Assessing the performance of $\Delta$SCF and the diagonal second-order self-energy approximation for calculating vertical core excitation energies

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Vertical core excitation energies are obtained using a combination of the $\Delta$SCF method and the diagonal second-order (D2) 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. The importance of both correlation and relaxation contributions to the vertical core-excited state energies, the concept of local and non-local core orbitals, and the consequences of breaking symmetry are discussed.

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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 \textit{ab initio} quantum chemical methods. As such, approaches based on density functional and wave function 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 properly accounting 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, CC\(_n\)), 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 have also seen successful application in this area.\(^{22-24}\) However, the steep scaling that accompanies some of these methods often go beyond the conventional \(O(N^5)\) integral transformation to the molecular orbital (MO) basis. For this reason, the computational cost of self-consistent field (SCF) methods, remains attractive.

Historically, the \(\Delta\text{SCF}\) approach with Hartree-Fock (HF) had been employed in the computation of ionization energies.\(^{25,26}\) In recent years, \(\Delta\text{SCF}\) has been used in conjunction with maximum overlap methods for computing core excitation energies and core binding energies due to the simplicity of separately optimizing the MOs of two reference states.\(^{27,28}\) Through \(\Delta\text{SCF}\), much of the orbital relaxation is accounted for—quite evidently so with core excitations. What remains to be accounted for is dynamical correlation via two (or
more) particle interactions.

With HF lacking correlation, logically, one may be inclined to use Kohn-Sham 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 non-degenerate HOMO-LUMO gap can of course cause complications for DFT as well. The restricted open-shell Kohn-Sham (ROKS) approach has been employed by Hait and Head-Gordon for obtaining accurate vertical core excitation energies.\(^{29,30}\) However, restricted open-shell HF (ROHF) or ROKS orbitals and orbital energies have ambiguous validity as solutions to the mean-field equations. Perhaps a fundamental, parameter-free, and physically meaningful starting point for computing excitation gaps can be adopted instead.

This work presents a method 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 long ago.\(^{31,32}\) 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. It follows that a similar reasoning can be applied to \(N\)-conserving electronic excitations. With a limiting step of generating the MO integrals, the \(O(OV^2)\) arithmetic scaling of diagonal second-order EPT is indeed a low-cost choice as a post-HF method. We will show the quality of excitation energies depends on the EPT results for the core orbital. Also, we show that the locality of the core and non-equivalency of neighboring atoms lead to accurate results with just ΔHF.
II. METHODS

A. Electron Propagator Theory

The electron propagator formalism\textsuperscript{33–38} 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 wave functions 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 non-relativistic molecular Hamiltonian $H$,

$$H = H_0 + V$$  \hspace{1cm} (1)

where $H_0$ is taken to be the Fock operator and the fluctuation potential $V$ is approximated as an energy dependent effective potential $\Sigma(E)$, 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 $G(E)$:

$$(G(E))^{-1} = (G_0(E))^{-1} - \Sigma(E)$$  \hspace{1cm} (2)

By taking the Fock operator resolvent $G_0(E)$ (the HF Green’s function) in a spin-orbital basis,

$$G_0(E) = (E \mathbb{1} - H_0)^{-1}$$  \hspace{1cm} (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 $G(E)$ lie, occur at the HF eigenvalues $\epsilon$. By requiring $(G(E))^{-1} = 0$, we can recast the problem into a system of linear equations and solve:

$$\det ((E \mathbb{1} - \epsilon - \Sigma(E))) = 0$$  \hspace{1cm} (4)
Since the lowest-order corrections to the orbital energies $\epsilon_i$ involve only the diagonal elements of the self-energy matrix, the above simplifies to

$$\prod_i ((E - \epsilon_i - \Sigma_{ii}(E)) = 0$$

(5)

For each correction to $\epsilon_i$, we solve for $E$,

$$E = \epsilon_i + \Sigma_{ii}(E)$$

(6)

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

$$\omega = \epsilon_i + \Sigma_{ii}(E)$$

(7)

When the $i$th orbital is occupied, $\omega$ is an electron detachment energy, when it is unoccupied, $\omega$ is an electron attachment energy. $\Sigma_{ii}(E)$ is evaluated at $\omega$ until the convergence criteria is met. The energies obtained arise from the diagonal quasiparticle equation:

$$[F + \Sigma_{ii}(E_i)] C_i^{Dyson} = C_i^{Dyson} \omega_i$$

(8)

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

$$\mathbf{G}(E) \equiv \langle \langle \mathbf{a}; \mathbf{a}^\dagger \rangle \rangle_E = \langle \mathbf{a}^\dagger | (E \mathbf{1} - \mathbf{H})^{-1} \mathbf{a}^\dagger \rangle$$

(9)

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

$$\mathbf{G}(E) = \langle \mathbf{a}^\dagger | \mathbf{h} | (E \mathbf{1} - \mathbf{H}) \mathbf{h}^{-1} \mathbf{h} | \mathbf{a} \rangle$$

(10)

The partitioned form of the propagator matrix becomes:

$$\mathbf{G}(E) = \begin{bmatrix} \langle \mathbf{a}^\dagger | \mathbf{a}^\dagger \rangle & \langle \mathbf{a}^\dagger | \mathbf{f} \rangle \\ \langle \mathbf{f} | \mathbf{a} \rangle & \langle \mathbf{f} | \mathbf{f} \rangle \end{bmatrix} \begin{bmatrix} \langle \mathbf{a}^\dagger | (E \mathbf{1} - \mathbf{H}) \mathbf{a}^\dagger \rangle & \langle \mathbf{a}^\dagger | (E \mathbf{1} - \mathbf{H}) \mathbf{f} \rangle \\ \langle \mathbf{f} | (E \mathbf{1} - \mathbf{H}) \mathbf{a} \rangle & \langle \mathbf{f} | (E \mathbf{1} - \mathbf{H}) \mathbf{f} \rangle \end{bmatrix}^{-1} \begin{bmatrix} \langle \mathbf{a}^\dagger | \mathbf{a} \rangle \\ \langle \mathbf{a}^\dagger | \mathbf{f} \rangle \end{bmatrix}$$

(11)
Given the orthogonality conditions \((a^\dagger|f) = 0\), this simplifies to:

\[
G(E) = \begin{bmatrix} 1 & 0 \\ \end{bmatrix} \begin{bmatrix} E1 - (a^\dagger|Ha^\dagger) - (a^\dagger|Hf) \\ - (f|Ha^\dagger) & (f|Hf) \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 0 \end{bmatrix}
\]  

(12)

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

\[
U\omega = HU
\]

(13)

Here, \(H\) is the superoperator Hamiltonian matrix. \(U\) contain the residues connected to the \(j^{th}\) pole \(\omega_j\). The matrix elements of \(U\) can be used to compute the Dyson orbitals of a particular pole,

\[
\phi_j^{\text{Dyson}} = \sum_i \phi_i U^*_ij
\]

(14)

The probability factor, or pole strength, is given by:

\[
\pi_j = \sum_i |Uij|^2
\]

(15)

In the diagonal approximation, a value of \(\pi \geq 0.85\) is normally indicative that the HF orbitals are a good reference for the Dyson orbitals.

Again, due to the orthogonality between primary and secondary spaces, the diagonal of \((h|(E1 - H)h)^{-1}\) is needed. The inverse propagator matrix is now:

\[
(G(E))^{-1} = (a^\dagger|(E1 - H)a^\dagger) - (a^\dagger|Hf) (f|(E1 - H)f)^{-1} (f|Ha^\dagger)
\]

(16)

which reduces further:

\[
(G(E))^{-1} = E1a - Haa - Haf (E1a - Hff)^{-1} Hfa
\]

(17)

Now, the set \(\{f_n\}\) represent 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 \(f_1 \equiv a^\dagger_p (p/h)\), \(f_3 \equiv a^\dagger_p a^\dagger_q a_r (2ph/2hp)\), \(f_5 \equiv a^\dagger_p a^\dagger_q a^\dagger_s a_r a_t (3p2h/3h2p)\), and so on. These operator “strings” are needed generate the \(N \pm 1\) states in a type of configuration interaction expansion in Hilbert space.

One can take the set of field operators in primary subspace \(a^\dagger\) to be the creation operator product \(f_1\) acting on the HF vacuum to generate a HF reference. Because we can choose the basis representation of the primary subspace, the first two terms in Eq. 17 result in the
inverse HF Green’s function \((G(E))_0^{-1}\). The final term is thus the energy dependent part of the self-energy matrix \(\sigma(E)\). The total self-energy,

\[
\Sigma(E) = \sigma(E) + \Sigma(\infty)
\] (18)

As \(E \rightarrow \infty\), \(\sigma(E)\) vanishes and we are left with the constant or energy independent form of the self-energy:

\[
\Sigma(\infty)_{pq} = \sum_{rs} \langle pr | qs \rangle \rho_c^{rs}
\] (19)

where \(\rho_c\) is the correction to the HF one-particle density \(\rho^{HF}\).

2. Self-Energy Approximations

The simplest approximation to the self-energy within EPT is to select the \(f_3\) operators to constitute the secondary space. This first-order approximation leads to the second-order self-energy matrix:

\[
\Sigma^{(2)}(E) = (a|Hf_3)^{(1)} \left(E \mathbb{1} - (f_3|Hf_3)^{(0)}\right)^{-1} (f_3|H a)^{(1)}
\] (20)

The superscripts represent the \(n^{th}\) order correction to the self-energy. The first correction \(n = 1\) thus begins at second-order perturbation. The poles of \(\Sigma^{(2)}(E)\) are recovered by diagonalizing the following superoperator Hamiltonian:

\[
H^{(1)} = \begin{bmatrix} (a|H a)^{(0)} & (a|H f_3)^{(1)} \\ (f_3|H a)^{(1)} & (f_3|Hf_3)^{(0)} \end{bmatrix}
\] (21)

Note that the matrix elements \((a|H a)^{(0)}\) and \((f_3|Hf_3)^{(0)}\) 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 the \(H^{(1)}\), 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 the expression:

\[
\Sigma^{(2)}_{pq}(E) = \frac{1}{2} \sum_{aij} \frac{\langle ij | qa \rangle \langle pa | ij \rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2} \sum_{iab} \frac{\langle pi | ab \rangle \langle ab | qi \rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b}
\] (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 2ph and
2hp terms. If the canonical HF orbitals are sufficient approximations to the Dyson orbitals, we only need to evaluate the diagonal of $\Sigma^{(2)}(E)$ by requiring pole index $p = q$:

$$\Sigma^{(2)}_{pp}(E) = \frac{1}{2} \sum_{aij} \frac{|\langle ap | i | j \rangle|^2}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2} \sum_{iab} \frac{|\langle pi | a | b \rangle|^2}{E + \epsilon_i - \epsilon_a - \epsilon_b}$$  \hspace{1cm} (23)

If we take the second term in Eq. 22 and separate terms with no dependency on $E$ and either $a$ or $b$, we actually 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 towards a more optimal set of one-electron orbitals. This amounts to the orbital relaxation term,

$$\Sigma^{R(2)}_{pp} = \sum_{ai} \frac{|\langle ap | i | p \rangle|^2}{\epsilon_a - \epsilon_i}$$  \hspace{1cm} (24)

Note that, for obvious reasons, $a \neq i$. This relaxation term $\Sigma^{R(2)}_{pp}$ is the second–order contribution to the ionization energy of orbital $p$ from a $\Delta$SCF calculation:

$$-I_p(\Delta\text{SCF}) = E_{HF}(N) - E_{HF}(N - 1)$$  \hspace{1cm} (25)

A generalization of relaxation contribution to the binding energy of orbital $p$ at the $\Delta$SCF level is presented as a correction to the HF eigenvalue $\epsilon_p$:

$$-I_p(\Delta\text{SCF}) \simeq \epsilon_p - \Sigma^{R(2)}_{pp}$$  \hspace{1cm} (26)

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

$$\Sigma^{C(2)}_{pp}(E) = \Sigma^{(2)}_{pp}(E) - \Sigma^{R(2)}_{pp}$$  \hspace{1cm} (27)

This comes out to be:

$$\Sigma^{C(2)}_{pp}(E) = \frac{1}{2} \sum_a \sum_{i \neq p} \sum_{j \neq p} \frac{|\langle pa | i | j \rangle|^2}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2} \sum_{i \neq p} \sum_a \sum_b \frac{|\langle pi | a | b \rangle|^2}{E + \epsilon_i - \epsilon_a - \epsilon_b}$$  \hspace{1cm} (28)

The first term describes the correlation contribution of pair interactions of occupied $i, j$ orbitals with unoccupied orbital $a$ the new virtual $p$—analogous to orbital relaxation, but for the $N - 1$ state. The second term, related to the 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 $p$. 
B. $\Delta$SCF $+$ $\Delta\Sigma$ Approach

Following the detailed protocol by Pickup and Goscinski\textsuperscript{33} together with developments\textsuperscript{31,32} in EPT at the Quantum Theory Project, one can recover an expression for the lowest-order correction to Koopmans’ theorem:

$$-I = -I_{p}(\Delta\text{SCF}) + \Sigma_{pp}^{C(2)}(E)$$

(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. An approximation of the excitation energy $\omega_{X}$ is proposed:

$$\omega_{X} \simeq E(\Delta\text{SCF}) + \Delta\Sigma_{C}^{C(2)}(E)$$

(30)

$$\simeq [E_{p\rightarrow r}(N) - E_{0}(N)] + \Sigma_{rr}^{C(2)}(E_{N+1}) - \Sigma_{pp}^{C(2)}(E_{N+1})$$

(31)

Here, $E(\Delta\text{SCF})$ is the difference between the excited ($E_{p\rightarrow r}$) and ground state ($E_{0}$) HF energies. $\Delta\Sigma_{C}^{C(2)}(E)$ is the difference between the correlation corrections to $\epsilon_{r}$ and $\epsilon_{p}$. These terms are computed for the $N+1$ determinant, the propagator reference, where orbitals $p$ and $r$ are both occupied. The anions are used simply as model configurations 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\textsuperscript{40} (PIMOM). The SCF excited-states are unrestricted Hartree-Fock (UHF) solutions obtained after an occupied-virtual orbital rotation. As a consequence of the symmetry dilemma, these excited-state solutions break spin and electronic state symmetry in exchange for a lower energy. For closed-shell systems, 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 UHF determinant, an estimate for the proper spin state energies of the excited states is computed using approximate projection\textsuperscript{41–43} (AP):

$$E_{AP} = \alpha E_{LS} + (1 - \alpha) E_{HS}$$

(32)
where the weight or single annihilation parameter $\alpha$ is

$$\alpha = \frac{\langle S_H^2 \rangle - S_{z,LS}(S_{z,LS} + 1)}{\langle S_H^2 \rangle - \langle S_{LS}^2 \rangle}$$  \hspace{1cm} (33)$$

$E_{LS}$ is the energy of the spin contaminated core-hole configuration and $E_{HS}$ is the energy of its $S + 1$ counterpart. AP is applied for all excited-state singlet $\Delta$SCF calculations.

C. Relativistic Corrections

Since we are dealing with core electrons, relativistic effects need to be considered. The relativistic shift in the ionization potential for a two-electron atom is defined by Bethe and Salpeter$^{44}$:

$$E_J = \alpha^2 \left[ -\frac{1}{8} Z^4 + \frac{1}{4} \langle p_1^4 \rangle - \pi Z \langle \delta^{(3)}(r_1) \rangle - \pi \langle \delta^{(3)}(r_{12}) \rangle - E_2 \right]$$  \hspace{1cm} (34)$$

Extensions of this to higher $Z$ and formulas for the expectation values above are provided by Perekis, Silverman, and Scherr.$^{45,46}$ For consistency, $E_J$ for a particular atom is added in an ad hoc fashion to the computed non-relativistic core excitation energy $\omega_X$. In this study, the corrections for C, N, O, F, and S are 0.1 eV, 0.2 eV, 0.4 eV, 0.7 eV, and 9.2 eV respectively.

III. RESULTS

An assortment of molecules was taken from the CGB data set.$^{47,48}$ These structures had been optimized with CCSD(T)/aug-cc-pVTZ. Geometries for molecules not present in the CGB set were obtained from the NIST CCCBDB database$^{49}$ at the same level of theory. All systems belong to their highest point group symmetry. 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 are generally good eigenstates of the total spin-squared operator $S^2$, except for the anions of the heterocyclic molecules. The furan, tetrazine, pyridine, and thiophene anions possess $\langle S^2 \rangle$ values that deviate from $S(S + 1)$ by $\sim 10\%$ to $18\%$. These errors are artifacts of the basis chosen for post-SCF treatment and the high degree of spin polarization.
at the HF level. Mean pole strengths for core and valence electron detachments are 0.75 and 0.91 respectively. All calculations were performed with a development version of Gaussian\textsuperscript{50}.

Shown in Table I are the vertical excitation energies obtained with only $\Delta$SCF. The absence of degenerate or quasi-degenerate core orbitals for a particular atom lessens the interactions of configurations relevant for describing the excited state, meaning the correlation contributions to the energy is much less than the orbital relaxation. For these systems, it is not surprising that the computed $\Delta$SCF energies are well in the vicinity of experimental values (MAE: 1.1 eV, RMSE: 2.5 eV) since the atomic cores of interest are unique and other core orbitals belonging to atoms of the same bonding class are not present. One exception is $\omega_X$ for the sulfur K-edge of thiophene. The significant deviation of this result ($\sim 11$ eV) from the experiment is largely attributed to the chosen relativistic correction as well as the relaxation and correlation not captured with $\Delta$SCF.

Systems for which core excitations are poorly quantified with $\Delta$SCF are thus candidates for treatment with EPT. To avoid double counting of orbital relaxation recovered with $\Delta$SCF, $\Delta \Sigma^{R(2)}$ must be removed from the self-energy correction to binding energies obtained with Koopmans' theorem. Results using the $\Delta$SCF + $\Delta \Sigma^{C(2)}$ method are displayed in Table II. With a MAE of 1.3 eV and a RMSE of 1.8 eV, 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 $\Delta$SCF 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 $\Delta$SCF result. Since the quality of the poles is connected to the quality of the reference orbitals, it is important to note an additional layer of error is present due to spin contamination in the anions. Whenever possible, propagator references with good intrinsic spin quantum numbers are preferred over lower UHF solutions.
TABLE I. ∆SCF vertical excitation energies $\omega_X$ for the lowest symmetry-allowed core to valence transitions.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Core</th>
<th>∆SCF (eV)</th>
<th>$\omega_X$ (eV)</th>
<th>Exp. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>C (C-O)</td>
<td>287.3</td>
<td>287.4</td>
<td>286.4$^{51}$</td>
</tr>
<tr>
<td>Acetone</td>
<td>O</td>
<td>531.0</td>
<td>531.4</td>
<td>531.4$^{53}$</td>
</tr>
<tr>
<td>Acrolein</td>
<td>C (C-O)</td>
<td>286.7</td>
<td>286.8</td>
<td>286.1$^{52}$</td>
</tr>
<tr>
<td>Acrolein</td>
<td>O</td>
<td>530.2</td>
<td>530.6</td>
<td>530.6$^{52}$</td>
</tr>
<tr>
<td>CH4</td>
<td>C</td>
<td>289.8</td>
<td>289.9</td>
<td>288.0$^{53}$</td>
</tr>
<tr>
<td>CO</td>
<td>C</td>
<td>288.4</td>
<td>288.5</td>
<td>287.4$^{54}$</td>
</tr>
<tr>
<td>CO</td>
<td>O</td>
<td>533.7</td>
<td>534.1</td>
<td>534.2$^{54}$</td>
</tr>
<tr>
<td>Furan</td>
<td>O</td>
<td>535.1</td>
<td>535.5</td>
<td>535.2$^{55}$</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>C</td>
<td>286.5</td>
<td>286.6</td>
<td>285.6$^{56}$</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>O</td>
<td>530.6</td>
<td>531.0</td>
<td>530.8$^{56}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>O</td>
<td>534.3</td>
<td>534.7</td>
<td>534.0$^{53}$</td>
</tr>
<tr>
<td>HF</td>
<td>F</td>
<td>687.3</td>
<td>688.0</td>
<td>687.4$^{57}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>N</td>
<td>401.1</td>
<td>401.3</td>
<td>400.8$^{53}$</td>
</tr>
<tr>
<td>Pyridine</td>
<td>N</td>
<td>398.8</td>
<td>399.0</td>
<td>398.8$^{58}$</td>
</tr>
<tr>
<td>Thiophene</td>
<td>S</td>
<td>2475.4</td>
<td>2484.6</td>
<td>2473.4$^{59}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>C</td>
<td>292.4</td>
<td>292.5</td>
<td>290.8$^{60}$</td>
</tr>
<tr>
<td>Imidazole</td>
<td>N (N-H)</td>
<td>403.2</td>
<td>403.4</td>
<td>402.3$^{61}$</td>
</tr>
<tr>
<td>Imidazole</td>
<td>N</td>
<td>400.4</td>
<td>400.6</td>
<td>399.9$^{61}$</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>N (N-N)</td>
<td>401.2</td>
<td>401.4</td>
<td>401.0$^{60}$</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>N (N-O)</td>
<td>404.7</td>
<td>404.9</td>
<td>404.6$^{60}$</td>
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<td>534.5</td>
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</tr>
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<td>HCN</td>
<td>C</td>
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<td>287.0</td>
<td>286.4$^{62}$</td>
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<tr>
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<td>400.0</td>
<td>400.2</td>
<td>399.7$^{62}$</td>
</tr>
</tbody>
</table>

Mean absolute error (MAE): 1.1 eV
Root-mean-square error (RMSE): 2.5 eV
TABLE II. $\Delta$SCF $+ \Delta \Sigma^{C(2)}$ vertical excitation energies $\omega_X$ for the lowest symmetry-allowed core to valence transitions.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Core</th>
<th>$\Delta$SCF (eV)</th>
<th>$\Delta \Sigma^{C(2)}$ (eV)</th>
<th>$\omega_X$ (eV)</th>
<th>Exp. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_2$</td>
<td>C</td>
<td>294.0</td>
<td>-9.3</td>
<td>284.8</td>
<td>285.4$^{63}$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>C</td>
<td>293.0</td>
<td>-9.2</td>
<td>283.8</td>
<td>284.7$^{63}$</td>
</tr>
<tr>
<td>C$_2$N$_2$</td>
<td>C</td>
<td>293.3</td>
<td>-8.5</td>
<td>284.9</td>
<td>286.3$^{62}$</td>
</tr>
<tr>
<td>C$_2$N$_2$</td>
<td>N</td>
<td>410.4</td>
<td>-11.6</td>
<td>398.9</td>
<td>398.9$^{62}$</td>
</tr>
<tr>
<td>F$_2$</td>
<td>F</td>
<td>695.2</td>
<td>-13.5</td>
<td>682.3</td>
<td>682.2$^{57}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>N</td>
<td>410.5</td>
<td>-10.5</td>
<td>400.2</td>
<td>400.9$^{64}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>O</td>
<td>542.0</td>
<td>-11.9</td>
<td>530.5</td>
<td>531.0$^{65}$</td>
</tr>
<tr>
<td>Pyridine</td>
<td>C</td>
<td>294.6</td>
<td>-9.7</td>
<td>285.0</td>
<td>285.3$^{58}$</td>
</tr>
<tr>
<td>Tetrazine</td>
<td>N</td>
<td>413.6</td>
<td>-14.4</td>
<td>399.4</td>
<td>398.8$^{66}$</td>
</tr>
<tr>
<td>Tetrazine</td>
<td>C</td>
<td>293.8</td>
<td>-7.6</td>
<td>286.3</td>
<td>285.2$^{66}$</td>
</tr>
<tr>
<td>Thiophene</td>
<td>C (C-S)</td>
<td>294.4</td>
<td>-8.5</td>
<td>286.0</td>
<td>285.4$^{59}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>O</td>
<td>554.3</td>
<td>-14.4</td>
<td>540.3</td>
<td>535.4$^{60}$</td>
</tr>
<tr>
<td>Furan</td>
<td>C</td>
<td>295.8</td>
<td>-8.2</td>
<td>287.7</td>
<td>286.5$^{55}$</td>
</tr>
<tr>
<td>C$_2$F$_4$</td>
<td>C</td>
<td>298.7</td>
<td>-10.8</td>
<td>287.9</td>
<td>290.1$^{67}$</td>
</tr>
<tr>
<td>C$_2$F$_4$</td>
<td>F</td>
<td>708.4</td>
<td>-21.8</td>
<td>687.3</td>
<td>690.7$^{67}$</td>
</tr>
</tbody>
</table>

Mean absolute error (MAE): 1.3 eV
Root-mean-square error (RMSE): 1.8 eV
IV. DISCUSSION

We have presented computational results for core excitation energies using $\Delta$HF and the diagonal second-order self-energy approximation. The qualitative utility of the $\Delta$SCF + $\Delta\Sigma$ method 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 $\Sigma^R$ and correlation $\Sigma^C$ contributions varies between the core and valence regimes.\textsuperscript{68,69} For ionizations of local, non-equivalent cores, $\Delta$SCF recovers the bulk of the relaxation effects.\textsuperscript{70,71} Presence of lone pairs and double bonds between equivalent atoms (which give rise to degenerate orbitals) demand incorporation of dynamical correlation effects involving the interaction of degenerate configurations. In cases of strong correlation, $\Delta$HF tends to overestimate the excitation energy. Cederbaum and Domcke\textsuperscript{72} explain 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 $\Sigma_{\mu\nu}^{(2)}(E)$. In the case of N$_2$, they show that the degeneracy of the delocalized symmetry orbitals, $\sigma_g$ and $\sigma_u$, causes the correlation part of the self energy to become competitive in magnitude to the relaxation part. With two symmetry orbitals close in energy, $\Delta$HF results will of course not include the now increased correlation effects. If one lifts the constraints of symmetry (i.e. reduce the molecular symmetry) and localize 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 $\Delta$SCF for K-shell electron detachments usually yield decent results 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 KS-DFT limits systematic improvements with perturbation theory.

Computing core excitation energies using $\Delta$SCF + $\Delta\Sigma^{C(2)}$ requires a balanced treatment of orbital relaxation and correlation effects. Correlation corrections to $\Delta$SCF 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. Additionally, varying the occupation number of the target core orbital via the transition operator method\textsuperscript{73,74} may also be a relevant approach towards increasing the quality of the self-energy. Also, studies of L-edge transitions and computation of oscillator strengths for
simulating spectra will be important diagnostics for this model. Further exploration of practical, low-scaling composite models for computing excitations energies with different electron propagator methods is underway.
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REFERENCES


