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ABSTRACT

Vertical core excitation energies are obtained using a combination of the ΔSCF method and the diagonal second-order self-energy approximation. These methods are applied to a set of neutral molecules and their anionic forms. An assessment of the results with the inclusion of relativistic effects is presented. For core excitations involving delocalized symmetry orbitals, the applied composite method improves upon the overestimation of ΔSCF by providing approximate values close to experimental K-shell transition energies. The importance of both correlation and relaxation contributions to the vertical core-excited state energies, the concept of local and nonlocal core orbitals, and the consequences of breaking symmetry are discussed.

I. INTRODUCTION

X-ray spectroscopy is a powerful experimental technique for elucidating the excited state physics of materials.[1–10] The features of the observed spectral profile create a "fingerprint" characteristic of the atom or molecule under optical excitation. In particular, x-ray absorption spectroscopy (XAS) is used to probe element specific core-excited state properties in the soft x-ray region. Interpretations of x-ray spectra often rely on calculations based on *ab initio* quantum chemical methods. As such, approaches based on density functional and wavefunction theories have been developed for the accurate simulation of various x-ray spectroscopies.[11]

The nature of a core-hole state generated by the excitation of a K-shell electron must be described by dynamical quantum many-body effects within the local electronic structure. The challenge for accurate and predictive simulation of these core-excited states is to properly account for orbital relaxation and correlation. State-of-the-art methods for the direct computation of core excitation energies, such as the algebraic diagrammatic construction[12–14] (ADC) and coupled cluster[15,16] (EOM-CC, CCn), in the core-valence separation (CVS) approximation, can reproduce x-ray spectra to a high degree of accuracy. Recent developments of excited state mean field theory[17] (ESMF) and non-orthogonal configuration interaction singles[18] (NOCIS) have produced viable results for K-edge excitation energies at reasonable cost. Multireference configuration interaction calculations have been used to accurately describe core excitations in small molecules.[19–21] Additionally, the multiconfigurational self-consistent field (MCSCF) class of methods along with perturbative spin–orbit treatments has also seen successful application in this area.[22–24] However, the steep computational scaling involved with such methods often limits their applicability to a small set of modest-sized systems. For this reason, the computational cost of self-consistent field (SCF) methods is especially attractive and ΔSCF based models remain quite popular in computational studies of core-excited states.

Historically, the ΔSCF approach with Hartree–Fock (HF) had been employed in the computation of ionization energies.[25,26] In recent years, ΔSCF has been used in conjunction with maximum

overlap methods for computing core excitation energies and binding energies due to the simplicity of separately optimizing the MOs of two reference states.[27–30] For weakly correlated systems, SCF determinants are often a good approximation for the ground electronic state. The reference orbitals of a good HF wavefunction are a viable guess basis for an excited SCF calculation. Through ΔSCF, much of the orbital relaxation is accounted for—quite evidently so with localized core ionizations and excitations.[31–33] What remains to be accounted for is the many-body correlation via two (or more) particle interactions.

With HF lacking correlation, one may be inclined to use Kohn–Sham density functional theory (DFT). However, the sensitivity to the approximate functional makes it difficult to control the inclusion of correlation in a ΔDFT calculation—possibly leading to inconsistent results. Systems involving degenerate configurations and transitions beyond a nondegenerate HOMO–LUMO gap can also be challenging for DFT. The restricted open-shell Kohn–Sham (ROKS) approach has been employed by Hait and Head-Gordon for obtaining accurate vertical core excitation energies.[34,35] Alternatively, we propose the adoption of Hartree–Fock solutions as a fundamental, parameter-free starting point for computing excitation gaps.

This work presents a composite model for computing vertical core excitation energies with ΔHF and diagonal second-order correlation corrections to Koopmans' theorem for ionization potentials using electron propagator theory (EPT). The combination of ΔSCF and post-HF methods in the context of core-excited states is seldom explored. However, an analogous method for computing binding energies was developed and tested some time ago.[36,37] It was proposed that the total relaxation effects contained within the ΔSCF result between the N and $N-1$ determinants and that the correlation contributions are contained in the second-order self-energy for an electron detachment. With that observation in mind, this work explores the potential for a similar reasoning applied to N-conserving electronic excitations. As shown below, the quality of excitation energies using this compound model chemistry approach depends on the quality of EPT results for the core orbital. It is also shown that the locality of core orbitals and non-equivalency of neighboring atoms often lead to accurate results using only ΔHF.

II. METHODS

To compute core excitation energies, we propose a composite model combining quantum chemical methods with ΔSCF that treat dynamical correlation, corrected spin state energetics from an approximate spin projection method, and relativistic effects.

A. Electron propagator theory

The electron propagator formalism[31,38–45] provides a systematic framework for the inclusion of correlation in the one-electron picture of molecular electronic structure. EPT calculations generate Dyson orbitals as well as correlated binding and detachment energies without the need for determining wavefunctions and eigenvalues of total electronic states. The electron propagator, or one-electron Green's function, provides an approach for obtaining both qualitative and quantitative descriptions of chemical bonding and interpretation of spectra. In this section, we will briefly cover the basics of EPT and the approximate methods selected for computing the results featured in this work.

1. One-electron Green's function

Beginning with the Møller–Plesset partitioning of the nonrelativistic molecular Hamiltonian H,

$$H = H_0 + V, \tag{1}$$

where H_0 is taken to be the Fock operator and the fluctuation potential V is approximated as an energy dependent effective potential $\mathbf{\Sigma}(E)$, coined the "self-energy," which can be expanded as a perturbative series to arbitrary order. We aim to solve the inverse Dyson equation for the electron propagator matrix $\mathbf{G}(E)$,

$$(\mathbf{G}(E))^{-1} = (\mathbf{G}_0(E))^{-1} - \mathbf{\Sigma}(E). \tag{2}$$

By taking the Fock operator resolvent $\mathbf{G}_0(E)$ (the HF Green's function) in a spin–orbital basis,

$$\mathbf{G}_0(E) = (E\mathbb{1} - H_0)^{-1}, \tag{3}$$

one can obtain the real-valued simple poles of the propagator. The poles, or energies where the singularities of one-electron Green's function $\mathbf{G}_0(E)$ lie, occur at the HF eigenvalues ϵ. By requiring $(\mathbf{G}(E))^{-1} = 0$, we can recast the problem into a system of linear equations and solve

$$\det((E\mathbb{1} - \epsilon - \mathbf{\Sigma}(E)) = 0. \tag{4}$$

Since the lowest-order corrections to the orbital energies ϵ_i involve only the diagonal elements of the self-energy matrix, the above expression simplifies to

$$\prod_i ((E - \epsilon_i - \mathbf{\Sigma}_{ii}(E)) = 0. \tag{5}$$

For each correction to ϵ_i, we solve for E,

$$E = \epsilon_i + \mathbf{\Sigma}_{ii}(E). \tag{6}$$

This is done iteratively by first evaluating $\mathbf{\Sigma}_{ii}(E)$ at a guess pole $E = \epsilon_i$. The corrected HF orbital energies are, thus,

$$\omega = \epsilon_i + \mathbf{\Sigma}_{ii}(E). \tag{7}$$

$\mathbf{\Sigma}_{ii}(E)$ is evaluated at ω and Eq. (7) is solved iteratively until the convergence criteria is met. When the ith orbital is occupied, ω is an electron detachment energy; when it is unoccupied, ω is an electron attachment energy. The energies obtained arise from the diagonal quasiparticle equation,

$$[\mathbf{F} + \mathbf{\Sigma}_{ii}(E_i)]C_i^{Dyson} = C_i^{Dyson}\omega_i. \tag{8}$$

The minimum approximation to the self-energy that recovers the qualitative correlation correction to Koopmans' theorem is performed at diagonal second-order, $\mathbf{\Sigma}_{ii}^{(2)}(E)$. Explicit matrix elements of $\mathbf{\Sigma}_{ii}^{(2)}(E)$ are generated through electron field operator couplings. The manifold, $\mathbf{h}$, of elements from the linear space of field operators separated into two orthogonal subspaces, $\mathbf{a}^\dagger$ (primary) and $\mathbf{f}$ (secondary), is applied to superoperator energy matrix $\mathbf{H}$ using Löwdin's

partitioning method.[46] The elements of $\mathbf{G}(E)$ for the primary space are then

$$\mathbf{G}(E) \equiv \langle\langle \mathbf{a}; \mathbf{a}^\dagger \rangle\rangle_E = \left(\mathbf{a}^\dagger | (E\mathbb{1} - \mathbf{H})^{-1} \mathbf{a}^\dagger\right). \tag{9}$$

Through inner projection of $\mathbf{h}$, we obtain another form of the propagator matrix,

$$\mathbf{G}(E) = \left(\mathbf{a}^\dagger|\mathbf{h}\right)(\mathbf{h}|(E\mathbb{1} - \mathbf{H})\mathbf{h})^{-1}\left(\mathbf{h}|\mathbf{a}^\dagger\right). \tag{10}$$

The partitioned form of the propagator matrix becomes

$$\mathbf{G}(E) = \begin{bmatrix}\left(\mathbf{a}^\dagger|\mathbf{a}^\dagger\right) & \left(\mathbf{a}^\dagger|\mathbf{f}\right)\end{bmatrix}\begin{bmatrix}\left(\mathbf{a}^\dagger|(E\mathbb{1} - \mathbf{H})\mathbf{a}^\dagger\right) & \left(\mathbf{a}^\dagger|(E\mathbb{1} - \mathbf{H})\mathbf{f}\right) \\ \left(\mathbf{f}|(E\mathbb{1} - \mathbf{H})\mathbf{a}^\dagger\right) & (\mathbf{f}|(E\mathbb{1} - \mathbf{H})\mathbf{f})\end{bmatrix}^{-1} \times \begin{bmatrix}\left(\mathbf{a}^\dagger|\mathbf{a}^\dagger\right) \\ \left(\mathbf{a}^\dagger|\mathbf{f}\right)\end{bmatrix}. \tag{11}$$

Given the orthogonality conditions $\left(\mathbf{a}^\dagger|\mathbf{f}\right) = 0$, this simplifies to

$$\mathbf{G}(E) = \begin{bmatrix}\mathbb{1} & 0\end{bmatrix}\begin{bmatrix}E\mathbb{1} - \left(\mathbf{a}^\dagger|\mathbf{H}\mathbf{a}^\dagger\right) & -\left(\mathbf{a}^\dagger|\mathbf{H}\mathbf{f}\right) \\ -\left(\mathbf{f}|\mathbf{H}\mathbf{a}^\dagger\right) & (\mathbf{f}|\mathbf{H}\mathbf{f})\end{bmatrix}^{-1}\begin{bmatrix}\mathbb{1} \\ 0\end{bmatrix}. \tag{12}$$

The poles of the electron propagator, occurring at values $E = \omega$, are determined through the following eigensystem:

$$\mathbf{U}\omega = \mathbf{H}\mathbf{U}. \tag{13}$$

Here, $\mathbf{H}$ is the superoperator Hamiltonian matrix and $\mathbf{U}$ contains the residues connected to the jth pole ω_j. The matrix elements of $\mathbf{U}$ can be used to compute the Dyson orbitals of a particular pole,

$$\phi_j^{Dyson} = \sum_i \phi_i U_{ij}^*. \tag{14}$$

The probability factor, or pole strength, is given by

$$\pi_j = \sum_i |U_{ij}|^2. \tag{15}$$

In the diagonal approximation, a value of $\pi \geq 0.85$ is typically taken as an indication that the HF orbitals are a good reference for the Dyson orbitals.[47] Again, due to the orthogonality between primary and secondary spaces, the diagonal of $(\mathbf{h}|(E\mathbb{1} - \mathbf{H})\mathbf{h})^{-1}$ is needed. The inverse propagator matrix is given by

$$(\mathbf{G}(E))^{-1} = \left(\mathbf{a}^\dagger|(E\mathbb{1} - \mathbf{H})\mathbf{a}^\dagger\right) - \left(\mathbf{a}^\dagger|\mathbf{H}\mathbf{f}\right)(\mathbf{f}|(E\mathbb{1} - \mathbf{H})\mathbf{f})^{-1}\left(\mathbf{f}|\mathbf{H}\mathbf{a}^\dagger\right), \tag{16}$$

which reduces further to

$$(\mathbf{G}(E))^{-1} = E\mathbb{1}_\mathbf{a} - \mathbf{H}_{\mathbf{aa}} - \mathbf{H}_{\mathbf{af}}(E\mathbb{1}_a - \mathbf{H}_{\mathbf{ff}})^{-1}\mathbf{H}_{\mathbf{fa}}. \tag{17}$$

The set $\{\mathbf{f}_\mathrm{n}\}$ represents vectors of length n containing creation operators exceeding annihilation operators by one for either particles (p) or holes (h). For example, with general orbital indices $p, q, r, s, t, \ldots$, we have $\mathbf{f}_1 \equiv a_p^\dagger$ (h/p), $\mathbf{f}_3 \equiv a_p^\dagger a_q^\dagger a_r$ (2hp/2ph), $\mathbf{f}_5 \equiv a_p^\dagger a_q^\dagger a_r^\dagger a_s a_t$ (3h2p/3p2h), and so on. These operator "strings" generate the $N \pm 1$ states in a type of configuration interaction expansion in Hilbert space.

The set of field operators in the primary subspace $\mathbf{a}^\dagger$ can be taken to be the creation operator product $\mathbf{f}_1$ acting on the HF vacuum to generate a HF reference. Because one can choose the basis representation of the primary subspace, the first two terms in Eq. (17) result in the inverse HF Green's function $(\mathbf{G}(E))_0^{-1}$. The final term is, thus, the energy dependent part of the self-energy matrix $\boldsymbol{\sigma}(E)$ and the total self-energy is

$$\boldsymbol{\Sigma}(E) = \boldsymbol{\sigma}(E) + \boldsymbol{\Sigma}(\infty). \tag{18}$$

As $E \longrightarrow \infty$, $\boldsymbol{\sigma}(E)$ vanishes to leave the constant, or energy independent, form of the self-energy given by

$$\boldsymbol{\Sigma}(\infty)_{pq} = \sum_{rs} \langle pr||qs\rangle \rho_{rs}^c, \tag{19}$$

where ρ^c is the correction to the HF one-particle density ρ^{HF}.

2. Self-energy approximations

The simplest approximation to the self-energy within EPT selects the $\mathbf{f}_3$ operators to constitute the secondary space. This first-order approximation leads to the second-order self-energy matrix,

$$\boldsymbol{\Sigma}^{(2)}(E) = (\mathbf{a}|\mathbf{H}\mathbf{f}_3)^{(1)}\left(E\mathbb{1} - (\mathbf{f}_3|\mathbf{H}\mathbf{f}_3)^{(0)}\right)^{-1}(\mathbf{f}_3|\mathbf{H}\mathbf{a})^{(1)}. \tag{20}$$

The superscripts represent the nth order correction to the self-energy. The first correction $n = 1$, thus, begins at second-order perturbation. Diagonalizing the superoperator Hamiltonian, $\mathbf{H}$,

$$\mathbf{H}^{(1)} = \begin{bmatrix}(\mathbf{a}|\mathbf{H}\mathbf{a})^{(0)} & (\mathbf{a}|\mathbf{H}\mathbf{f}_3)^{(1)} \\ (\mathbf{f}_3|\mathbf{H}\mathbf{a})^{(1)} & (\mathbf{f}_3|\mathbf{H}\mathbf{f}_3)^{(0)}\end{bmatrix}, \tag{21}$$

gives the poles of $\boldsymbol{\Sigma}^{(2)}(E)$. Note that the matrix elements $(\mathbf{a}|\mathbf{H}\mathbf{a})^{(0)}$ and $(\mathbf{f}_3|\mathbf{H}\mathbf{f}_3)^{(0)}$ rely on just the Fock operator. Terms in the primary-secondary coupling blocks that also rely on the Fock operator are omitted to preserve the Hermiticity of $\mathbf{H}^{(1)}$; otherwise, these spurious terms will vanish as the reference configuration is improved to a sufficient order. Algebraic or diagrammatic derivation of the second-order self-energy-matrix elements yields

$$\boldsymbol{\Sigma}_{pq}^{(2)}(E) = \frac{1}{2}\sum_{aij}\frac{\langle ij||qa\rangle\langle pa||ij\rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2}\sum_{iab}\frac{\langle pi||ab\rangle\langle ab||qi\rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b}. \tag{22}$$

The hole indices $\{i, j, \ldots\}$ represent occupied spin–orbitals and particle indices $\{a, b, \ldots\}$ represent virtual spin–orbitals. The first and second summations of Eq. (22) are the 2hp and 2ph terms. If the canonical HF orbitals are sufficient approximations to the Dyson orbitals, we only need to evaluate the diagonal of $\boldsymbol{\Sigma}^{(2)}(E)$ by requiring pole index $p = q$,

$$\boldsymbol{\Sigma}_{pp}^{(2)}(E) = \frac{1}{2}\sum_{aij}\frac{|\langle pa||ij\rangle|^2}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2}\sum_{iab}\frac{|\langle pi||ab\rangle|^2}{E + \epsilon_i - \epsilon_a - \epsilon_b}. \tag{23}$$

If we take the second sum in Eq. (22) and separate terms with no dependency on E and set either a or b equal to i, we recover the contribution of single-particle excitations in the second-order energy. These singles substitutions are meant to improve the occupied space of the $N-1$ system toward a more optimal set of one-electron orbitals. This amounts to the orbital relaxation term

$$\Sigma_{pp}^{R(2)} = \sum_{ai} \frac{|\langle ap||ip\rangle|^2}{\epsilon_a - \epsilon_i}. \tag{24}$$

Note that $a \neq i$. The relaxation term $\Sigma_{pp}^{R(2)}$ is the second-order contribution to the ionization energy of orbital p from a ΔSCF calculation,

$$-I_p(\Delta\text{SCF}) = E_{HF}(N) - E_{HF}^{p}(N-1). \tag{25}$$

A generalization of relaxation contribution to the binding energy of orbital p at the ΔSCF level is presented as a correction to the HF eigenvalue ϵ_p,

$$-I_p(\Delta\text{SCF}) \simeq \epsilon_p - \Sigma_{pp}^{R(2)}. \tag{26}$$

Additionally, the correlation part of the diagonal second-order self-energy can be extracted as follows:

$$\Sigma_{pp}^{C(2)}(E) = \Sigma_{pp}^{(2)}(E) - \Sigma_{pp}^{R(2)}, \tag{27}$$

which can be rewritten as

$$\Sigma_{pp}^{C(2)}(E) = \frac{1}{2}\sum_{a}\sum_{i\neq p}\sum_{j\neq p} \frac{|\langle pa||ij\rangle|^2}{E+\epsilon_a-\epsilon_i-\epsilon_j} + \frac{1}{2}\sum_{i\neq p}\sum_{a}\sum_{b} \frac{|\langle pi||ab\rangle|^2}{E+\epsilon_i-\epsilon_a-\epsilon_b}. \tag{28}$$

The first term in Eq. (28) describes the correlation contribution of pair interactions of occupied i,j orbitals with unoccupied orbital a and the new virtual p, which is analogous to orbital relaxation but for the $N-1$ state. The second term in Eq. (28), related to typical second-order HF perturbation theory for the N-particle system, contains the correlation effects of losing pairwise interactions due to the removal of orbital p.[31,48]

B. ΔSCF + ΔΣ approach

Following the detailed protocol by Pickup and Goscinski[31] together with developments[36,37] in EPT by Öhrn, Ortiz, and others, one can recover an expression for the lowest-order correction to Koopmans' theorem,

$$-I = -I_p(\Delta\text{SCF}) + \Sigma_{pp}^{C(2)}(E). \tag{29}$$

This interpretation of the true binding energy retains a complete second-order description of relaxation and correlation contributions.

What has yet to be explored in great detail is the application of this concept to excitation energies for one-electron transitions. Following from the discussion above, we propose an approximation of the excitation energy ω_X given by

$$\omega_X \simeq E(\Delta\text{SCF}) + \Delta\Sigma^{C(2)}(E), \tag{30}$$

$$\simeq [E_{p\to r}(N) - E_0(N)] + \left[\Sigma_{rr}^{C(2)}(E_{N+1}) - \Sigma_{pp}^{C(2)}(E_{N+1})\right], \tag{31}$$

where $E(\Delta\text{SCF})$ is the difference between the excited $(E_{p\to r})$ and ground state (E_0) HF energies. $\Delta\Sigma^{C(2)}(E)$ is the difference between the correlation corrections to ϵ_r and ϵ_p. These terms are computed for the $N+1$ determinant, the propagator reference, where orbitals p and r are both occupied. This anionic species is used to provide a model configuration for obtaining correlation energy gaps.

Since core-hole configurations are often subject to variational collapse in the SCF procedure, we make use of a maximum overlap algorithm to obtain representative single determinant excited state solutions of the desired configuration. Here, we have chosen the projected initial maximum overlap method (PIMOM).[49] The SCF excited states are unrestricted Hartree–Fock (UHF) solutions obtained after an occupied-virtual orbital rotation.

As a consequence of the symmetry dilemma,[50] these excited state solutions often break spin and electronic state symmetry in exchange for a lower energy. For closed-shell initial states, the core excitation process should involve a linear combination of open-shell configurations, since either the up-spin or down-spin electron can be substituted. With a single unrestricted determinant, an estimate for the energy of a proper spin eigenstate for the excited state is computed using approximate projection (AP) according to[51–53]

$$E_{AP} = aE_{LS} + (1-a)E_{HS}, \tag{32}$$

where the weight or single annihilation parameter a is

$$a = \frac{\langle \mathcal{S}_{HS}^2\rangle - S_{z,LS}(S_{z,LS}+1)}{\langle \mathcal{S}_{HS}^2\rangle - \langle \mathcal{S}_{LS}^2\rangle}. \tag{33}$$

Here, E_{LS} is the energy of the spin contaminated core-hole configuration and E_{HS} is the energy of its $S+1$ counterpart. AP is then applied for excited state ΔSCF calculations.

C. Relativistic corrections

To attain a proper description of core electron physics, relativistic effects need to be considered. Bethe and Salpeter defined the relativistic shift in the ionization potential for a two-electron atom as[54]

$$E_J = \alpha^2\left[-\frac{1}{8}Z^4 + \frac{1}{4}\langle p_1^4\rangle - \pi Z\langle\delta^{(3)}(\mathbf{r}_1)\rangle - \pi\langle\delta^{(3)}(\mathbf{r}_{12})\rangle\right] - E_2. \tag{34}$$

Extensions of this model to higher Z and formulas for the expectation values above have been provided by Pekeris, Silverman, and Scherr.[55,56] For consistency, E_J for a particular atom is included in our model in an *ad hoc* fashion to the computed nonrelativistic core excitation energy to obtain ω_X. Following this protocol, our calculated corrections for C, N, O, and F are 0.1, 0.2, 0.4, and 0.7 eV, respectively. We note that these values agree with those previously reported.[14,57]

III. RESULTS AND DISCUSSION

A test set has been selected from the Chong-Gritsenko-Baerends (CGB) dataset, which has been reported in prior

publications.[58,59] These structures were optimized using coupled-cluster with singles, doubles, and perturbative triples [CCSD(T)] model with the aug-cc-pVTZ basis set. Additional molecules were selected from the NIST CCCBDB[60] and were optimized using the same level of theory. All calculations were performed with a development version of GAUSSIAN.[61] Reference single-point SCF calculations used the aug-cc-pVTZ basis. Diagonal second-order (D2) calculations used the cc-pVTZ basis with a full MO integral transformation window. Neutral and anion reference determinants were generally eigenstates of the total spin-squared operator $\mathcal{S}^2$, except for the heterocyclic molecules. Furan, imidazole, tetrazine, pyridine, and thiophene anions possess $\langle \mathcal{S}^2 \rangle$ values that deviate from $S(S+1)$ by ~10%–18%. Mean pole strengths for core and valence electron detachments are 0.73 and 0.92, respectively.

Table I reports the vertical excitation energies obtained with only ΔSCF. The absence of degenerate or quasi-degenerate core orbitals for a particular atom tends to minimize the interactions of configurations relevant for describing the excited state, meaning that the correlation contribution to the energy is much less than the orbital relaxation in these cases. As such, it is not surprising that the computed ΔSCF energies with relativistic corrections are well in the vicinity of experimental values (see Table II) since the atomic cores of interest are unique and other core orbitals belonging to atoms of the same bonding class are not present. The differences in the measure of errors between excitation energies computed with (MAE: 0.6 eV, RMSE: 0.8 eV) and without relativistic effects (MAE: 0.6 eV, RMSE: 0.7 eV) are shown to be minimal for this dataset.

TABLE I. ΔSCF vertical excitation energies ω_X for the lowest symmetry-allowed core to valence transition.

Molecule	Core	ΔSCF (eV)	ω_X (eV)	Expt. (eV)
Acetone	C (C–O)	287.3	287.4	286.4[67]
Acetone	O	531.0	531.4	531.4[67]
Acrolein	C (C–O)	286.7	286.8	286.1[68]
Acrolein	O	530.2	530.6	530.6[68]
CH4	C	289.8	289.9	288.0[69]
CO	C	288.4	288.5	287.4[70]
CO	O	533.7	534.1	534.2[70]
Furan	O	535.1	535.5	535.2[71]
H_2CO	C	286.5	286.6	285.6[72]
H_2CO	O	530.6	531.0	530.8[72]
H_2O	O	534.3	534.7	534.0[69]
HF	F	687.3	688.0	687.4[73]
NH_3	N	401.1	401.3	400.8[69]
Pyridine	N	398.8	399.0	398.8[74]
CO_2	C	292.4	292.5	290.8[75]
Imidazole	N (N–H)	403.2	403.4	402.3[76]
Imidazole	N	400.4	400.6	399.9[76]
N_2O	N (N–N)	401.2	401.4	401.0[75]
N_2O	N (N–O)	404.7	404.9	404.6[75]
N_2O	O	534.1	534.5	534.6[75]
HCN	C	286.9	287.0	286.4[77]
HCN	N	400.0	400.2	399.7[77]
CF_2O	C	292.2	292.3	290.9[78]
CF_2O	O	532.7	533.1	532.7[78]
NO	N	400.0	400.2	399.7[79]
NO	O	532.2	532.6	532.7[79]
CH_3OH	C	289.0	289.1	288.1[80]
CH_3OH	O	534.3	534.7	534.1[67]
CH_3NH_2	C	288.2	288.3	287.5[80]
CH_3NH_2	N	401.2	401.4	400.6[80]

TABLE II. Mean absolute error (MAE) and root-mean-square error (RMSE) in eV.

	ΔSCF with rel.	ΔSCF
MAE	0.6	0.6
RMSE	0.8	0.7

Systems for which core excitations are poorly described using ΔSCF are thus candidates for treatment with EPT based models. To avoid double counting of orbital relaxation recovered with ΔSCF, $\Delta\Sigma^{R(2)}$ must be removed from the self-energy correction to binding energies obtained with Koopmans' theorem. Results using the ΔSCF + $\Delta\Sigma^{C(2)}$ method are given in Tables III and IV. ΔSCF results for core excitations in the set of molecules with equivalent atoms highly overestimate experimental values—with errors exceeding 10 eV. Significant improvements are made when $\Delta\Sigma^{C(2)}$ is added along with relativistic corrections for each atom type (MAE: 1.3 eV, RMSE: 1.7 eV). Errors here slightly increase when relativistic effects are ignored.

Although the ΔSCF method is satisfactory for the molecules in Table I, an evaluation of changes in the data with the introduction of D2 self-energy corrections is performed for completeness and summarized in Tables V and VI. The addition of $\Delta\Sigma^{C(2)}$ consistently underestimates experiment and overcorrects ΔSCF energies. This is a residual, nonphysical effect of using the difference in the

TABLE III. ΔSCF + $\Delta\Sigma^{C(2)}$ vertical excitation energies ω_X for the lowest symmetry-allowed core to valence transition.

Molecule	Core	ΔSCF (eV)	$\Delta\Sigma^{C(2)}$ (eV)	ω_X (eV)	Expt. (eV)
C_2H_2	C	294.0	−9.3	284.8	285.9[81]
C_2H_4	C	293.0	−9.2	283.8	284.7[81]
C_2H_6	C	294.5	−8.6	286.0	286.9[81]
C_2N_2	C	293.3	−8.5	284.9	286.3[77]
C_2N_2	N	410.4	−11.6	398.9	398.9[77]
F_2	F	695.2	−13.5	682.3	682.2[73]
N_2	N	410.5	−10.5	400.2	400.9[82]
O_2	O	542.0	−11.9	530.5	530.8[79]
Pyridine	C	294.6	−9.7	285.0	285.3[74]
Tetrazine	N	413.6	−14.4	399.4	398.8[83]
Tetrazine	C	293.8	−7.6	286.3	285.2[83]
Thiophene	C (C–S)	294.4	−8.5	286.0	285.4[84]
CO_2	O	546.6	−14.4	532.6	535.4[75]
Furan	C	295.8	−8.2	287.7	286.6[71]
CF_2O	F	700.9	−16.4	685.3	689.2[78]
C_2F_4	C	298.7	−10.8	287.9	290.1[85]
C_2F_4	F	708.4	−21.8	687.3	690.7[85]

TABLE IV. Mean absolute error (MAE) and root-mean-square error (RMSE) in eV.

	ΔSCF + $\Delta\Sigma^{C(2)}$ with rel.	ΔSCF + $\Delta\Sigma^{C(2)}$	ΔSCF with rel.	ΔSCF
MAE	1.3	1.4	10.6	10.4
RMSE	1.7	1.9	11.0	10.7

correlation terms of the D2 approximation for two independent ionizations in the anions.

Reducing point group symmetry or applying effective core potentials (ECP) can localize the core orbital and improve estimates to ω_X. Table VII contains energies computed with ΔSCF alone for the dataset in Table III but with broken molecular symmetry. For molecules with $D_{\infty h}$, D_{3d}, or D_{2h} symmetry, multi-electron Wood–Boring ECPs (MWB2) are applied to all atoms except hydrogen and the atom of interest. For all other molecules, the symmetries are reduced to C_1. With this pragmatic approach, errors (see Table VIII) are reduced to about half of an electron volt (MAE: 0.5 eV, RMSE: 0.5 eV). This remarkable but well-known effect ameliorates the problems that arise from quasi-degeneracy and delocalization at the cost of losing symmetry and its usefulness for theoretical assignment spectral signatures.

A qualitative effect of adding correlation corrections to Hartree–Fock energy gaps is apparent. However, quantitative predictions of vertical core excitation energies with this method can vary as there are multiple factors at play. For example, modeling excited states of neutral molecules through electron detachments within the $N + 1$ configurations lacks a one-to-one correspondence with respect to the relaxation of the target N electron core-hole state. For errors that manifest in ΔSCF calculations, different non-Aufbau SCF solutions representing an excited state configuration can be obtained depending on basis projections, overlap metrics, and convergence criteria—all of which can alter the ΔSCF result. Since the quality of the poles is dependent on the quality of the reference determinant, it is important to note an additional layer of error is present

TABLE V. ΔSCF + $\Delta\Sigma^{C(2)}$ vertical excitation energies ω_X for the lowest symmetry-allowed core to valence transition.

Molecule	Core	ΔSCF (eV)	$\Delta\Sigma^{C(2)}$ (eV)	ω_X (eV)	Expt. (eV)
Acetone	C (C–O)	287.3	−3.5	283.9	286.4[67]
Acetone	O	531.0	−1.6	529.8	531.4[67]
Acrolein	C (C–O)	286.7	−3.4	283.5	286.1[68]
Acrolein	O	530.2	−2.2	528.4	530.6[68]
CH4	C	289.8	−3.5	286.3	288.0[69]
CO	C	288.4	−3.5	285.1	287.4[70]
CO	O	533.7	−2.5	531.6	534.2[70]
Furan	O	535.1	−2.4	533.1	535.2[71]
H_2CO	C	286.5	−4.5	282.1	285.6[72]
H_2CO	O	530.6	−3.1	527.8	530.8[72]
H_2O	O	534.3	−5.2	529.5	534.0[69]
HF	F	687.3	−5.5	682.6	687.4[73]
NH_3	N	401.1	−2.7	398.6	400.8[69]
Pyridine	N	398.8	−3.6	395.3	398.8[74]
CO_2	C	292.4	−5.3	287.2	290.8[75]
Imidazole	N (N–H)	403.2	−1.4	402.0	402.3[76]
Imidazole	N	400.4	−2.5	398.1	399.9[76]
N_2O	N (N–N)	401.2	−1.5	399.9	401.0[75]
N_2O	N (N–O)	404.7	−2.4	402.5	404.6[75]
N_2O	O	534.1	−1.4	533.1	534.6[75]
HCN	C	286.9	−3.2	283.8	286.4[77]
HCN	N	400.0	−2.6	397.6	399.7[77]
CF_2O	C	292.2	−4.7	287.6	290.9[78]
CF_2O	O	532.7	−4.7	528.4	532.7[78]
NO	N	400.0	−3.2	397.0	399.7[79]
NO	O	532.2	−2.1	530.4	532.7[79]
CH_3OH	C	289.0	−3.6	285.4	288.1[80]
CH_3OH	O	534.3	−4.6	530.1	534.1[67]
CH_3NH_2	C	288.2	−3.1	285.1	287.5[80]
CH_3NH_2	N	401.2	−3.7	397.7	400.6[80]

TABLE VI. Mean absolute error (MAE) and root-mean-square error (RMSE) in eV.

	ΔSCF + $\Delta\Sigma^{C(2)}$ with rel.	ΔSCF + $\Delta\Sigma^{C(2)}$	ΔSCF with rel.	ΔSCF
MAE	2.6	2.9	0.6	0.6
RMSE	2.8	3.1	0.8	0.7

TABLE VII. ΔSCF vertical excitation energies ω_X for the lowest symmetry-allowed core to valence transition with core localization.

Molecule	Core	ΔSCF (eV)	ω_X (eV)	Expt. (eV)
C_2H_2	C	286.0	286.1	285.9[81]
C_2H_4	C	285.0	285.1	284.7[81]
C_2H_6	C	287.2	287.3	286.9[81]
C_2N_2	C	286.3	286.4	286.3[77]
C_2N_2	N	398.6	398.8	398.9[77]
F_2	F	680.7	681.4	682.2[73]
N_2	N	400.7	400.9	400.9[82]
O_2	O	530.9	531.3	530.8[79]
Pyridine	C	285.9	286.0	285.3[74]
Tetrazine	N	398.2	398.4	398.8[83]
Tetrazine	C	286.2	286.3	285.2[83]
Thiophene	C (C–S)	286.1	286.2	285.4[84]
CO_2	O	535.1	535.5	535.4[75]
Furan	C	287.0	287.1	286.6[71]
CF_2O	F	689.2	689.9	689.2[78]
C_2F_4	C	290.5	290.6	290.1[85]
C_2F_4	F	690.4	691.1	690.7[85]

TABLE VIII. Mean absolute error (MAE) and root-mean-square error (RMSE) in eV.

	ΔSCF with rel.	ΔSCF
MAE	0.5	0.4
RMSE	0.5	0.6

when there is spin contamination in the anions. Whenever possible, propagator references with good intrinsic spin quantum numbers are preferred.[62,63]

Finally, the choice of relativistic correction may vary the magnitude of ω_X significantly with increasing atomic number and heightened many-electron correlation in the core region. In addition to the technique applied in this study, there many other methods in relativistic quantum chemistry to choose from.[64–66] Nonetheless, the composite model introduced here provides a reasonable estimate to core excitation energies and appears to balance static and dynamic correlation effects well with affordable computational cost.

The qualitative utility of the ΔSCF + ΔΣ model for predicting vertical core excitation energies is reflected in the moderate deviations from experimental values. The "relaxation error" is pronounced for K-shell ionizations or excitations, more so when the core orbitals are delocalized, and the relative importance of relaxation $\mathbf{\Sigma}^R$ and correlation $\mathbf{\Sigma}^C$ contributions varies between the core and valence regimes.[86,87] For ionizations of local, nonequivalent cores, ΔSCF recovers the bulk of the relaxation effects.[88,89]

Lone pairs and double bonds between equivalent atoms (which give rise to degenerate orbitals) enhance the correlation effects involving the interaction of degenerate configurations. In cases of strong correlation, ΔHF tends to overestimate the excitation energy. Cederbaum and Domcke[90] have explained that when there are no degenerate or closely degenerate core orbitals, the correlation energy becomes very small in comparison to the relaxation energy found in $\mathbf{\Sigma}^{(2)}_{pp}(E)$. In the case of homonuclear diatomics (e.g., N_2), they have shown that the degeneracy of the delocalized orbitals with *gerade* and *ungerade* symmetry, σ_g and σ_u, causes the correlation contribution to the self-energy to become competitive in magnitude to the relaxation component. With two delocalized, symmetry orbitals close in energy, ΔHF results will not include the now increased correlation effects.

If one lifts the symmetry constraints (i.e., reduce the molecular symmetry) and localizes the basis for the cores, the total SCF relaxation energy becomes a mixture of orbital relaxation and pair correlation in the relaxed $N-1$ state. This explains why ΔSCF for K-shell electron detachments often yields good agreement with experiment when the core orbitals are localized. However, by breaking symmetry, the admixture of orbital relaxation and correlation effects in the excited SCF solutions obtained with HF or Kohn-Sham DFT limits its systematic improvements with perturbation theory. More recent studies have further explored the errors that arise from using localized/delocalized core orbitals with a variety of methods for modeling x-ray spectroscopy.[91]

Computing core excitation energies using ΔSCF + $\Delta\Sigma^{C(2)}$ requires a balanced treatment of orbital relaxation and correlation effects. Correlation corrections to ΔSCF are heavily modulated by the quality of the pole of the excited core orbital. Higher-order approximations to the self-energy beyond D2 may be needed to obtain accurate core binding energies. Computing self-energy gaps with electron affinities starting from a core-hole cation reference state may be an alternative to an ionization-based approach, although, some precautions must be taken to deal with numerical instabilities that may accompany a non-Aufbau core-hole reference with post-HF methods.[92] Additionally, varying the occupation number of the target core orbital via the transition operator method[93,94] may also be a relevant approach toward increasing the quality of the self-energy.

IV. CONCLUSIONS

We have presented computational results for core excitation energies using ΔHF and the diagonal second-order self-energy approximation. The efficacy of obtaining accurate excitation energies with only ΔHF when core orbitals are localized is reaffirmed. Without reducing molecular symmetry, the results calculated with the proposed ΔSCF + ΔΣ composite method for chemical species with degenerate C, N, O, and F core orbitals are in good agreement with experimental energies. Separating the orbital relaxation energy recovered with ΔSCF and correlation energy gaps determined with the D2 self-energy approximation provides a step toward a systematic approach for estimating vertical core excitation energies. With a limiting step of generating the MO integrals, the $\mathcal{O}(OV^2)$ arithmetic scaling of diagonal second-order EPT is indeed a low-cost choice as a post-HF method to be used with ΔSCF for calculating core excitation energies.

Studies of K- and L-edge transitions beyond second period elements and computation of cross sections for simulating spectra will be important diagnostics for this model and will be examined in a future work. Further exploration of practical, low-scaling composite models for computing excitation energies with different electron propagator methods is also underway.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Abdulrahman Y. Zamani: Investigation (lead); Methodology (lead); Validation (lead); Writing – original draft (lead); Writing – review & editing (lead). **Hrant P. Hratchian**: Funding acquisition (equal); Methodology (equal); Resources (equal); Software (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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