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ABSTRACT

We present an *ab initio* computational study of the Auger electron spectrum of benzene. Auger electron spectroscopy exploits the Auger–Meitner effect, and although it is established as an analytic technique, the theoretical modeling of molecular Auger spectra from first principles remains challenging. Here, we use coupled-cluster theory and equation-of-motion coupled-cluster theory combined with two approaches to describe the decaying nature of core-ionized states: (i) Feshbach–Fano resonance theory and (ii) the method of complex basis functions. The spectra computed with these two approaches are in excellent agreement with each other and also agree well with experimental Auger spectra of benzene. The Auger spectrum of benzene features two well-resolved peaks at Auger electron energies above 260 eV, which correspond to final states with two electrons removed from the $1e_{1g}$ and $3e_{2g}$ highest occupied molecular orbitals. At lower Auger electron energies, the spectrum is less well resolved, and the peaks comprise multiple final states of the benzene dication. In line with theoretical considerations, singlet decay channels contribute more to the total Auger intensity than the corresponding triplet decay channels.

I. INTRODUCTION

X-ray spectroscopies are widely used for probing the electronic structure of molecules and materials.[1–3] Based on transitions involving core electrons, they exploit special features of the core orbitals—their localized nature, the element specificity of their energies, and the sensitivity to the environment of these energies.[1–7] Progress in experimental techniques such as laser technology and, more specifically, the higher quality of x-ray beams has motivated recent efforts to advance the theoretical capabilities for modeling core-level transitions.[5,8,9]

Irradiation with x-rays creates vacancies in the core orbitals, producing highly excited or ionized states. Alternatively, core-hole states can also be created by nuclear transformations such as electron capture or internal conversion of some radionuclides. In molecules with light atoms—C, N, and O—which are most relevant to organic chemistry, core-hole states relax predominantly via autoionization processes, collectively referred to as the Auger–Meitner effect.[10,11] In non-radiative Auger decay, a valence electron fills the core vacancy, liberating sufficient energy to eject another electron, called the Auger electron, into the continuum. Different types of this process are shown in Fig. 1: core-ionized states, produced, for example, in x-ray photoionization spectroscopy (XPS), undergo regular Auger decay, whereas core-excited states, produced in x-ray absorption spectroscopy (XAS), undergo resonant participator or spectator Auger decay. Less common are double and triple Auger decay in which two or three electrons are simultaneously emitted, resulting in multiply charged cations.[12,13]

In Auger electron spectroscopy,[15] the intensity of the emitted Auger electrons is recorded as a function of their kinetic energy. Auger electron spectroscopy benefits from the element- and environment-sensitivity of core orbitals and, therefore, can provide information about the electronic structure not accessible by other techniques.[1] It has been employed to characterize with high accuracy and high spatial resolution the chemical composition of surfaces,[16–19] materials,[20–22] nanostructures,[23,24] and gas-phase molecules.[25–28]

Auger electrons find uses beyond spectroscopy, e.g., in radiotherapy and precision medicine.[29–32] Because Auger decay produces multiple electron tracks in the vicinity of the emission site, typically within 500 nm, it can deposit large amounts of energy into the surrounding molecules. This ability of Auger emitters to deliver considerable levels of radiation to a specific target[33–35] has motivated

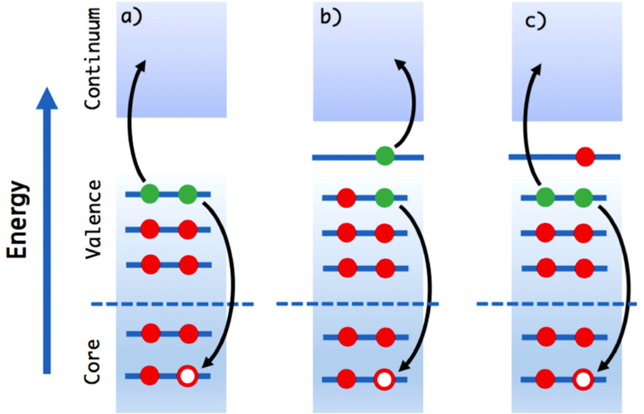


FIG. 1. Different types of Auger decay: (a) regular Auger decay, (b) resonant participator decay, and (c) resonant spectator decay. Reproduced with permission from W. Skomorowski and A. I. Krylov, "Feshbach–Fano approach for calculation of Auger decay rates using equation-of-motion coupled-cluster wave functions. I. Theory and implementation," J. Chem. Phys. **154**, 08124 (2021). Copyright 2021 AIP Publishing LLC.

the therapeutic use of molecules labeled with radionuclides that emit Auger electrons upon nuclear decay.

Theoretical modeling of Auger processes is difficult owing to the metastable nature of core-ionized and core-excited states, which are embedded in the ionization continuum. Conventional quantum chemistry methods are formulated for discrete bound states with L^2-integrable wavefunctions and thus cannot describe states subject to electronic decay. One can circumvent this problem by artificial stabilization of core-hole states by means of the core-valence separation[36] (CVS). This approach, in which decaying states are approximated as bound states, delivers excellent energies in most cases. However, energies alone are not sufficient for modeling Auger spectra because a complete description requires decay widths as well.

In this contribution, we compute decay widths for the core-ionized states of benzene and construct its Auger spectrum. As a prototypical aromatic molecule, benzene is often used as a model system to test new spectroscopic techniques[37–42] and benchmark theoretical methods.[43–50] The high symmetry and multiple core orbitals make Auger decay in benzene particularly interesting, which motivated several experimental and theoretical studies.[51–57]

In the early experiment by Spohr *et al.*, Auger electrons were generated by electron impact,[51] which likely produces highly excited molecules, giving rise to an Auger spectrum containing regular and resonant contributions. Later, Rennie and co-authors used x-ray radiation to produce core-ionized states;[52] they reported an Auger spectrum of benzene obtained with 390 eV radiation, which they referred to as the sudden limit, as well as an Auger spectrum obtained using lower excitation energies closer to XAS transitions. It is expected that the former spectrum should be dominated by non-resonant Auger decay, whereas the latter spectrum should feature resonant contributions. The most recent experiment by Carniato *et al.* employed higher-energy radiation (510 eV) and measured Auger electrons in coincidence with photoelectrons in order to eliminate the resonant contributions to the spectrum.[53]

Figure 2 shows the Auger spectra of benzene from the three experiments. The spectra have similar shapes but show noticeable differences both in the peak positions and the intensities. The position of the lowest peak (labeled L in Fig. 2) differs by 0.58 eV, and even more troubling is the fact that it is not possible to align the positions of all major peaks with a constant shift. For example, if the spectra are aligned by the lowest peak, then the position of the highest peak (labeled H in Fig. 2) varies by 1.44 eV, and so on. This is illustrated in Figs. S1–S3 in the supplementary material.

Theoretically, Auger decay in benzene was studied by Tarantelli *et al.* using a statistical approach, which assumes that all decay channels have identical partial widths.[55] Specifically, they computed the decay channels, i.e., the dicationic states of benzene, with second-order algebraic diagrammatic construction [ADC(2)][58,59] and constructed the spectrum using the density of states as a proxy for the intensities. On the basis of these calculations, Tarantelli *et al.* were able to interpret the main features in the Auger spectrum.[55]

In view of the challenges faced by quantitative experimental measurements of Auger spectra and the noticeable discrepancies between the three experimental Auger spectra of benzene, there is a need for accurate theoretical modeling. By using a high-level description of the electronic structure and computing the Auger decay widths explicitly, we hope to clarify the nature of the main spectral features in the Auger spectrum of benzene and to provide a benchmark for future experiments and computational studies.

We use two different theoretical approaches to compute the decay widths of the core-ionized states: Feshbach–Fano resonance theory[60–62] and the method of complex basis functions (CBF),[63] which is based on complex scaling.[64,65] The comparison between these different theoretical approaches and between theory and

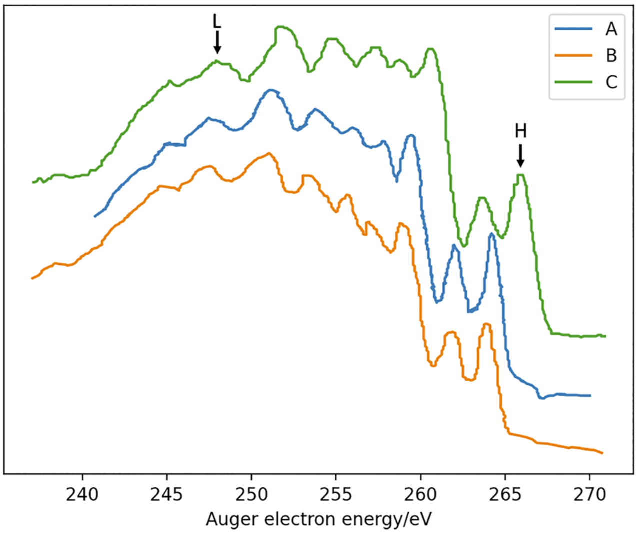


FIG. 2. Auger spectra of benzene from (a) Spohr *et al.*,[51] (b) Rennie *et al.*,[52] and (c) Carniato *et al.*[53]

experiment provides insights into the Auger spectrum of benzene and Auger decay in general.

Both approaches originate from non-Hermitian quantum mechanics, which offers a powerful and elegant framework for treating molecular electronic resonances.[66–70] The Schrödinger equation is reformulated such that the resonances are separated from the continuum and become isolated states with L^2-integrable wavefunctions and complex energies,

$$E_{\rm res} = E - i\frac{\Gamma}{2}, \qquad (1)$$

where the real part E describes the energy of a resonance and the imaginary part gives its decay width Γ, which is inversely proportional to the lifetime. The Feshbach–Fano approach and the method of complex basis functions represent two techniques to achieve such reformulation in practice.[67–70]

These ideas were recently exploited to model molecular Auger decay rates in the framework of coupled-cluster (CC) theory[71] and its equation-of-motion (EOM) extensions:[72–74] Skomorowski and Krylov have developed a method based on the Feshbach–Fano formalism,[14,75] whereas Matz and Jagau have developed methods based on CBFs.[76,77] Among related recent developments, Coriani and co-workers have reported an implementation of the Feshbach–Fano approach combined with a one-center approximation of free electrons and multi-reference wavefunctions.[78]

The structure of the paper is as follows: Sec. II outlines the details of our theoretical modeling, Sec. III presents the numerical results, and Sec. IV offers concluding remarks.

II. THEORETICAL AND COMPUTATIONAL DETAILS

A. Relevant electronic states of benzene

Figure 3 shows the occupied molecular orbitals (MOs) of benzene and their irreducible representations. The electronic configuration of the ground state of neutral benzene is

$$\begin{aligned} \mathrm{X}\ {}^1\mathrm{A}_{1g} = {}& (\mathrm{core})^{12}(2a_{1g})^2(2e_{1u})^4(2e_{2g})^4(3a_{1g})^2(2b_{1u})^2(1b_{2u})^2 \\ & \times (3e_{1u})^4(1a_{2u})^2(3e_{2g})^4(1e_{1g})^4, \end{aligned} \qquad (2)$$

where the core comprises six doubly occupied orbitals

$$(\mathrm{core})^{12} = (1a_{1g})^2(1e_{1u})^4(1e_{2g})^4(1b_{1u})^2. \qquad (3)$$

Following Wentzel,[81,82] we treat Auger decay as a two-step process in which the second step, the filling of the core hole and ejection of the Auger electron, is independent of the first step, the creation of the core vacancy. Thus, our theoretical treatment focuses on the second step. Figure 4 shows a sketch of the electronic states relevant for our modeling: the neutral ground state, the core-ionized states, which are the initial states in the Auger process, and the doubly ionized valence states, which represent the final states. The core-ionized states are metastable and decay, producing free electrons and doubly ionized valence states. Different doubly ionized states correspond to different decay channels, giving rise to Auger electrons with specific energies. The rates of decay into the respective doubly ionized target states determine the intensities in the Auger spectrum: Faster decay rates correspond to a higher probability of decay into the respective doubly ionized target state.

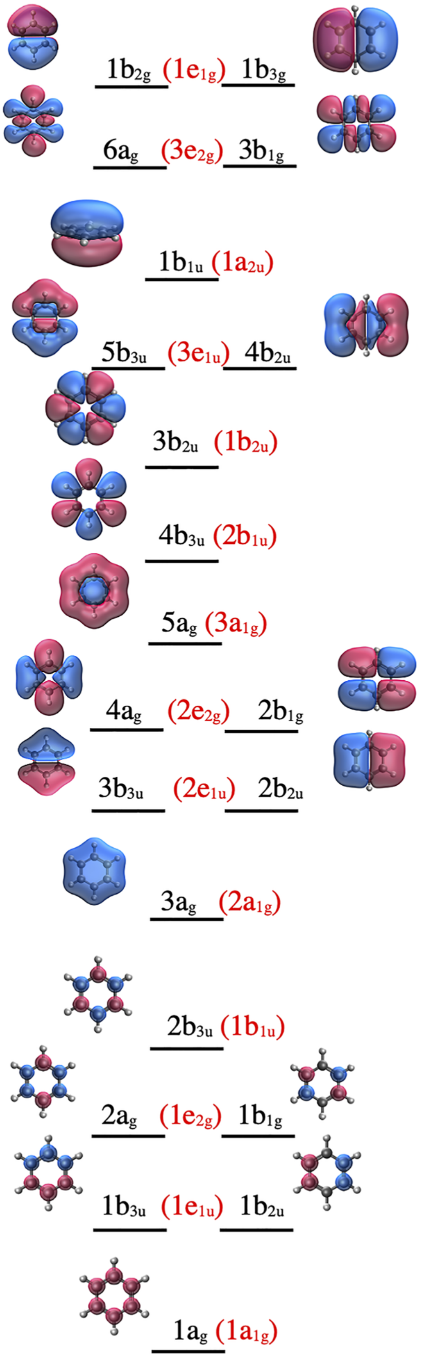


FIG. 3. Occupied molecular orbitals of benzene. Irreducible representations are given for the D_{6h} point group (in red) using the Mulliken convention[79] and for the largest Abelian subgroup (D_{2h}, in black), using Q-Chem's symmetry notation.[80]

Given that the four core-ionization energies (IEs) of benzene differ by only 0.1 eV, we assume that any of the six core orbitals can be ionized, i.e., all four core-ionized states (${}^2\mathrm{A}_{1g}$, ${}^2\mathrm{E}_{1u}$, ${}^2\mathrm{E}_{2g}$, ${}^2\mathrm{B}_{1u}$)

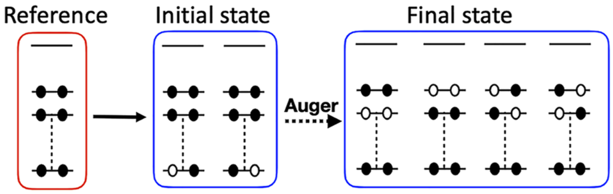


FIG. 4. Initial and final states in regular Auger decay.

contribute equally to the total Auger spectrum barring the two degeneracies. A rough estimate of the number of possible Auger transitions is $6 \times 15 \times 15 = 1,350$ because the core vacancy can be filled by an electron taken from any valence shell and the Auger electron can also originate from any valence shell. In this estimate, we do not take into account degenerate shells and the spin multiplicity of the doubly ionized target states. Moreover, we do not include channels resulting from three-electron processes, i.e., those leading to 3-hole-1-particle $(3h1p)$ target states of the dication, because these channels are expected to have lower intensity. Furthermore, we do not consider resonant Auger decay and focus on the non-resonant Auger process. This is justified by the setup of the most recent measurement, which supposedly excludes contributions from resonant Auger decay.[53]

Using a one-electron picture and Koopmans' theorem, the energies of the Auger electrons are[83]

$$E_{\text{Auger}} = \epsilon_{v1} + \epsilon_{v2} - \epsilon_{\text{core}}, \tag{4}$$

where ϵ_{v1} and ϵ_{v2} are the energies of the valence holes created by the Auger decay, and ϵ_{core} is the energy of the core orbital with the hole. In correlated treatments, different $2h$ configurations can mix, giving rise to correlated doubly ionized states, which we call DIP (double ionization potential) states. The positions of the peaks in the Auger spectrum are then

$$E_{\text{Auger}} = E_{\text{DIP}} - E_{\text{coreIP}}. \tag{5}$$

Furthermore, correlated treatments are able to distinguish singlet and triplet Auger channels. As per Fig. 3, the highest-energy Auger electrons should correspond to the DIP states with two holes in the $1e_{1g}$ highest occupied molecular orbital (HOMO) of benzene.

Because the IEs of the core orbitals are very close (~0.1 eV), one can anticipate that the positions of the peaks in the Auger spectrum of benzene follow the energies of the DIP states and that the intensity pattern follows the density of DIP states. Indeed, this approach has been used in earlier theoretical treatments of the Auger spectrum of benzene.[55] Although the density of correlated DIP states can provide a zero-order picture of the Auger spectrum, a quantitative treatment needs to account for the different probabilities associated with different decay channels.[82–84] These probabilities are proportional to the partial widths of the metastable core-ionized states for decay into a particular channel. If all decay channels are considered, these partial widths sum up to Γ from Eq. (1). In the following two sections (II B and II C) we discuss and compare our two approaches for computing these partial widths, i.e., Feshbach–Fano resonance theory and the CBF method. We show that accounting for partial widths leads to significant changes in the Auger intensities as compared to an estimate based on the density of DIP states.

We note that the contributions of triplet decay channels are expected to be smaller than the contributions of singlet decay channels.[83,85] The dominance of singlet channels is also confirmed by experiments on atoms, where the peaks in the Auger spectrum can be unambiguously mapped onto the decay channels.[86] In the Appendix, we analyze the contributions of singlet and triplet channels for the two many-body approaches used in this work.

Specific details of theoretical protocols are given below. All calculations were carried out using the Q-Chem package.[87,88]

B. Feshbach–Fano approach

For the Feshbach–Fano calculations, we employ CC and EOM-CC theories with single and double substitutions (CCSD and EOM-CCSD, respectively)[72–74,89] and their extensions to core-level states using CVS.[43,90–98] The reference state in these calculations corresponds to neutral benzene and is treated by CCSD,

$$|\Psi^{\text{CC}}\rangle = e^{T}|\Phi_0\rangle, \tag{6}$$

$$T = T_1 + T_2 = \sum_{ia} t_i^a\, a^\dagger i + \frac{1}{4}\sum_{ijab} t_{ij}^{ab}\, a^\dagger b^\dagger j i, \tag{7}$$

where $|\Phi_0\rangle$ is the Hartree–Fock reference determinant, which defines the separation between occupied and virtual orbital spaces. Following the standard notation, indices $i, j, k, \ldots$ denote orbitals from the occupied space, indices $a, b, c, \ldots$ denote orbitals from the virtual space, and indices $p, q, r, \ldots$ denote orbitals that can be either occupied or virtual.

The core-hole states are described by EOM-IP-CCSD as

$$|\Psi^{\text{IP}}\rangle = R^{\text{IP}} e^{T}|\Phi_0\rangle, \tag{8}$$

$$R^{\text{IP}} = R_1^{\text{IP}} + R_2^{\text{IP}} = \sum_i r_i\, i + \frac{1}{2}\sum_{ija} r_{ij}^{a}\, a^\dagger j i, \tag{9}$$

and the EOM-IP amplitudes r_i and r_{ij}^a are found by diagonalizing the similarity transformed Hamiltonian, $\bar{H} = e^{-T} H e^{T}$ in the space of $1h$ and $2h1p$ determinants. The IEs are directly obtained as eigenvalues of the EOM-IP-CCSD equations. We use the CVS scheme, where the EOM-IP operators R_1^{IP} and R_2^{IP} are restricted to operators that include at least one core orbital.[90–93] This makes the core-ionized states artificially bound and separates them from the double-ionization continuum. The doubly ionized target states are described by the DIP variant of EOM-CCSD,[99–101]

$$|\Psi^{\text{DIP}}\rangle = R^{\text{DIP}} e^{T}|\Phi_0\rangle, \tag{10}$$

$$R^{\text{DIP}} = R_1^{\text{DIP}} + R_2^{\text{DIP}} = \frac{1}{2}\sum_{ij} r_{ij}\, ij + \frac{1}{6}\sum_{ijka} r_{ijk}^{a}\, a^\dagger kji, \tag{11}$$

and the EOM-DIP amplitudes r_{ij} and r^a_{ijk} are determined by diagonalization of $\bar{H}$ in the space of $2h$ and $3h1p$ determinants.

In the Feshbach–Fano approach, a resonance state is obtained as the result of the interaction between a bound discrete state and continuum states.[60–62] The Feshbach projection operators Q and P divide the full Hilbert space into bound and continuum subspaces, respectively,[61] and these subspaces are coupled via the matrix elements of the many-body Hamiltonian between the bound and continuum configurations. By using the Löwdin partitioning technique,[62] the problem of computing the resonance energy is formulated as an eigenproblem of a non-Hermitian effective Hamiltonian $\mathcal{H}_{QQ}$ defined in the Q-space,

$$\mathcal{H}_{QQ}\,|\tilde{\Psi}\rangle = \tilde{\mathcal{E}}\,|\tilde{\Psi}\rangle, \tag{12}$$

$$\tilde{\mathcal{E}} = \mathcal{E} - i\frac{\Gamma}{2}, \tag{13}$$

$$\mathcal{H}_{QQ} = H_{QQ} + H_{QP}\,G_P^{(+)}(E)\,H_{PQ}, \tag{14}$$

$$G_P^{(+)}(E) = \lim_{\epsilon\to 0}\frac{1}{E + i\epsilon - H_{PP}}. \tag{15}$$

In practice, Eqs. (12)–(15) are solved perturbatively. In zeroth order, one computes the eigenstates $|\Psi\rangle$ of the bound-space Hamiltonian H_{QQ}. Then, the complex resonance energy $\tilde{\mathcal{E}}$ is computed using the first-order correction, i.e., by computing a matrix element between the bound and continuum states

$$\tilde{\mathcal{E}} \approx E + E^{(1)} = E + \langle\Psi\,|\,H_{QP}\,G_P^{(+)}\,H_{PQ}\,|\,\Psi\rangle, \tag{16}$$

giving rise to

$$\begin{aligned}\mathcal{E} &= \mathrm{Re}\langle\Psi|\mathcal{H}_{QQ}|\Psi\rangle\\ &\approx E + \sum_\mu P.V.\int_0^\infty dE'\,\frac{\langle\Psi|H_{QP}|\chi^\pm_{\mu,E'}\rangle\langle\chi^\pm_{\mu,E'}|H_{PQ}|\Psi\rangle}{E - E_\mu - E'},\end{aligned} \tag{17}$$

$$\begin{aligned}\Gamma &= -2\,\mathrm{Im}\langle\Psi|\mathcal{H}_{QQ}|\Psi\rangle\\ &\approx \sum_\mu 2\pi\,\langle\Psi|H_{QP}|\chi^\pm_{\mu,E-E_\mu}\rangle\langle\chi^\pm_{\mu,E-E_\mu}|H_{PQ}|\Psi\rangle = \sum_\mu \Gamma_\mu.\end{aligned} \tag{18}$$

Here, μ denotes the decay channels and E_μ the associated threshold energies, while $\chi^\pm_{\mu,E}$ refers to scattering states, which are normalized according to $\langle\chi^\pm_{\mu,E}|\chi^\pm_{\mu',E'}\rangle = \delta_{\mu\mu'}\,\delta(E - E')$.

The Feshbach–Fano approach has recently been applied by Skomorowski and Krylov to compute Auger decay rates using EOM-CC wave functions.[14] In their approach, CVS was used to define the projector Q. The bound part of a resonance state, that is, Ψ from Eqs. (17) and (18), can be computed by CVS-EOM-IP-CCSD and the continuum states $\chi^\pm_{\mu,E}$ are represented as products of EOM-DIP-CCSD states and free-electron states.

In this approach, the final expression for the partial width corresponding to the decay of an initial core-hole state into channel μ is

$$\begin{aligned}\Gamma_\mu = 2\pi g_\alpha \int d\Omega_{\mathbf{k}}&\left(\sum_p h^{\ \mu}_{p\mathbf{k}}\gamma^p + \frac{1}{2}\sum_{pqr}\langle pq\|\mathbf{k}r\rangle\,{}^\mu\Gamma^{pq}_r\right)\\ &\times\left(\sum_p h^{\ \mu}_{\mathbf{k}p}\gamma_p + \frac{1}{2}\sum_{pqr}\langle\mathbf{k}r\|pq\rangle\,{}^\mu\Gamma^r_{pq}\right),\end{aligned} \tag{19}$$

where g_α accounts for spin degeneracy and $\Omega_{\mathbf{k}}$ for the angle of the emitted electron with momentum $\mathbf{k}$. $h_{p\mathbf{k}}$ and $\langle pq\|\mathbf{k}r\rangle$ are matrix elements of the one-electron and two-electron parts of the Hamiltonian.

Because of the two-electron nature of Auger decay, the dominant contribution to Eq. (19) comes from the two-body Dyson orbitals Γ^{pq}_r and Γ^r_{pq},[84] which connect EOM-IP-CCSD (Ψ^{N-1}) and EOM-DIP-CCSD (Ψ^{N-2}) states corresponding to the channel μ

$$\Gamma^p_{qr} = \langle\Psi^{N-2}|p^\dagger qr|\Psi^{N-1}\rangle, \tag{20}$$

$$\Gamma^{pq}_r = \langle\Psi^{N-1}|p^\dagger q^\dagger r|\Psi^{N-2}\rangle. \tag{21}$$

These are contracted with two-electron integrals in which index $\mathbf{k}$ corresponds to a continuum orbital,

$$\langle\Psi^{N-2}|a_{\mathbf{k}}O_2|\Psi^{N-1}\rangle = \frac{1}{2}\sum_{pqr}\langle\mathbf{k}r\|pq\rangle\Gamma^r_{pq}, \tag{22}$$

$$\langle\Psi^{N-1}|O_2 a^\dagger_{\mathbf{k}}|\Psi^{N-2}\rangle = \frac{1}{2}\sum_{pqr}\langle pq\|\mathbf{k}r\rangle\Gamma^{pq}_r. \tag{23}$$

Here, $a^\dagger_{\mathbf{k}}$ denotes the creation operator corresponding to a free electron with momentum $\mathbf{k}$ and O_2 is the two-electron part of the Hamiltonian.[82,84] Because the EOM-CC Hamiltonian is not symmetric, both left and right Dyson orbitals, i.e., Γ^{pq}_r and γ^p as well as Γ^r_{pq} and γ_p, need to be computed.

In this work, we describe the continuum orbital $\mathbf{k}$ by plane waves. Complete expressions and details of the calculations of mixed Gaussian-plane-wave integrals are available in Ref. 14. The integration over $\Omega_{\mathbf{k}}$ is carried out using Lebedev's quadrature, and we found that for benzene, a very fine integration grid of order 17 is needed for converged results; calculations with the default grid of order 5 yield partial widths that break symmetry-imposed constraints. Sample inputs are given in the supplementary material.

The structure of benzene was optimized with RI-MP2/cc-pVTZ; the respective Cartesian coordinates are given in the supplementary material. The fully uncontracted 6-311(2+,+)G** basis set was used in the CVS-EOM-IP-CCSD and EOM-DIP-CCSD calculations[45,102] to evaluate the partial widths according to Eq. (19). In line with the frozen-core (fc) CVS approach, the core electrons, that is, the K-shells on carbons, were frozen in all valence calculations.[92] The decay widths were convoluted with a Gaussian function with a fixed full width at half maximum equal to 1.15 eV. The so-obtained Auger intensities were then combined with the Auger electron energies calculated according to Eq. (5) to generate the final Auger spectra. To analyze the many-body wave functions in terms of a molecular orbital framework, we also computed natural orbitals (NOs).[103,104]

C. Complex basis function approach

In the CBF method, we describe the metastable core-ionized states directly by CCSD, without invoking CVS. In these calculations, $|\Phi_0\rangle$ from Eq. (6) is a determinant with a core hole. To obtain the required high-energy solutions of the unrestricted Hartree–Fock equations, we used the MOM (maximum orbital overlap) algorithm.[105,106] The IEs are then computed as differences between the total CCSD energies of the core-ionized states and that of the neutral molecule, hence the name ΔCCSD.

In the CBF method,[63,107,108] the description of Auger decay is based on an L^2-representation of the resonance wave function obtained through analytical continuation of the Hamiltonian to the complex plane. A particular advantage of this approach is that no assumptions need to be made about the functional form of the wave function of the Auger electron. The complex resonance energy from Eq. (1) is computed as eigenvalue of a non-Hermitian Hamiltonian without invoking perturbation theory and the total decay width is obtained as $\Gamma = -2\,\mathrm{Im}(E_{\mathrm{res}})$.

The CBF method is related to complex scaling of the Hamiltonian[64,68] through the identity

$$E_{\mathrm{res}} = \frac{\langle\Psi(r)|\hat{H}(re^{i\theta})|\Psi(r)\rangle}{\langle\Psi(r)|\Psi(r)\rangle} = \frac{\langle\Psi(re^{-i\theta})|\hat{H}(r)|\Psi(re^{-i\theta})\rangle}{\langle\Psi(re^{-i\theta})|\Psi(re^{-i\theta})\rangle}, \tag{24}$$

with θ $(0 < \theta < \pi/4)$ as the complex-scaling angle. In the CBF method, the complex-scaled wave function on the right-hand side of Eq. (24) is expressed in terms of Gaussian functions with a scaled exponent that take the form

$$\chi_\mu(r, A) = N_\mu(\theta)\, S_\mu(r_A)\, \exp[-\alpha\, e^{-2i\theta} r_A^2], \tag{25}$$

where N_μ is a normalization constant and S_μ is a polynomial that depends on the angular quantum number of χ_μ. By scaling only selected basis functions, one obtains a finite-basis representation of the exterior complex-scaled Hamiltonian.[109,110] In contrast to complex scaling of the Hamiltonian, the CBF method is compatible with the Born–Oppenheimer approximation and thus applicable not only to atomic but also to molecular electronic resonances.

While the resonance energy E_{res} is independent of the scaling angle θ in the complete basis set limit, a dependence does exist when working with a finite basis. We determine the optimal value for θ through minimization of $|d(E_{\mathrm{res}} - E_0)/d\theta|$, where E_0 is the energy of neutral benzene in the present case. While $\mathrm{Im}(E_0)$ would be zero in the complete basis set because the ground state of benzene is stable against loss of electrons, this is not the case in a finite basis. Previous applications have shown that minimizing this energy difference generally leads to better results than minimizing $|dE_{\mathrm{res}}/d\theta|$.[76,111–113] Further theoretical details of the CBF method can be found elsewhere.[63,70,112,114]

We note that a variety of applications have shown that CBFs combined with CC theory provide an accurate description not only of Auger decay but of other types of electronic resonances such as temporary anions and molecules in static electric fields as well.[112–115]

To compute partial Auger decay widths in the framework of the CBF approach, Matz and Jagau developed two different procedures.[76,77] The first one can be viewed as a generalization of CVS.[36] In this procedure, partial widths are evaluated by applying projectors that are specific to a particular Auger decay channel.[77] The approach works well combined with CCSD, EOM-CCSD, and configuration interaction singles (CIS) wave functions but has the disadvantage that each decay channel requires a separate calculation.

The second approach is based on a decomposition of the imaginary energy and works only for CCSD wave functions.[76] This approach, which has the advantage that all partial widths can be evaluated with a single calculation, was used in the present work. The partial width of a particular decay channel is computed as the contribution to the imaginary part of the CCSD energy,

$$E_{\mathrm{CCSD}} = E_{\mathrm{HF}} + \sum_{ijab}\left(\frac{1}{4}t_{ij}^{ab} + \frac{1}{2}t_i^a t_j^b\right)\langle ij\|ab\rangle \tag{26}$$

from those amplitudes t_{ij}^{ab}, where a or b refers to the core hole, and i and j are the occupied valence orbitals that are empty in the target state. Note that, because of the two-electron nature of Auger decay, the Hartree–Fock energy would be real-valued in the complete basis set limit, and the non-zero value of $\mathrm{Im}(E_{\mathrm{HF}})$ results from using a finite basis.

In the CBF approach, where partial decay widths are evaluated using Eq. (26) alone, there seemingly is no need to compute the wave functions of the doubly ionized target states. However, the energies of these target states are needed to construct the Auger spectrum. As a first approximation, we used Eq. (4) and the orbital energies obtained in the Hartree–Fock calculations of the core-ionized states for this purpose. However, Eq. (4) is a rather crude approximation of the Auger electron energy, and Eq. (5) represents a natural improvement.

In contrast to the Feshbach–Fano approach based on EOM-CC wave functions, there is no obvious way to evaluate Eq. (5) in the framework of the CBF approach based on CCSD wave functions for the core-ionized states. In the present work, we evaluated Eq. (5) in the same way as in Sec. II B, that is, as differences between EOM-DIP-CCSD and EOM-IP-CCSD energies. However, we found that the assignment of the partial widths computed with CCSD using Eq. (26) to channel energies computed with EOM-DIP-CCSD is not straightforward. This is because the EOM-DIP-CCSD eigenvectors R^{DIP} are often not represented by a single transition but have contributions from several orbitals. We constructed the partial width for each DIP state by summing up those CCSD partial widths whose involved orbitals i and j correspond to the leading EOM-DIP-CCSD amplitudes $(r_{ij} > 0.1)$. We then weighted the contributions by the corresponding DIP amplitudes r_{ij} and linearly combined the resulting widths for the DIP states with leading amplitudes corresponding to the same transition. We only considered DIP states with dominant $2h$ character because $3h1p$ configurations do not contribute to the Auger decay process.

The structure of benzene was taken from Ref. 76. This structure differs from the one used in Sec. II B on the order of 0.001 Å, which is irrelevant for our purposes. All calculations were carried out using a modified cc-pCVTZ basis set, where s- and p-shells were replaced by those from cc-pCV5Z. In the CBF-CCSD calculations, three complex-scaled s-, p-, and d-shells were added to all C atoms. The resulting basis set is denoted cc-pCVTZ(5sp)+3(*spd*) and is provided in the supplementary material.

The optimal complex-scaling angle θ_{opt} was determined as 12° by minimization of $|d(E_{\text{res}} - E_0)/d\theta|$. For this purpose, the CBF-CCSD energies of neutral benzene and of the core-ionized $^2A_{1g}$ state were recalculated in the range 6°–16° in steps of 1°. The same optimal value for θ was assumed for the other core-ionized states since there is evidence that θ_{opt} varies little between resonances with similar electronic structures.[70]

Benzene has four distinct core-ionized states, two of which are doubly degenerate. When starting from reference determinants with a core hole, six core-ionized states can be constructed because the degeneracy of the $^2E_{1u}$ and $^2E_{2g}$ states is artificially lifted. Accordingly, we computed six sets of partial widths corresponding to the six core-ionized states. The effect of this artificial symmetry breaking on the results is discussed in Sec. III. The final Auger spectra were built by applying a Gaussian broadening function with a full width at half maximum equal to 1.15 eV to all decay widths in complete analogy to Sec. II B.

III. RESULTS AND DISCUSSION

A. Energies of core-ionized and valence doubly ionized states

Table I shows the IEs of benzene. As anticipated, they are very close, spanning the energy range from 290.78 to 290.86 eV at the CVS-EOM-IP-CCSD/u6-311(2+,+)G** level. The computed IEs agree well with the experimentally determined core-ionization threshold for benzene of 290.42 eV.[52] Using the larger cc-pCVTZ(5sp) basis improves the agreement by about 0.1 eV. We note that the excellent agreement of fc-CVS-EOM-IP-CCSD with the experiment might be due to fortuitous cancellation of errors in this approach.[92] In order to establish the absolute accuracy of this protocol, it is necessary to go beyond the CCSD level of theory and include triple excitations as well as relativistic and vibrational corrections.

The comparison of the different theoretical methods reveals that CBF-EOM-IP-CCSD yields energies that are systematically too high by about 1.5 eV. CBF-ΔCCSD yields energies that are even higher by ~1 eV, which can be explained by a better description of core relaxation in this approach. The last column of Table I shows that the degeneracy of the $^2E_{1u}$ and $^2E_{2g}$ states is lifted in the ΔCCSD calculations. This artificial splitting amounts to about 1 eV.

In the simulation of the Auger spectrum using the Feshbach–Fano approach, we computed 143 EOM-DIP-CCSD states (73 singlets and 70 triplets) with dominant 2*h* character, whereas in the simulation using the CBF approach, we computed 166 EOM-DIP-CCSD states (88 singlets and 78 triplets). These states span the range from 24 to 43 eV, which corresponds to Auger electrons with energies of 244–267 eV. In both simulations, the number of computed target states is less than the estimated total number of 2*h* configurations because of configuration mixing, which stabilizes some states while destabilizing others. The destabilized states appear at much higher energies and mix with 3*h*1*p* configurations, which reduces their contributions to the Auger spectrum. Our calculations do not include decay channels corresponding to Auger electrons with energies below 244 eV.

Table II shows the energies and the characters of the 14 lowest DIP states. The basic structure of the double ionization spectrum is consistent with Koopmans' theorem, i.e., the energies of the orbitals involved in the ionization process. Our DIP energies and the character of the corresponding wave functions also agree well with the ADC(2) results from Ref. 55. In accordance with well-known trends for excitation energies, ADC(2) yields double ionization energies that are consistently lower than EOM-DIP-CCSD energies by 1.5–2.0 eV.

In agreement with Hund's rules, the ground state of doubly ionized benzene is a triplet ($^3A_{2g}$), which is described as ionization from the doubly degenerate HOMO ($1e_{1g}$). According to EOM-DIP-CCSD calculations, its double-ionization energy is 24.85 eV, which is close to the experimentally determined value of 24.65 eV.[116] The two singlet states, which also result from ionization of the HOMO ($^1E_{2g}$ and $^1A_{1g}$), appear just 0.6 and 1.1 eV above the ground state.

Above these three states, there is a gap of almost 2 eV, followed by a cluster of seven states, which span a range of 0.4 eV from 27.85 to 28.25 eV. Six of them are ionizations from HOMO and HOMO − 1 ($1e_{1g} \otimes 3e_{2g} = {}^{1/3}E_{1g} \oplus {}^{1/3}B_{1g} \oplus {}^{1/3}B_{2g}$), whereas the last one is a triplet state ($^3E_{1u}$) corresponding to the ionization of HOMO and HOMO − 2 ($1e_{1g} \otimes 1a_{2u}$). Interestingly, the corresponding singlet state ($^1E_{1u}$) is 3 eV higher in energy, while the singlet-triplet

TABLE I. Core ionization energies (in eV) of benzene.

		CVS-EOM-IP-CCSD	CVS-EOM-IP-CCSD	CBF-EOM-IP-CCSD	CBF-ΔCCSD
State[a]	Core orbital[b]	u6-311(2+,+)G**[c]	cc-pCVTZ(5sp)[c]	cc-pCVTZ(5sp) + 3 (*spd*)[c]	cc-pCVTZ(5sp) + 3 (*spd*)[c]
$^2A_{1g}$	$1a_g$	290.86	290.74	292.04	293.10
$^2E_{1u}$	$1b_{3u}$	290.85	290.72	292.02	291.82
$^2E_{1u}$	$1b_{2u}$	290.85	290.72	292.02	292.81
$^2E_{2g}$	$2a_g$	290.80	290.68	291.98	291.82
$^2E_{2g}$	$1b_{1g}$	290.80	290.68	291.98	292.77
$^2B_{1u}$	$2b_{3u}$	290.78	290.66	291.96	293.03

[a] Irreducible representations are given for the full molecular point group, D_{6h}, using Mulliken's convention.

[b] Irreducible representations are given for the computational point group, D_{2h}, using Q-Chem's convention.

[c] For the definition of basis sets, see Secs. II B and II C. CBF calculations were performed with a scaling angle of 12°.

TABLE II. Double ionization energies (eV) of the 14 lowest doubly ionized states of benzene. The composition of the wave functions in terms of the leading DIP amplitudes is also given.

State	Energy[a]	Energy[b]	Energy[c]	Composition[a]
$^3A_{2g}$	24.85	25.17	23.34	$1e_{1g}^{-2}$ (0.67)
$^1E_{2g}$	25.48	25.80	23.96	$1e_{1g}^{-2}$ (0.66)
$^1A_{1g}$	25.92	26.25	24.59	$1e_{1g}^{-2}$ (0.64), $1a_{2u}^{-2}$ (0.28)
$^3B_{1g}$	27.85	28.14	26.19	$3e_{2g}^{-1}1e_{1g}^{-1}$ (0.47)
$^3E_{1u}$	27.90	28.26	26.07	$1e_{1g}^{-1}1a_{2u}^{-1}$ (0.67)
$^3E_{1g}$	27.96	28.24	26.30	$3e_{2g}^{-1}1e_{1g}^{-1}$ (0.47)
$^1B_{1g}$	28.05	28.33	26.44	$3e_{2g}^{-1}1e_{1g}^{-1}$ (0.46), $1a_{2u}^{-1}1b_{2u}^{-1}$ (0.11)
$^3B_{2g}$	28.07	28.35	26.41	$3e_{2g}^{-1}1e_{1g}^{-1}$ (0.47)
$^1E_{1g}$	28.16	28.43	26.55	$3e_{2g}^{-1}1e_{1g}^{-1}$ (0.46), $1a_{2u}^{-1}3e_{1u}^{-1}$ (0.11)
$^1B_{2g}$	28.25	28.52	26.63	$3e_{2g}^{-1}1e_{1g}^{-1}$ (0.47)
$^1A_{1u}$	29.90	30.16	28.08	$1e_{1g}^{-1}3e_{1u}^{-1}$ (0.47)
$^3E_{2u}$	29.98	30.26	28.32	$1e_{1g}^{-1}3e_{1u}^{-1}$ (0.41), $3e_{2g}^{-1}1a_{2u}^{-1}$ (0.11), $1e_{1g}^{-1}1b_{2u}^{-1}$ (0.11)
$^3A_{1u}$	30.04	30.29	28.22	$1e_{1g}^{-1}3e_{1u}^{-1}$ (0.47)
$^1E_{2u}$	30.04	30.31	28.39	$1e_{1g}^{-1}3e_{1u}^{-1}$ (0.37), $3e_{2g}^{-1}1a_{2u}^{-1}$ (0.38), $1e_{1g}^{-1}1b_{2u}^{-1}$ (0.15)

[a] Computed with EOM-DIP-CCSD/u6-311(2+,+)G**.
[b] Computed with EOM-DIP-CCSD/cc-pCVTZ(5sp).
[c] Computed with ADC(2), taken from Tarantelli *et al.*[55]

splittings of the states described as HOMO ⊗ HOMO − 1 amount to at most 0.2 eV. This difference arises due to the very different values of the respective exchange integrals, $\langle 1e_{1g}1e_{1g}|1a_{2u}1a_{2u}\rangle \approx 0.341$ hartree, $\langle 1e_{1g}1e_{1g}|3e_{2g}3e_{2g}\rangle \approx 0.036$ hartree, which were computed by summing over all degenerate orbitals.

Next comes a second distinct gap of 1.7 eV, after which the structure of the DIP spectrum becomes less resolved. The next group of doubly ionized states, which is only partly included in Table II, results from ionization from HOMO and HOMO − 3, but these states are separated by only 1 eV from higher-lying ones. Notably, the lowest-lying state in this group is a singlet ($^1A_{1u}$) and not a triplet. This can be explained by the low value of the exchange integral $\langle 1e_{1g}1e_{1g}|3e_{1u}3e_{1u}\rangle \approx 0.067$ hartree.

As one can see from Table II, the low-lying DIP states are well represented by a single $2h$ configuration. However, this changes at higher energies, where we observe considerable configuration mixing so that many states cannot be described by a single $2h$ configuration. This has also been observed in the ADC(2) study of doubly ionized benzene by Tarantelli *et al.*[55] and in an ADC(2) study of doubly ionized fluorinated benzenes.[57] We note that some of the higher-lying DIP states also show considerable $3h1p$ character. The lowest state with predominant $3h1p$ character appears at around 36.5 eV corresponding to an Auger electron energy of 255.0 eV. While the energy of these satellite states is overestimated by EOM-DIP-CCSD, the effect on the Auger spectrum is small because of their small contribution to the two-body Dyson orbital [Eqs. (20) and (21)].

The analysis of the EOM-DIP-CCSD wave functions in terms of NOs and their populations shown in Fig. 5 confirms these observations. For the neutral ground state, the shape of the NOs is very similar to that of the canonical Hartree–Fock MOs from Fig. 3.

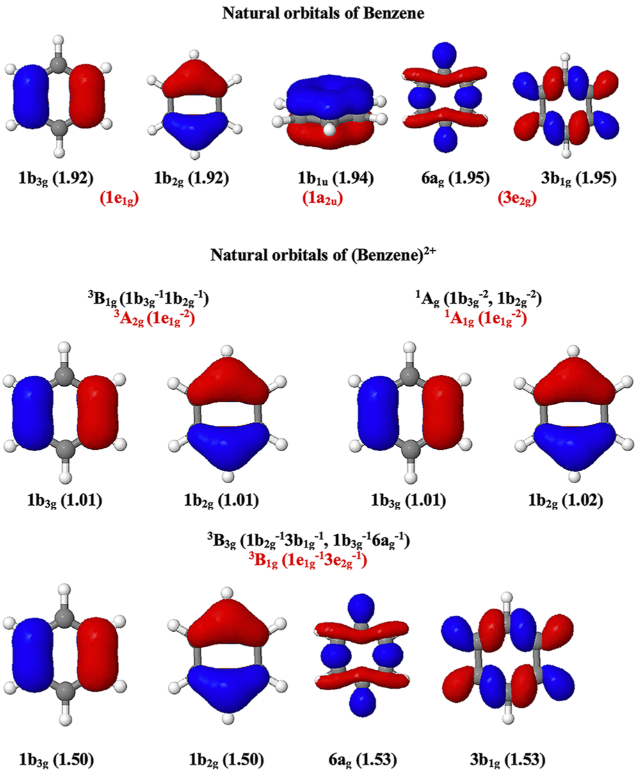


FIG. 5. Frontier NOs and their occupation numbers for the ground state of benzene and selected doubly ionized states. Irreducible representations are given for the D_{6h} point group (in red) and for the largest Abelian subgroup (D_{2h}, in black).

By comparing the NO occupations of the DIP states with those of the neutral reference state, one can infer the character of the orbitals from which the electrons are removed in the course of Auger decay. For example, for the $^3\mathrm{A}_{2g}$ state at 24.85 eV and the $^1\mathrm{A}_{1g}$ state at 25.92 eV, the occupation numbers of the $1b_{3g}$ and $1b_{2g}$ NOs change from 1.92 to 1.01 relative to the neutral reference. This implies that a total of 1.82 electrons are removed from these NOs, which together represent the $1e_{1g}$ shell in the full point group, while 0.18 electrons are removed from other orbitals. For the $^3\mathrm{B}_{1g}$ state at 27.85 eV, the occupation numbers of the $6a_g$ and $1b_{3g}$ NOs change from 1.95 to 1.53, and those of the $3b_{2g}$ and $1b_{2g}$ NOs from 1.92 to 1.50. This means that a total of 1.68 electrons are removed from the $1e_{1g}$ and $3e_{2g}$ shells, and 0.32 electrons are removed from other orbitals.

B. Density of states

Figure 6 shows the densities of singlet and triplet DIP states computed with EOM-DIP-CCSD together with the ADC(2) results from Ref. 55. As discussed in Sec. II A and in Ref. 55, the density of DIP states can be considered a crude approximation to the Auger spectrum.

Figure 6 illustrates that, after application of a broadening function, most DIP states are no longer individually discernible. Rather, a spectrum with a few broad peaks, each comprising many DIP states, is obtained. An exception is the lowest peak in the triplet manifold at 25 eV, which corresponds to the $^3\mathrm{A}_{2g}$ state. This state (the first entry in Table II) originates from the double ionization of the doubly degenerate HOMO. The lowest-lying singlet peak at around 26 eV is composed of two states ($^1\mathrm{E}_{2g}$ and $^1\mathrm{A}_{1g}$), which are derived by ionization of the HOMO (see Table II). The next two peaks, which are well separated from the higher-lying ones, comprise four triplet and three singlet channels, respectively, as detailed in Table II. Beyond 30 eV, each peak in the singlet and triplet spectrum comprises an even larger number of DIP states.

Figure 6 shows that, after application of a uniform shift, the agreement between EOM-DIP-CCSD and ADC(2) is very good for the lowest two peaks in each panel, still acceptable for the third peak, and substantially worse at higher energies. While the uniform shift can be justified by the well-known performances of EOM-CCSD and ADC(2) (see Sec. III A), the reason for deteriorating agreement at higher energies is less obvious. It may be related to the increasing admixture of $3h1p$ configurations that we observe in the higher-lying DIP states. ADC(2) treats these doubly excited configurations at a lower level than EOM-CCSD, which may lead to a poor description of states in which the weight of these configurations becomes comparable to the weight of the $2h$ configurations.

Importantly, Fig. 6 only provides a crude picture of the Auger spectrum. The most important shortcoming is that it suggests equal contributions of singlet and triplet channels to the spectrum, whereas it is clear from theoretical considerations that the contributions of triplet states are smaller (see Appendix). One needs to compute the partial widths of the decay channels for quantitative modeling, and we do so in Sec. III C.

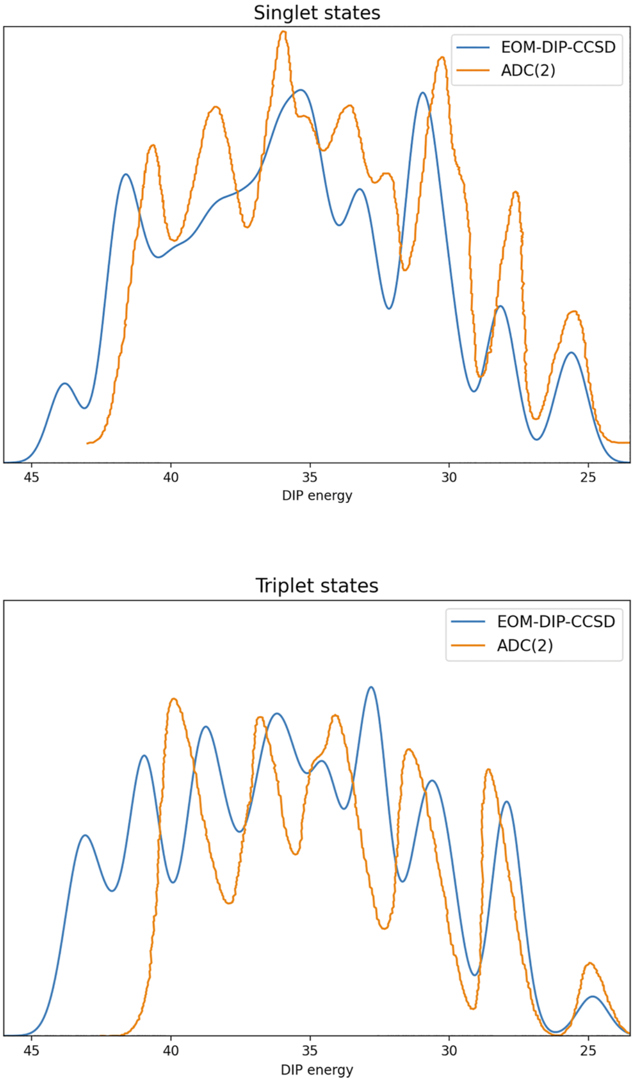


FIG. 6. Density of singlet and triplet DIP states in benzene computed with EOM-DIP-CCSD/u6-311(2+,+)G** and ADC(2) (from Ref. 55). To match the lowest-lying EOM-DIP-CCSD peaks, the ADC(2) data were shifted by 2.15 and 1.33 eV for singlet and triplet states, respectively.

C. Total Auger spectrum

The non-resonant Auger spectra of benzene computed with the two different methods discussed in Sec. II (Feshbach–Fano and CBFs) are shown in Fig. 7. The largest partial widths are given in Tables S1 and S3 in the supplementary material. Notably, there are many channels with partial widths of the same order of magnitude, and there is not a single channel with a width of more than 2 meV. Thus, the data in the tables cannot be interpreted without actually constructing the spectrum.

The comparison of the two spectra in Fig. 7 illustrates the very good agreement between the two theoretical approaches, despite the vastly different treatment of the outgoing electron. This cross-validates our two approaches. For the CBF method, Fig. S4 in the supplementary material shows how using Eq. (4) instead of Eq. (5) for the peak positions leads to a substantially different Auger spectrum. This demonstrates the importance of using a high-level electronic-structure model.

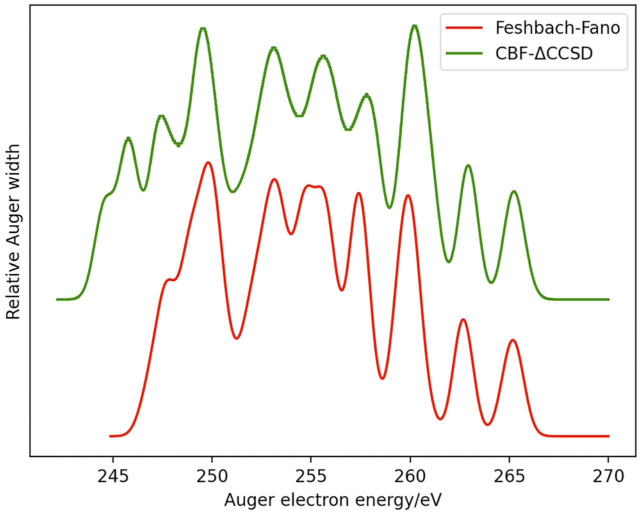


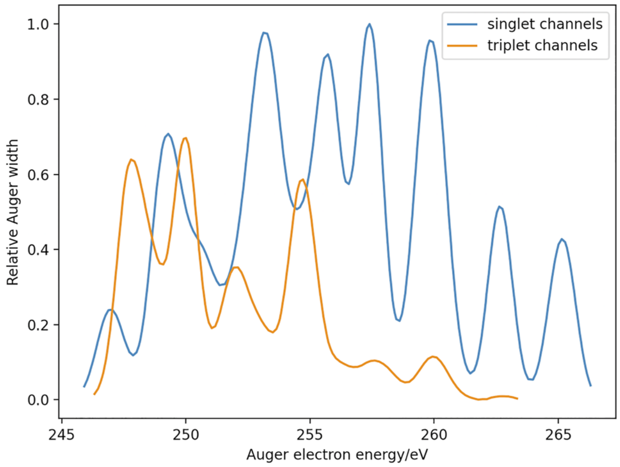
FIG. 7. The non-resonant Auger spectrum of benzene computed using the Feshbach–Fano approach (red curve) and the CBF approach (green curve). The DIP energies needed for the positions of the peaks were computed with EOM-DIP-CCSD for both approaches (see Secs. II B and II C).

The two spectra in Fig. 7 have eight and nine distinct peaks, respectively, which we loosely group into the following categories based on the Auger electron energies: (a) peaks above 262 eV, (b) peaks between 252 and 262 eV, and (c) peaks below 252 eV. The two peaks above 262 eV are the easiest to describe. They correspond to the two lowest peaks in the density of singlet states (see Fig. 6) and arise from double ionization of the HOMO and mixed ionization of HOMO/HOMO − 1, respectively.

In the range between 252 and 262 eV, each peak is composed of many decay channels. As one would expect, contributions from lower-lying orbitals become more important with decreasing Auger electron energy. We observe that the final states in this energy range have a predominant 2*h* character and are thus well represented by EOM-DIP-CCSD. Below 252 eV, contributions from lower-lying orbitals gain even more weight, and the final states develop substantial 3*h*1*p* character, which makes their description by EOM-DIP-CCSD less reliable. This affects both spectra in Fig. 7 equally.

Additionally, we investigated the contributions of singlet and triplet states to the computed spectra. As discussed in the Appendix and in Refs. 55 and 83, singlet channels are expected to have notably larger Auger intensities in comparison to triplet channels. Figure 8 shows that this is indeed the case with both approaches—the Auger spectrum of benzene is dominated by contributions from singlets.

Interestingly, the $^3A_{2g}$ ground state of the benzene dication has zero Auger intensity in both of our approaches (Feshbach–Fano and CBF). Likewise, the contributions of the low-lying triplets listed in Table II are very small. Only below 260 eV, the triplet contributions become noticeable. At these energies, they visibly affect the shape of the spectrum. This is most evident for the peak around 250 eV, which becomes the most intense peak in the spectrum due to the combined contributions of singlets and triplets. We reiterate that such differences in the Auger intensity of singlet and triplet channels are not apparent from the density of states shown in Fig. 6. Thus, a mere analysis of decay channels does not provide a complete picture of Auger decay.



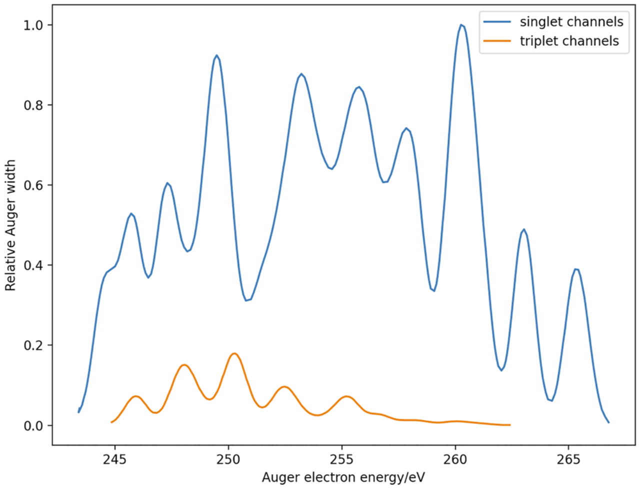


FIG. 8. Contributions from singlet and triplet decay channels to the non-resonant Auger spectrum of benzene. Top: Feshbach–Fano approach, bottom: CBF approach.

Furthermore, we note that the triplet contributions are overestimated by the Feshbach–Fano approach as compared to the CBF approach. Such overestimation of triplet intensities was observed in previous studies, where it was attributed to the limitations of the plane-wave treatment of the Auger electron.[75] It was also shown that using Coulomb waves improved the results.[14,75] Despite this limitation of the plane-wave treatment, the overall spectrum in Fig. 7 is barely affected; Feshbach–Fano and CBF agree well with each other in the entire energy range.

D. Auger spectra corresponding to individual core-ionized states

To analyze the contributions of the four different core-ionized states ($^2A_{1g}$, $^2E_{1u}$, $^2E_{2g}$, $^2B_{1u}$) to the overall Auger spectrum in Fig. 7, we plotted the spectra resulting from selective ionization in Fig. 9. Here, the contributions of degenerate core orbitals (e_{1u}, e_{2g}) were added together. We anticipate that our results will provide useful insights into Auger spectroscopy experiments using narrow-band x-rays, which may lead to selective core-ionization.

Our results show that the symmetry of the core holes impacts the intensity pattern despite their very similar energies. Although the individual spectra have a general structure that is similar to that of the overall spectrum in Fig. 7, the decay width corresponding to a particular Auger electron energy differs. For example, the $^2B_{1u}$ state produces enhanced intensity in the Auger electron energy regime around 250 eV, whereas the $^2A_{1g}$ state mostly stimulates an energy regime closer to 255 eV.

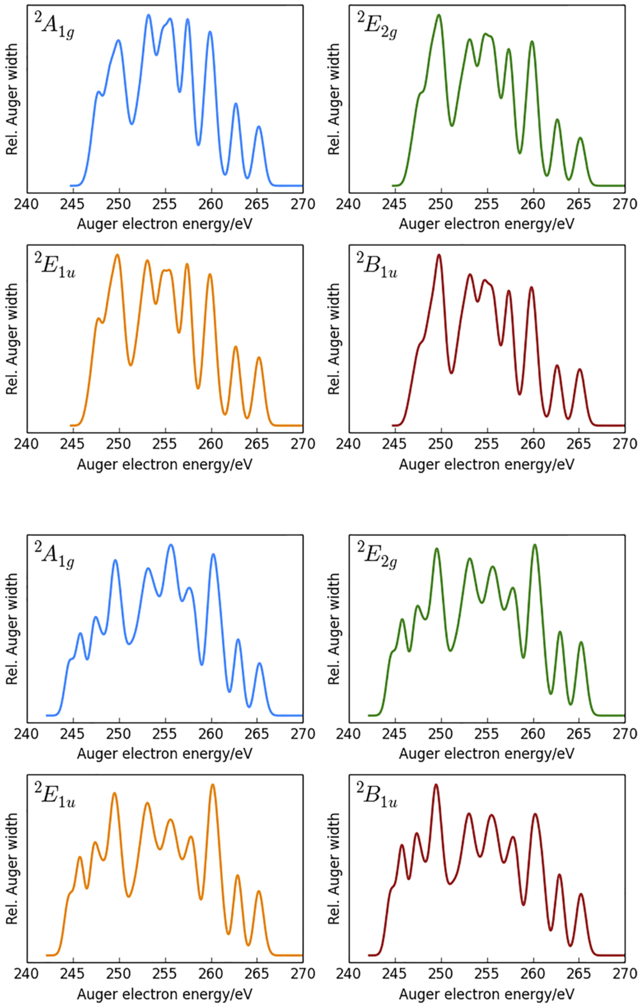


FIG. 9. Auger spectra of benzene corresponding to selective ionization of each core orbital. The spectra are normalized individually, and the degenerate core orbitals (e_{1u} and e_{2g}) are treated together. Top four panels: Feshbach–Fano approach. Bottom four panels: CBF approach.

The inspection of Fig. 9 also illustrates more substantial differences between the Feshbach–Fano and the CBF approach that are not visible in the overall spectrum in Fig. 7. For example, it appears that the CBF approach overestimates the intensity of the decay channels around 260 eV for the degenerate core holes (e_{2g} and e_{1u}). This may be due to the shortcoming of the CBF/CCSD approach discussed in Sec. III A, namely that the degeneracy of the e_{2g} and e_{1u} core orbitals is lifted. Fig. S5 shows the same data as in Fig. 9, but normalized together rather than individually, illustrating the effect of the artificial symmetry breaking on the CBF spectra. In addition, Fig. S5 shows that there is more variation among the individual spectra in the CBF approach than in the Feshbach–Fano approach for the non-degenerate core-hole states as well.

E. Total decay widths

We also calculated the total decay widths of all core-ionized states; the results are shown in Table III. The variation in the width among the core holes does not exceed 15%, which is not surprising given that all states are derived from C(1s) orbitals. However, the widths computed with CBFs are about a factor of two larger than those computed with the Feshbach–Fano approach: 80 vs 45 meV, corresponding to lifetimes of 8.3 and 14.6 fs, respectively. This is most likely due to the latter calculations including only a limited number of decay channels. The issue of underestimation of total decay widths in Feshbach–Fano approaches has been noted most recently by Coriani and co-workers, who reported that the theory gives higher lifetimes than experiment: 9 fs were computed as the lifetime for core-excited ozone, as compared to 4 fs obtained for water from a O 1s photoelectron spectrum.[117]

In contrast, in the CBF approach, the total decay width is computed directly without considering individual decay channels. We note that both approaches violate symmetry-imposed constraints, yielding different widths for degenerate orbitals. In the Feshbach–Fano calculations, the core-hole states are exactly degenerate, and the mismatch in widths occurs because a different number of decay channels are included in the calculations. In the CBF approach, the symmetry violation is more pronounced and happens because the core-hole states are described based on independent open-shell CCSD calculations.

TABLE III. Total decay widths of the core-ionized states of benzene in meV.

Core orbital	Feshbach–Fano	CBF
$1a_g$ ($1a_{1g}$)	41.70	76.45
$1b_{2u}$ ($1e_{1u}$)	44.20	78.84
$1b_{3u}$ ($1e_{1u}$)	43.10	84.80
$2a_g$ ($1e_{2g}$)	46.20	84.63
$1b_{1g}$ ($1e_{2g}$)	47.30	78.02
$2b_{3u}$ ($1b_{1u}$)	48.60	75.23
Average width	45.17	79.66

A quantitative assessment of the computed total decay widths in Table III is difficult because no experimental values have been reported for benzene. However, several experiments have been conducted for methane.[118–121] Values for the natural linewidth of the C(1s) core-hole state reported from these measurements vary significantly between 83 ± 10 meV (7.9 fs) and 120 ± 10 meV (5.5 fs), which underpins our supposition that the Feshbach–Fano calculations underestimate the total decay widths and the CBF results are more accurate.

F. Comparison to the experimental Auger spectrum

Figure 10 compares the Auger spectrum from the most recent experiment[53] (see Fig. 2, spectrum C) and our theoretical Auger spectra from Fig. 7. The experimental spectrum has a broad structure with various unresolved bands. Eight distinct peaks can be distinguished, two of which are in the high Auger electron energy regime above 262 eV. The latter two peaks, which are relatively well resolved in the experimental spectrum, can be, on the basis of our calculations, unambiguously assigned to final states arising from double ionization of the HOMO and HOMO/HOMO − 1, respectively.

However, the intensity pattern of these two peaks differs between theory and experiment. We note that our two theoretical spectra agree with the one reported by Tarantelli *et al.*;[55] on the other hand, the three experimental spectra agree with each other as well in this respect. Provided that the experimental intensity pattern is real and not an artifact of calibration or detection, a possible explanation for the mismatch could be the contribution of resonant Auger decay to the experimental spectra. Both participator and spectator resonant Auger decay contribute intensity, especially for the higher-energy Auger electrons. The mismatch could also be due to the effect of nuclear motion, which is neglected in the present treatment. For example, it has been shown for the water molecule that vibrational effects can modify Auger intensities considerably.[122] We will explore the intensity mismatch between theory and experiment in future work.

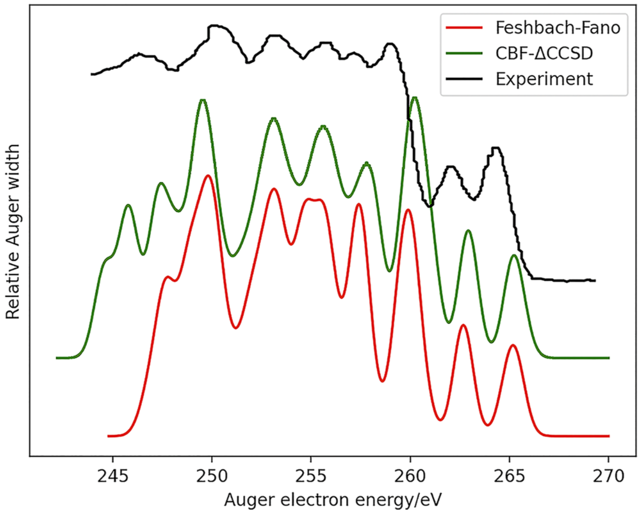


FIG. 10. The theoretical Auger spectra of benzene from Fig. 7 computed using Feshbach–Fano and CBF approaches compared to the most recent experiment.[53] The experimental spectrum is shifted by −1.60 eV to match the theory peak at 253.15 eV.

At lower Auger electron energies, the experimental spectrum has five peaks in the region between 250 and 260 eV and one peak below 250 eV. Both theoretical spectra reproduce the intensity pattern of these peaks quite well: (a) all peaks are more intense than the two above 260 eV, (b) the peak below 250 eV is somewhat less intense than the ones between 250 and 260 eV, and (c) the most intense peak is the one around 250–251 eV. The weak trend in the intensity between 250 and 260 eV is captured better by the Feshbach–Fano approach, whereas the CBF approach seems to overestimate the intensity of the peak at around 260 eV. However, the CBF spectrum is superior below 250 eV, where two well-resolved peaks are obtained, whereas the Feshbach–Fano spectrum only has a weak shoulder this is likely because we computed fewer DIP states for the latter spectrum.

We also note that the higher electron-energy peaks in the experimental spectrum do not fully align with those in the theoretical spectra, even after the experimental spectrum is shifted by 1.60 eV. This misalignment may be either due to an insufficient level of correlation treatment in EOM-IP-CCSD or some problems in the experiments. We reiterate that there is a noticeable disagreement between the three measurements, as seen in Fig. 2 and in the supplementary material.

IV. CONCLUSIONS

We have reported a theoretical *ab initio* study of Auger decay in benzene. Partial Auger decay widths were computed with two methods from non-Hermitian quantum chemistry combined with CC and EOM-CC theory. Namely, we used the Feshbach–Fano projection operator approach and, independently, the method of CBFs. In total, we considered over 1000 transitions corresponding to Auger electron energies in the range from 245 to 270 eV, which illustrates the complexity of Auger decay in benzene.

Our two theoretical Auger spectra are in excellent agreement with each other and in reasonable agreement with experimental Auger spectra as well. This showcases the power of non-Hermitian quantum chemistry and cross-validates the Feshbach–Fano and the CBF approaches. Our Auger spectra are also in qualitative agreement with an Auger spectrum derived from the density of doubly ionized valence states, which validates the statistical approach of Tarantelli *et al.*[55]

Our work illustrates the strengths and weaknesses of the Feshbach–Fano and the CBF approaches. On the one hand, Feshbach–Fano calculations are computationally less expensive because there is no need for optimizing the complex-scaling angle or complex algebra altogether. Also, smaller basis sets as compared to CBF calculations appear to be sufficient. Moreover, our Feshbach–Fano calculations preserve the degeneracy of the benzene core holes, whereas this is not the case in the CBF treatment, which is based on core-hole reference states. The latter problem could, however, be circumvented by using a closed-shell reference in the CBF calculations.

On the other hand, CBF calculations provide direct access to total decay widths, whereas Feshbach–Fano calculations only yield partial widths. Moreover, the Feshbach–Fano approach overestimates the contributions of triplet decay channels, likely due to using plane waves for representing the Auger electron, whereas the CBF approach gives more realistic singlet-triplet branching ratios. This shortcoming of the Feshbach–Fano approach can likely be remedied by improving the free-electron description.

We note that we could not resolve a conspicuous discrepancy between theory and experiment regarding the intensity of the two peaks in the spectrum with the highest Auger electron energies. This suggests possible extensions of our current work that are worthwhile to pursue: the consideration of resonant contributions to the Auger spectrum as well as the study of vibrational effects.

In conclusion, we see our work as a testament to the power and usefulness of non-Hermitian extensions of *ab initio* quantum-chemical methods. We also expect that our work will motivate further theoretical and experimental work in the area of Auger decay.

SUPPLEMENTAL MATERIAL

Supplementary material is available: an analysis of the experimental spectra; additional data, and the results of the calculations.

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AUTHOR DECLARATIONS

Conflict of Interest

A.I.K. is the president and a part-owner of Q-Chem, Inc.

Author Contributions

Nayanthara K. Jayadev: Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal). **Anthuan Ferino-Pérez**: Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal). **Florian Matz**: Investigation (supporting); Validation (supporting); Writing – original draft (supporting). **Anna I. Krylov**: Conceptualization (lead); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Supervision (lead); Validation (equal); Writing – original draft (equal). **Thomas-C. Jagau**: Conceptualization (lead); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Supervision (lead); Validation (equal); Writing – original draft (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

APPENDIX A: AUGER INTENSITIES OF SINGLET VERSUS TRIPLET CHANNELS IN THE FESHBACH–FANO APPROACH

Following Ågren and co-workers,[82,84] we analyze the expressions of the Auger intensity, Eq. (23), in terms of different spin blocks of the two-body Dyson orbitals to explain differences in relative intensities of triplet and singlet channels. We analyze the contribution to the total intensity due to Γ_r^{pq}; a similar analysis can be carried out for Γ_{pq}^r (left and right Dyson orbitals are slightly different because of the non-Hermitian nature of EOM-CC; for the sake of brevity, only the right part of the transition amplitude is shown in the following equations).

Here, we are interested in the two-electron part of the width, which is computed by contracting the two-body Dyson orbitals[84] Γ_r^{pq}—that connect EOM-IP (Ψ^{N-1}) and EOM-DIP (Ψ^{N-2}) states—with two-electron integrals in which one index corresponds to the plane wave.

From the definition of Γ_r^{pq} [Eq. (21)] and Fig. 4 one can see that index r corresponds to the core orbital and indices p and q to the valence orbitals. Since the operators for the core and valence orbitals operate in different orbital subspaces, they commute. Therefore, the expression for the two-body Dyson orbital connecting the core-hole state and a DIP state can be written as

$$\Gamma_r^{pq} = \langle \Psi_0 | p^\dagger q^\dagger | \Psi^{N-2} \rangle, \tag{A1}$$

where Ψ_0 is the neutral CCSD reference state re-created from the EOM-IP state by filling the core hole with operator r. Equation (A1) shows that the leading contribution to Γ is given by the 2h DIP amplitudes.

Following these preparations, we can now analyze the spin symmetry of Γ_r^{pq}. First, for a state with an α core-hole, Γ_α^{pq} is non-zero and Γ_β^{pq} is zero; the converse is true for a state with a β hole. For the DIP states with $M_s = 0$, $\Gamma_r^{\alpha\alpha}$ and $\Gamma_r^{\beta\beta} = 0$. By using the spin symmetry of the singlet and triplet states with the same orbital occupations, we can write that for a singlet DIP state

$$\Gamma_r^{\alpha\beta} = -\Gamma_r^{\beta\alpha} \tag{A2}$$

and for a triplet DIP state

$$\Gamma_r^{\alpha\beta} = \Gamma_r^{\beta\alpha}. \tag{A3}$$

To estimate the relative contributions to the Auger intensity, we need to carry out spin integration of the two-electron integrals. The expression for the partial width in terms of different spin blocks can be written as follows by considering an α core hole and the spin symmetry of $\mathbf{k}$ to be β:

$$\begin{aligned}\widetilde{\Gamma} &= \frac{1}{2}\sum_{pqr} \langle pq \| \mathbf{k} r_\alpha \rangle \Gamma_{r_\alpha}^{pq} \\ &= \frac{1}{2}\sum_{pqr} \langle p_\alpha q_\beta \| \mathbf{k}_\beta r_\alpha \rangle \Gamma_{r_\alpha}^{p_\alpha q_\beta} + \frac{1}{2}\sum_{pqr} \langle p_\beta q_\alpha \| \mathbf{k}_\beta r_\alpha \rangle \Gamma_{r_\alpha}^{p_\beta q_\alpha}\end{aligned}$$

$$
\begin{aligned}
&= \frac{1}{2}\sum_{pqr}\left[\langle p_\alpha q_\beta|\mathbf{k}_\beta r_\alpha\rangle - \langle p_\alpha q_\beta|r_\alpha \mathbf{k}_\beta\rangle\right]\Gamma^{p_\alpha q_\beta}_{r_\alpha} \\
&\quad + \frac{1}{2}\sum_{pqr}\left[\langle p_\beta q_\alpha|\mathbf{k}_\beta r_\alpha\rangle - \langle p_\beta q_\alpha|r_\alpha \mathbf{k}_\beta\rangle\right]\Gamma^{p_\beta q_\alpha}_{r_\alpha} \\
&= \frac{1}{2}\sum_{pqr}\left[-\langle p_\alpha q_\beta|r_\alpha \mathbf{k}_\beta\rangle\Gamma^{p_\alpha q_\beta}_{r_\alpha} + \langle p_\beta q_\alpha|\mathbf{k}_\beta r_\alpha\rangle\Gamma^{p_\beta q_\alpha}_{r_\alpha}\right]. \qquad \text{(A4)}
\end{aligned}
$$

Integrating the spins out and substituting Eqs. (A2) and (A3), the partial widths become

$$
\begin{aligned}
\widetilde{\Gamma}_{singlet} &= \frac{1}{2}\sum_{pqr}\left[\langle pq|\mathbf{k}r\rangle + \langle pq|r\mathbf{k}\rangle\right]\Gamma^{pq}_{r}, \\
\widetilde{\Gamma}_{triplet} &= \frac{1}{2}\sum_{pqr}\left[\langle pq|\mathbf{k}r\rangle - \langle pq|r\mathbf{k}\rangle\right]\Gamma^{pq}_{r}.
\end{aligned} \qquad \text{(A5)}
$$

In the above expressions, indices p, q, and r correspond to spatial orbitals. As one can see, in the singlet contribution, the two two-electron integrals, which can be interpreted as Coulomb interaction between the core hole, the valence electrons, and a free electron, are connected by a plus sign, whereas in the triplet contribution, they are connected by a minus sign, leading to partial cancellation.

APPENDIX B: AUGER INTENSITIES OF SINGLET VERSUS TRIPLET CHANNELS IN THE COMPLEX BASIS FUNCTION APPROACH

As discussed in Sec. II C, the Auger intensities can be computed from the partial decay widths obtained through energy decomposition analysis of the imaginary part of the CBF-CCSD energy in Eq. (26). For the purpose of this work, the contribution of the single amplitudes is negligible[76] and is, therefore, omitted in the following discussion. The partial decay width of a specific channel μ can then be written as

$$
\begin{aligned}
-\frac{\Gamma_\mu}{2} &= \frac{1}{4}\,\mathrm{Im}\left[t^{ab}_{ij}\langle ij\|ab\rangle + t^{ab}_{ji}\langle ji\|ab\rangle + t^{ba}_{ij}\langle ij\|ba\rangle + t^{ba}_{ji}\langle ji\|ba\rangle\right] \\
&= \mathrm{Im}\left[t^{ab}_{ij}\langle ij\|ab\rangle\right], \qquad \text{(B1)}
\end{aligned}
$$

where a, b, i, and j refer to those spin orbitals, which give rise to decay channel μ. Note that Eq. (B1) does not include any summation. We now consider the CBF-CCSD energy of a core-ionized state where the core hole has β spin. Then, if index a refers to the core hole, b represents the outgoing Auger electron and can have α or β spin. i and j are valence orbitals and can also have either α or β spin. Thus, we end up with three spin cases: $t^{a_\beta b_\beta}_{i_\beta j_\beta}$, $t^{a_\beta b_\alpha}_{i_\beta j_\alpha}$, $t^{a_\beta b_\alpha}_{i_\alpha j_\beta}$.

Recalling that b stands for the outgoing Auger electron and that the core hole has β spin, the $\beta\beta$ spin case can be related to a triplet final state, while the $\alpha\beta$ and $\beta\alpha$ spin cases correspond to singlet final states. This assignment is necessarily approximate for an open-shell CCSD wave function, which is not a spin eigenfunction. However, it would be exact, for example, for an EOM-IP-CCSD wave function. Note, in particular, that for EOM-IP-CCSD, the $\alpha\beta$ and $\beta\alpha$ spin cases do not contribute to the $M_S = 0$ components of the triplet channels.[77]

The contributions to the decay width can thus be written as

$$
-\frac{\Gamma^{\text{triplet}}_\mu}{2} = \mathrm{Im}\left[t^{a_\beta b_\beta}_{i_\beta j_\beta}\left(\langle a_\beta b_\beta|i_\beta j_\beta\rangle - \langle a_\beta b_\beta|j_\beta i_\beta\rangle\right)\right], \qquad \text{(B2)}
$$

$$
\begin{aligned}
-\frac{\Gamma^{\text{singlet}}_\mu}{2} &= \mathrm{Im}\Big[t^{a_\beta b_\alpha}_{i_\beta j_\alpha}\left(\langle a_\beta b_\alpha|i_\beta j_\alpha\rangle - \langle a_\beta b_\alpha|j_\alpha i_\beta\rangle\right) \\
&\quad + t^{a_\beta b_\alpha}_{i_\alpha j_\beta}\left(\langle a_\beta b_\alpha|i_\alpha j_\beta\rangle - \langle a_\beta b_\alpha|j_\beta i_\alpha\rangle\right)\Big] \\
&= \mathrm{Im}\left[t^{a_\beta b_\alpha}_{i_\beta j_\alpha}\langle a_\beta b_\alpha|i_\beta j_\alpha\rangle - t^{a_\beta b_\alpha}_{i_\alpha j_\beta}\langle a_\beta b_\alpha|j_\beta i_\alpha\rangle\right]. \qquad \text{(B3)}
\end{aligned}
$$

Equations (B2) and (B3) represent contributions to the imaginary part of the same-spin and opposite-spin correlation energies. From this, we can conclude that the partial widths of the triplet channels are smaller than those of the singlet channels because it is well known that the opposite-spin correlation energy is usually considerably higher than the same-spin correlation energy.[123]

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