by over 50 eV. This error is not affected by improving the quality of the basis set. The failure of TD-B3LYP and other standard functionals has been documented previously in the literature.^{9,12,13,43,44} One view of this error is that it is similar to the error observed for charge transfer states. Since core orbitals are localized on the nuclei, there is little overlap between these orbitals and typical valence orbitals, such as π^* . The failure of TDDFT in describing electronic excitations of this nature is well documented and understood^{45,46} and arises from the electron self-interaction error present in approximate exchange-correlation functionals. Although for core excited states the self-interaction error at long and short ranges may be important.^{15,16} Consistent with this analysis, greater accuracy can be achieved by increasing the proportion of HF exchange in the functional.^{9,13,43} However, the

TABLE III. Deviations of computed excitation energies (in eV) and computed B3LYP oscillator strengths (f) for the second row atoms with the u6-311(2+,2+)G** basis set.

Excitation	Exp. ^a	TD-B3LYP	MP2	B3LYP	f
SiH ₄ Si(1s) → σ^*	1842.5	-40.4	+2.8	+0.5	0.16
SiH ₄ Si(2p) → σ^*	102.8	-5.0	+2.2	+2.0	0.01
PH ₃ P(1s) → σ^*	2145.8	-44.7	+3.7	+0.5	0.11
PH ₃ P(2p) → σ^*	132.3	-5.8	+2.6	+2.3	0.03
H ₂ S S(1s) → σ^*	2473.1	-49.3	+1.8	-2.4	0.42
H ₂ S S(1s) → 4p	2476.3	-50.8	+1.1	-2.7	0.12
H ₂ S S(2p) → σ^*	164.5	-6.0	+1.3	+0.6	0.11
H ₂ S S(2p) → 4s	166.5	-7.9	+1.6	-1.2	0.06
SO ₂ S(1s) → π^*	2473.8	-49.4	+2.0	-2.7	0.48
SO ₂ S(1s) → 4p	2478.4	-48.3	+3.0	-1.1	0.36
SO ₂ S(2p) → π^*	164.4	-5.5	+1.9	+0.3	0.00
SO ₂ S(2p) → 4s	171.3	-7.7	+0.9	+0.2	0.11
HCl Cl(1s) → σ^*	2823.9	-53.4	+2.0	-2.6	0.35
HCl Cl(1s) → 4p _{π}	2827.8	-54.9	+1.6	-2.8	0.22
HCl Cl(2p) → σ^*	201.0	-6.9	+0.8	+0.3	0.13
HCl Cl(2p) → 4p _{π}	204.6	-8.1	+0.6	+0.2	0.01
Cl ₂ Cl(1s) → σ_u^*	2821.3	-53.2	+1.7	-2.8	0.48
Cl ₂ Cl(1s) → 4p	2828.5	-54.4	+1.6	-2.7	0.15
Cl ₂ Cl(2p) → σ_u^*	198.7	-7.1	+0.3	-0.3	0.09
MAD ^b	...	29.4	1.8	1.5	...

^aReference 19 and references therein.^bMean absolute deviation.

fraction of HF exchange required is dependent on the atomic number of the nuclei on which the core orbital is located and, for heavier nuclei, the principal quantum number of the core orbital, with a larger fraction of HF exchange required for heavier nuclei. A physical interpretation of this may be the more compact the core orbital, the resulting overlap with the valence orbitals will be reduced and a greater proportion of HF exchange in the functional required.

Within a Δ Kohn–Sham framework, local exchange is not problematic for computing these states and the resulting core excitation energies do not show a systematic underestimation observed for the TD-B3LYP calculations. Initially, we will discuss the 1s excitations for the first row elements computed with the u6-311(2+,2+)G** basis set (Table II). The MAD for B3LYP of 0.5 eV represents a good agreement with experiment and is comparable to the accuracy that is achieved for valence excitations. At the MP2 level of theory, the MAD of 0.7 eV is slightly higher. These values compare with MADs of 0.5 and 0.9 eV for the 6-311(2+,2+)G** basis set with contracted core (data not shown). Consequently, uncontracting the core orbital gives a small improvement in accuracy for MP2. Overall, an error of 0.5 eV represents a good agreement with experiment and only slightly worse than would be expected for a comparable set of valence (UV) excited states. Table II also shows oscillator strengths computed using B3LYP. Detailed qualitative analysis of oscillator strengths is not feasible. However, some qualitative analysis is possible. Transitions to valence orbitals are predicted to have greater intensity than transitions to Rydberg orbitals, in agreement with experiment. For example, the K -edge spectrum of CO₂ shows an intense band with two weaker bands at higher energy, corresponding to 3s and 3p excitations.⁴⁷ The calculated oscillator strengths for

the π^* , 3s, and 3p excitations are 0.57, 0.04, and 0.09, respectively, which is consistent with the experimental spectrum.

Table III shows the computed core-excitation energies for excitations from 1s and 2p orbitals localized on second row atoms. The TD-B3LYP results continue to show the underestimation in the excitation energy and this becomes more severe as the nuclear charge of the atoms increase. Similar to the results for the first row atoms, B3LYP provides slightly more accurate results than MP2. However, for both methods there is an increase in the error compared to the first row elements. Although if expressed as a percentage, the error is small; for interpreting experimental spectra it is useful to have accurate predictions of the absolute excitation energy. For the second row atoms the relativistic effects become more important. For the Si, P, S, and Cl atoms, the lowering of the 1s orbital due to relativity is computed to be 4.4, 6.0, 7.8, and 10.2 eV, respectively. For the 2p orbitals, the effect of relativity is much smaller, and is less than 0.2 eV. It is likely that our current description of the relativistic effects does introduce some error into the calculations and for heavier elements this may constitute a significant part of the observed error. Based on energy level splitting arising from spin orbit coupling reported elsewhere,⁴⁸ it is possible to adjust the 2p excitations to the weighted average of the excitations including spin-orbit coupling. Overall, this leads to a small improvement in the calculated excitation energies. However, due to the relatively small number of 2p excitations in the data the MAD does not change.

Another important feature of the calculations on heavier elements is the basis set. The more compact core holes associated with the elements of higher nuclear charge will also place greater demands on the basis set. If the standard

TABLE IV. Computed excitation energies (in eV) for CuCl_4^{2-} and plastocyanin. Experimental data from Refs. 49, 51, and 53.

Excitation	Exp.	TD-B3LYP	B3LYP	B3LYP
		6-311(2+,2+)G ^{**a}	6-311(2+,2+)G ^{**a}	u6-311(2+,2+)G ^{**a}
CuCl_4^{2-}				
$\text{Cu}(1s) \rightarrow 3d$	8979	8867	8986	8980
$\text{Cu}(2p) \rightarrow 3d$	931	932	946	936
$\text{Cl}(1s) \rightarrow 3d$	2820	2765	2840	2818
Plastocyanin				
$\text{Cu}(1s) \rightarrow 3d$	8978	8863	8986	8980
$\text{Cu}(2p) \rightarrow 3d$	931	929	946	936
$\text{S}(1s) \rightarrow 3d$	2469	2417	2465	2466

^a6-31(2+,2+)G^{**} for Cu.

6-311(2+,2+)G^{**} basis set with contracted basis functions is used, MADs of 2.6 and 3.5 eV are obtained for B3LYP and MP2, respectively. Consequently, uncontracting the basis functions does lead to a significant improvement and is evidence that a large number of uncontracted basis functions provides greater flexibility, particularly for the core region, to describe the core excited states of the heavier elements.

C. X-ray absorption spectra of plastocyanin

Plastocyanin is a copper-containing metalloprotein involved in electron transfer. The highest occupied MO of the active site of plastocyanin is a singly occupied orbital that is a mixture of the $3d_{x^2-y^2}$ orbital of copper and the $3p$ orbitals of the sulfur ligands. The electronic structure of the active site can be probed by x-ray absorption spectroscopy.^{49–52} The accurate calculation of these core excitations represents a significant challenge for theory. These studies have measured excitations from the copper center and the ligand. Table IV shows the computed excitation energies for the pre-edge features for plastocyanin and the related model system CuCl_4^{2-} . The calculations use geometries taken from the crystal structures (see Fig. 1) and the 6-311(2+,2+)G^{**} basis set. Unfortunately, this basis set is not available for copper and the 6-31(2+,2+)G^{**} basis set was used for the copper atoms.

For both CuCl_4^{2-} and plastocyanin, the TD-B3LYP core excitation energies are too low. However, the exception is for the $\text{Cu}(2p) \rightarrow 3d$ excitation, which is close to the value from experiment. This is in part because of the underestimation of TDDFT for excitations from $2p$ orbitals is much less than for $1s$ excitations. The predicted excitation energies for the MOM with the 6-311(2+,2+)G^{**} basis set with contracted

basis functions are much closer to the experiment. However, the magnitude of the errors for some of the states is large and overall the results are not satisfactory. In particular, the $\text{Cu}(2p) \rightarrow 3d$ excitation and $\text{Cl}(1s) \rightarrow 3d$ excitation energies are predicted to be too large by 10 eV or greater. Again, the source of this error is likely to be associated with the correction for relativity and the basis set used. If the basis functions are uncontracted there is a significant improvement in the predicted excitation energies and errors of 2–5 eV are obtained. This represents a much more satisfactory agreement with experiment, and, since this basis set is of a relatively modest size, it can be applied to large systems like metalloproteins. The computed intensities are only nonzero for the excitations from the $2p$ orbitals, where oscillator strengths of 0.05 and 0.03 are predicted for CuCl_4^{2-} and plastocyanin, respectively. This is consistent with experiment where excitations for the K -edge are evident in other types of spectroscopy, such as magnetic circular dichroism.

IV. CONCLUSIONS

Δ SCF methods provide a convenient method for computing CEBEs. In this work, we used the MOM to prevent the variational collapse and converge the SCF calculation for the core excited state. For these calculations, it is important that the basis set can describe the core region adequately. In calculations of CEBEs, uncontracting the basis functions of the 6-311G^{**} basis set can improve the results to a quality that matches the much larger cc-pCVQZ basis set. This provides a computationally inexpensive approach that can be applied to large systems. For calculations involving excitations of core electrons, relativistic effects are important. Even for calculations of CEBEs for first row atoms, incorporating a relativistic correction leads to a closer agreement with experiment for B3LYP and MP2.

For core excitations B3LYP predicts more accurate core excitation energies than MP2 for excitations from core orbitals on both first and second row atoms. For the 6-311(2+,2+)G^{**} basis set with uncontracted basis functions, a MAD of 0.5 and 0.7 eV is obtained for the first row atoms with B3LYP and MP2, respectively. A MAD of 0.5 eV represents a good agreement with experiment, which is only slightly worse than the typical accuracy of DFT calculations for excitations of the valence electrons. For core excitations

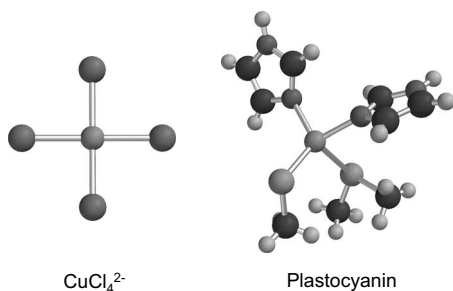


FIG. 1. Structure of CuCl_4^{2-} and the active site of plastocyanin.

from atoms of higher nuclear charge, two factors become more significant. The basis set requires the flexibility to describe compact core holes and the magnitude of the relativistic correction increases. The first of these problems can be addressed by uncontracting the basis functions. With the $u6-311(2+,2+)G^{**}$ basis set a MAD of 1.5 and 1.8 eV is obtained for the core excitations from second row nuclei. This represents a significant improvement on MADs of 2.6 and 3.5 eV for the same basis set with contracted functions. The remaining rise in error is likely associated with an increase in the size of the relativistic effects. In this work, these have been estimated from relativistic calculations on the corresponding atoms. This is likely to introduce some error and it would be more desirable to incorporate the relativistic calculation directly within the MOM calculations for the ground and core excited states. We are planning to pursue this development. Calculations of the pre-edge features of plastocyanin and $CuCl_4^{2-}$ illustrate these issues further. With the standard $6-311(2+,2+)G^{**}$ basis set, the computed excitation energies have large errors. However, uncontracting the basis functions leads to more satisfactory results with errors of 2–5 eV. Overall, if relativistic effects are taken into account and care is taken with the choice of basis set, ΔSCF approaches provide an accurate and convenient method for computing core excited states that can be applied to large systems.

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