

Complex-Energy Second-Order Approximate Coupled-Cluster Methods for Electronic Resonances

Cansu Utku, Garrette Pauley Paran, and Thomas-C. Jagau

Department of Chemistry, KU Leuven, Belgium

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Abstract

Electronic resonances are metastable states with finite lifetimes, encountered in processes such as photodetachment, electron transmission, and Auger decay. Resonances appear in Hermitian quantum mechanics as increased density of states in the continuum rather than as discrete energy levels. To describe resonances accurately, including their coupling to the continuum, methods based on non-Hermitian quantum mechanics can be used, which yield complex energies. In this work, we combine the complex absorbing potential (CAP) and complex basis functions (CBF) techniques with the RI-CC2 method. The second-order coupled cluster method (CC2) offers a good balance between accuracy and computational cost by approximating equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) theory, making it suitable for studying of electronic resonances in larger molecules. The resolution-of-the-identity (RI) approximation further reduces computational demands without significant loss in accuracy. We investigate the numerical performance of the new complex-energy RI-CC2 methods focusing on temporary anions. Negative electron affinities and decay widths can be computed using the electron-attachment (EA) variant of RI-CC2. For N_2 , C_2H_4 , CH_2O , and HCOOH , EA-CC2 yields affinities about 0.1–0.2 eV smaller than EOM-EA-CCSD, while deviations reach 0.5 eV for larger anions such as uracil, naphthalene, cyanonaphthalene, and pyrene. As a result of these trends, EA-CC2 is in better agreement with experiment for the negative electron affinities than EOM-EA-CCSD for all studied anions. The corresponding resonance widths from EA-CC2 calculations are about 0.05–0.25 eV smaller compared to EOM-EA-CCSD. Semi-empirical spin-scaling increases electron affinities by 0.3–0.5 eV and broadens resonance widths, improving the agreement with EOM-EA-CCSD but worsening the agreement with experiment.

I. INTRODUCTION

The characterization of metastable electronic states plays an important role in understanding processes such as dissociative electron attachment[1, 2], autoionization, Auger-Meitner decay[3, 4], and intermolecular Coulombic decay[5]. These processes mediate key steps in chemical reactions including, for example, energy transfer,[6, 7] plasmonic catalysis,[8–10] and radiation damage in materials and biological systems.[11, 12] Metastable states are also essential for interpreting Auger,[13] photoionization,[14] photodetachment,[15], electron scattering,[16, 17] and electron-energy loss spectra.[18] Their study and understanding are thus essential for advancing fields ranging from quantum chemistry and spectroscopy to plasma physics, astrochemistry, and biomedical science.

Metastable states lie in the continuum above the detachment or ionization threshold and cannot be described within the conventional bound-state framework. Electronic resonances have been studied using a variety of theoretical approaches that include both extensions of bound-state techniques and explicit scattering methods. Stabilization methods identify resonances by tracking the variation of eigenvalues upon introducing external charges or scaling the diffuseness of basis functions.[19, 20] The Feshbach-Fano formalism partitions the Hilbert space into bound and continuum subspaces and treats the coupling perturbatively.[21, 22] Scattering-based techniques such as the R-matrix[23] method solve the electron-molecule scattering problem directly, yielding resonance positions and widths from the scattering matrix.[24]

A further approach for the theoretical treatment of resonances involves non-Hermitian extensions of quantum chemistry methods.[25, 26] Complex absorbing potentials[27, 28] (CAPs) and complex basis functions (CBFs)[29–31] provide a route to compute resonance energies and lifetimes within the framework of bound-state electronic structure methods.

These approaches yield complex energy and have been implemented for a variety of electronic-structure methods. CAPs have been employed with density functional theory (DFT),[32] multireference configuration interaction (MRCI)[33, 34], Fock space multireference coupled-cluster,[35] symmetry-adapted cluster configuration interaction (SAC-CI)[36], algebraic diagrammatic construction [ADC(n)][37–40], second-order multiconfigurational quasidegenerate perturbation theory (XMCQDPT2),[41] complete-active-space second-order perturbation theory (CASPT2),[42] and equation-of-motion coupled-cluster with singles and

doubles (EOM-CCSD).[43–47] The CAP-EOM-CCSD method has been extended beyond energies and lifetimes to transition properties[48] and analytic gradients.[49–51]

We note that there are different variants of CAP-SAC-CI, CAP-ADC, and CAP-EOM-CCSD available, in which the potential is added to the Hamiltonian at different steps of the calculation. For example, in EOM-CCSD, one can either include the CAP in the Hartree-Fock (HF) calculation [45], or add it only at the EOM-CCSD step[43], or construct the CAP Hamiltonian in a basis of real-valued EOM-CCSD pseudocontinuum states.[46] By means of the OpenCAP software,[52] the latter approach has been extended to arbitrary electronic-structure methods that yield mutually orthogonal pseudocontinuum states.

The CBF method relies on complex scaling[53–55] (CS) and has been combined with HF theory,[31, 56, 57] MRCI,[58–60] resolution-of-the-identity second-order Møller-Plesset perturbation theory (RI-MP2), [61, 62] and EOM-CCSD.[47, 63]

In this work, we present an implementation of the electron attachment (EA) variant of the resolution-of-the-identity second-order approximate coupled-cluster (RI-CC2) method[64–66] combined with both CAPs and CBFs. In analogy to CC2 for bound states, which is suited well for electronically excited states in large systems, our implementation provides an appealing alternative to EOM-CCSD for resonances in larger systems. The computational cost scales as $\mathcal{O}(N^5)$ with system size N as compared to $\mathcal{O}(N^6)$ for EOM-CCSD, balancing accuracy and efficiency. The memory requirements are reduced from $\mathcal{O}(N^4)$ to $\mathcal{O}(N^3)$ by decomposing the four-index two-electron integrals by means of the RI approximation into three-index quantities.[67–69] We note that the latter can also be achieved by means of Cholesky decomposition (CD)[70–72], but this is beyond the present work.

Our RI-CC2 implementation is based on the algorithm presented in Ref. [65]. This algorithm is based on an effective Jacobian that only has the dimensions of the CI singles eigenvalue equations because the double excitation amplitudes are treated implicitly. As a result, the matrix elements of the Jacobian depend on the excitation energy, i.e., the eigenvalue that is sought. Therefore, the Davidson algorithm, commonly applied to solve the EOM-CCSD equations, cannot be applied to RI-CC2 without modifications. To address this, we implemented a modified algorithm that is also based on Ref. [65].

Extending the original formulation for electron-number and spin conserving excitations,[64, 65] further RI-CC2 methods have been implemented for spin-flipping (SF) excitations,[73] ionization (IP),[74] and electron attachment.[75] The numerical performance of the IP

and EA variants is not satisfactory, but it can be improved significantly using spin scaling factors[76] resulting in the spin-component-scaled (SCS)[77] and spin-opposite-scaled (SOS)[78] RI-CC2 methods.[79] For example, in the case of valence anions, the error of RI-EA-CC2 relative to EOM-EA-CCSD is 0.47 eV, but decreases to 0.07 eV with SCS and 0.14 eV with SOS.[80] Very similar results were found for the spin-scaled ADC(2) methods.[81] This suggests that complex-energy RI-EA-CC2 may also benefit from spin scaling and, therefore, we also implemented the SCS and SOS variants.

To assess the performance of complex-energy RI-CC2 methods for resonance states, we apply our new methods to several molecular temporary anions. These include the small anions N_2^- , C_2H_4^- , CH_2O^- , HCOOH^- , for which EOM-EA-CCSD are feasible, as well as anions of uracil, naphthalene, cyanonaphthalene, and pyrene as examples of larger molecules. The anion of uracil is of interest in the context of radiation-induced damage to RNA. The anions of the polycyclic aromatic hydrocarbons (PAHs) are astrochemically relevant,[82] because PAHs are widespread in the interstellar medium and believed to contribute to diffuse interstellar bands.

The remainder of the article is structured as follows: In Section II, we discuss the theory of complex-energy techniques and the RI-CC2 electronic-structure method. Thereafter, we present the details of our implementation in Section III. The computational details and numerical results of the application of RI-CC2 to temporary anions are presented in Sections IV and V, respectively. Our conclusions about the new complex-energy RI-CC2 methods are given in Section VI.

II. THEORY

A. Complex-energy methods

The accurate description of electronic states embedded in the detachment continuum requires theoretical methods that go beyond a bound-state treatment. Complex-energy methods offer a systematic framework to characterize metastable states in terms of their energy and lifetime. These methods rely on a non-Hermitian formulation of the Schrödinger equation, achieved either by adding a CAP[27, 28] or by complex scaling the coordinates of the Hamiltonian[53, 54] or the exponents of Gaussian basis functions.[29, 30] The resulting com-

plex eigenvalues of the Schrödinger equation are called Siegert energies and can be expressed as:[83]

$$E = E_R - i \Gamma/2 \quad (1)$$

where the real part E_R corresponds to the energy of the resonance and the imaginary part $\Gamma/2$ is connected to the lifetime τ of the metastable state via $\Gamma = 1/\tau$. In the context of temporary anion states, E_R is also referred to as resonance position and the difference between E_R and the energy of the parent neutral molecule yields the electron affinity, which is negative.

B. Complex absorbing potentials

The CAP Hamiltonian has the form:

$$H_\eta = H - i \eta W, \quad (2)$$

where η is the CAP strength and W defines the shape of the absorbing potential. In this work, we employ a quadratic box potential

$$W = \sum_{\alpha} W_{\alpha}, \quad W_{\alpha}(r_{\alpha}) = \begin{cases} 0 & \text{if } |r_{\alpha} - o_{\alpha}| \leq r_{\alpha}^0, \\ (|r_{\alpha} - o_{\alpha}| - r_{\alpha}^0)^2 & \text{if } |r_{\alpha} - o_{\alpha}| > r_{\alpha}^0. \end{cases} \quad (3)$$

Here, $\alpha = x, y, z$ refers to the Cartesian coordinates, $o_{\alpha} = (o_x, o_y, o_z)$ is the origin of the CAP, and r_{α}^0 is the size of the box. We also compare to results computed with a smooth Voronoi potential, where each atom is enclosed within a cutoff sphere.[46, 84] The smooth Voronoi CAP has the form

$$W(r) = \begin{cases} (r_{\text{av}}(r) - r^0)^2 & \text{if } r_{\text{av}} > r^0, \\ 0 & \text{else,} \end{cases} \quad r_{\text{av}}(r) = \sqrt{\frac{\sum_A w_A(r) r_A^2(r)}{\sum_A w_A(r)}} \quad (4)$$

and depends on a single parameter r_0 . The index A refers to the nuclei, w_A are the weighting factors, and r_{av} is the weighted average of the electron-nucleus distances.

The CAP absorbs the diverging tail of the resonance wave function, forcing it into a square-integrable form. The eigenvalues of the CAP Hamiltonian depend on η as well as r_{α}^0 . In this work, we derive the onset parameters r_{α}^0 from the extent of the wave function of the neutral ground state[44] and optimize η according to the criterion $\min |\eta (dE/d\eta)|$. [28]

This necessitates series of calculations with different values of η . This parameter has no strict upper bound and optimal values can range from 10^{-4} a.u. to 10^{-1} a.u. In the CAP calculations presented in this work, the trajectory is sampled over 30–40 η values, ranging from 0.00025 to 0.01 a.u. with increments of 0.00025 a.u. An alternative approach, in which the CAP strength η is fixed and the onset parameters r_α^0 are optimized, has been introduced recently,[85] and entails a similar number of calculations.

The need to compute trajectories and the resulting computational overhead motivate the projected CAP technique.[34] In this approach, the Schrödinger equation is first solved without CAP for a number of pseudocontinuum states and the CAP Hamiltonian from Eq. (2) is then constructed in the basis of these states. This significantly reduces the cost of generating the η trajectory as only one electronic-structure calculation needs to be carried out. However, the resulting Siegert energies depend on the size of the subspace. The required number of states is system dependent and cannot be predicted *a priori*: For example, for projected CAP-EOM-EA-CCSD, 4 pseudocontinuum states were sufficient for N_2^- , whereas anionic states of uracil required as many as 55 states.[86]

Lastly, we note that Siegert energies computed with CAP methods can often be improved somewhat by means of perturbation theory, i.e., by subtracting the expectation value of $-i\eta W$ from the corresponding eigenvalue of H_η . [28, 44] In Section V, these results are referred to as “first-order”.

C. Complex basis functions

The method of complex basis functions (CBFs)[29, 31] extends CS[53, 54] to molecular resonances. This is achieved by using a Gaussian basis set in which the exponents α of some functions χ_A are complex-scaled yielding $\alpha e^{-2i\theta}$ with θ as scaling angle:

$$\chi_A(r, \theta) = N(\theta) (x - x_A)^k (y - y_A)^l (z - z_A)^m \exp \left[-\alpha e^{-2i\theta} (r - R_A)^2 \right] \quad (5)$$

$N(\theta)$ is a normalization constant and R_A the position of nucleus A . Whereas the CAP method has been used primarily for temporary anions, the CBF method has been applied to various types of resonances. This includes molecules in static electric fields[61, 62, 87, 88], Rydberg states[47, 89], Auger decay[90–93], and intermolecular Coulombic decay[94] in addition to temporary anions.[31, 63, 95] The exponents of the complex-scaled functions

are related to the kinetic energy of the emitted electrons,[90] meaning that diffuse functions need to be scaled for low-lying temporary anions and steeper functions for Auger decay.

The complex scaling angle θ is restricted to $0 < \theta < \pi/4$, [25] which is a practical advantage over the CAP method where no upper bound exists for the CAP strength η . Nonetheless, an optimal scaling angle θ_{opt} must be determined by minimizing the variation of the resonance energy with respect to changes in θ , following the condition $\min |dE/d\theta|$. [96] Identifying θ_{opt} requires multiple calculations with different θ values. For the temporary anions studied in the present work, θ_{opt} was determined by scanning the range from 0° to 45° in increments of 4° to identify an approximate value, followed by a finer search in the vicinity of this estimate. This strategy reduces the number of calculations required to determine θ_{opt} compared to CAP calculations. Often, only 10–12 calculations are needed. Also, the minima in $|dE/d\theta|$ are typically more pronounced than those in $|\eta dE/d\eta|$ for CAP calculations.

D. The RI-CC2 reference state

CC2 is a second-order approximate coupled-cluster method in which the single amplitude equations are identical to those from CCSD and the double amplitude equations are truncated to first order in perturbation theory.[64] A general CC wave function is expressed using an exponential ansatz as

$$|\Psi_{\text{CC}}\rangle = e^T |\Phi_0\rangle \quad (6)$$

with $|\Phi_0\rangle$ as the reference determinant and the cluster operator defined as $T = T_1 + T_2 + \dots + T_n$ for n electrons. For CCSD and CC2 alike, T is truncated to the singles and doubles cluster operators, which are given by

$$T_1 = \sum_{ai} t_i^a a^\dagger i, \quad T_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} a^\dagger i b^\dagger j \quad (7)$$

Here, $i, j, \dots$ denote occupied molecular orbitals, while $a, b, \dots$ refer to virtual orbitals. $p, q, \dots$ will be used to denote generic orbitals. In second quantization notation,[97] $a^\dagger$ creates a particle in spin orbital φ_a and i removes a particle from spin orbital φ_i and thus creates a hole.

The amplitudes t_i^a and t_{ij}^{ab} are determined from the CC equations, which are derived by inserting Eq. (6) into the Schrödinger equation and applying e^{-T} from the left, followed by

projection on the singly and doubly excited determinants,

$$\Omega_i^a = \langle \Phi_i^a | e^{-T} H e^T | \Phi_0 \rangle = 0 \quad \forall \langle \Phi_i^a |, \quad (8)$$

$$\Omega_{ij}^{ab} = \langle \Phi_{ij}^{ab} | e^{-T} H e^T | \Phi_0 \rangle = 0 \quad \forall \langle \Phi_{ij}^{ab} |, \quad (9)$$

where $e^{-T} H e^T$ is the similarity-transformed Hamiltonian. The CC energy is obtained from projection onto the reference determinant,

$$E_{\text{CC}} = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle = E_0 + \sum_{ai} F_a^i t_i^a + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}, \quad (10)$$

where F_a^i is an element of the Fock matrix and $\langle ij || ab \rangle$ a two-electron repulsion integral.

In CC2 theory, Eq. (9) is simplified based on a perturbative analysis. The Hamiltonian

$$H = E_0 + F + W = E_0 + \sum_{pq} F_p^q \{p^\dagger q\} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{p^\dagger q^\dagger sr\} \quad (11)$$

is partitioned into a zeroth-order term $E_0 + F$ and a first-order term W . T_1 and T_2 are assigned to zeroth order and first order, respectively. Keeping only terms that are at most first order in Eq. (9) yields the CC2 double amplitude equations

$$\Omega_{ij}^{ab} = \langle \Phi_{ij}^{ab} | \tilde{H} + [F, T_2] | \Phi_0 \rangle = 0 \quad \forall \langle \Phi_{ij}^{ab} | \quad (12)$$

where $\tilde{H} = e^{-T_1} H e^{T_1}$ is a Hamiltonian similarity-transformed by T_1 and has the same particle rank as H . An explicit expression in terms of spin orbitals is

$$\begin{aligned} 0 = & \langle ab || ij \rangle + P(ab) \sum_c F_c^b t_{ij}^{ac} - P(ab) \sum_{kc} F_c^k t_k^b t_{ij}^{ac} - P(ij) \sum_k F_j^k t_{ik}^{ab} - P(ij) \sum_{kc} F_c^k t_j^c t_{ik}^{ab} \\ & - P(ab) \sum_k \langle kb || ij \rangle t_k^a + P(ij) \sum_c \langle ab || cj \rangle t_i^c + \sum_{cd} \langle ab || cd \rangle t_i^c t_j^d + \sum_{kl} \langle kl || ij \rangle t_k^a t_l^b \\ & - P(ij|ab) \sum_{kc} \langle kb || cj \rangle t_i^c t_k^a + P(ab) \sum_{kcd} \langle kb || cd \rangle t_i^c t_k^a t_j^d + P(ij) \sum_{klc} \langle kl || cj \rangle t_i^c t_k^a t_l^b \\ & + \sum_{klcd} \langle kl || cd \rangle t_i^c t_j^d t_k^a t_l^b \end{aligned} \quad (13)$$

$$= \langle \hat{a}\hat{b} || \hat{i}\hat{j} \rangle + P(ab) \sum_c \tilde{F}_c^b t_{ij}^{ac} - P(ij) \sum_k \tilde{F}_j^k t_{ik}^{ab} \quad \forall i > j, a > b \quad (14)$$

Here, $P(ab)$, $P(ij)$, and $P(ij|ab)$ are antisymmetric permutation operators and $\langle \hat{a}\hat{b} || \hat{i}\hat{j} \rangle$ denotes the T_1 -transformed electron-repulsion integrals that arise as matrix elements of $\tilde{W} = e^{-T_1} W e^{T_1}$. Note that for a generic electron-repulsion integral $\langle \hat{p}\hat{q} || \hat{r}\hat{s} \rangle$, the T_1 -transformation

affects p and q only if they are virtual orbitals and r and s only if they are occupied orbitals because T_1 is a pure excitation operator.

$\tilde{F}$ is the T_1 -transformed Fock matrix that is constructed from the T_1 -transformed one-electron Hamiltonian $\tilde{h} = e^{-T_1} h e^{T_1}$ and $\tilde{W}$. If $|\Phi_0\rangle$ is a canonical HF wave function, Eq. (14) can be rearranged to obtain an explicit expression for the double amplitudes as a function of the single amplitudes as

$$t_{ij}^{ab} = \frac{\langle \hat{a}\hat{b} || \hat{i}\hat{j} \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (15)$$

The significance of Eq. (15) is that it enables an implementation in which the double amplitudes t_{ij}^{ab} need not be stored.

The CC2 single amplitude equations are identical to those from CCSD and can be written as

$$\Omega_i^a = \langle \Phi_i^a | \tilde{H} + [\tilde{H}, T_2] | \Phi_0 \rangle = 0 \quad \forall \langle \Phi_i^a |, \quad (16)$$

with the explicit expression

$$\begin{aligned} 0 = & F_i^a + \sum_{kc} F_c^k t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle ak || cd \rangle t_{ik}^{cd} - \frac{1}{2} \sum_{klc} \langle kl || ic \rangle t_{kl}^{ac} + \sum_c F_c^a t_i^c - \sum_k F_i^k t_k^a \\ & + \sum_{kc} \langle ak || ic \rangle t_k^c - \frac{1}{2} \sum_{klcd} \langle lk || cd \rangle t_l^a t_{ik}^{cd} - \frac{1}{2} \sum_{klcd} \langle kl || dc \rangle t_i^d t_{kl}^{ac} + \sum_{klcd} \langle kl || cd \rangle t_k^c t_{li}^{da} \\ & - \sum_{kc} F_c^k t_i^c t_k^a + \sum_{kcd} \langle ak || cd \rangle t_i^c t_k^d - \sum_{klc} \langle kl || ic \rangle t_k^a t_l^c - \sum_{klcd} \langle kl || cd \rangle t_i^c t_k^a t_l^d \end{aligned} \quad (17)$$

$$= \tilde{F}_i^a + \sum_{kc} \tilde{F}_c^k t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle \hat{a}k || cd \rangle t_{ik}^{cd} - \frac{1}{2} \sum_{klc} \langle kl || \hat{i}c \rangle t_{kl}^{ac} \quad \forall i, a \quad (18)$$

To avoid the computation of the four-index electron-repulsion integrals, the RI approximation can be applied to Eqs. (15), (18), and (10). [67, 98, 99] A generic four-index integral, written as $(pq|rs)$ using Mulliken notation, is decomposed as

$$(pq|rs) = \sum_P B_{pq}^P B_{rs}^P = \sum_{PQ} (pq|P) J_{PQ}^{-1} (Q|rs), \quad B_{pq}^P = \sum_Q (pq|Q) J_{QP}^{-1/2} \quad (19)$$

Here, P and Q denote auxiliary basis functions and $(pq|P)$ and J_{PQ} are, respectively, three-center and two-center electron-repulsion integrals.

E. Computation of excitation energies with EOM-EE-CC2 theory

From the time evolution of the CC2 wave function, excited-state energies and state and transition properties can be computed within the framework of CC linear-response theory. [100–

104] However, similar to other CC models, the same working equations for the excitation energies can also be obtained in the framework of EOM-CC theory. Here, an excitation operator R acts on the CC reference wave function to generate the target state $|\Psi_k\rangle$

$$|\Psi_k\rangle = R_k |\Psi_{\text{CC}}\rangle = R_k e^T |\Phi_0\rangle . \quad (20)$$

In EOM-CC2 theory, the excitation operator for excited states has the same form as in EOM-CCSD theory,

$$R^{\text{EE}} = R_0 + R_1 + R_2 = r_0 + \sum_{ai} r_i^a a^\dagger i + \frac{1}{4} \sum_{abij} r_{ij}^{ab} a^\dagger i b^\dagger j . \quad (21)$$

The energies ω_k of the target states can be obtained by solving the eigenvalue equation

$$\mathbf{A} r_k = \omega_k r_k \quad \Leftrightarrow \quad \begin{pmatrix} \mathbf{A}_{\text{SS}} & \mathbf{A}_{\text{SD}} \\ \mathbf{A}_{\text{DS}} & \mathbf{A}_{\text{DD}} \end{pmatrix} \begin{pmatrix} r_{\text{S}} \\ r_{\text{D}} \end{pmatrix} = \omega \begin{pmatrix} r_{\text{S}} \\ r_{\text{D}} \end{pmatrix} \quad (22)$$

where r_k denotes the right eigenvector corresponding to state $|\Psi_k\rangle$ and $\mathbf{A}$ is the CC2 Jacobian. The elements of the latter matrix are obtained by differentiating the CC2 amplitude equations (Eqs. (12) and (16)) with respect to t_i^a and t_{ij}^{ab} . This yields

$$\mathbf{A} = \begin{pmatrix} d\Omega_i^a/dt_k^c & d\Omega_i^a/dt_{kl}^{cd} \\ d\Omega_{ij}^{ab}/dt_k^c & d\Omega_{ij}^{ab}/dt_{kl}^{cd} \end{pmatrix} = \begin{pmatrix} \langle \Phi_i^a | [\tilde{H} + [\tilde{H}, T_2], \{c^\dagger k\}] | \Phi_0 \rangle & \langle \Phi_i^a | [\tilde{H}, \{c^\dagger k d^\dagger l\}] | \Phi_0 \rangle \\ \langle \Phi_{ij}^{ab} | [\tilde{H}, \{c^\dagger k\}] | \Phi_0 \rangle & \langle \Phi_{ij}^{ab} | [F, \{c^\dagger k d^\dagger l\}] | \Phi_0 \rangle \end{pmatrix} \quad (23)$$

Similar to Eq. (15), the second row of Eq. (22) can be rearranged to express the double amplitudes r_{ij}^{ab} in terms of the single amplitudes r_i^a , because $\mathbf{A}_{\text{DD}}$ is diagonal with the diagonal elements given by $\Delta_{ij}^{ab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$. This results in

$$r_{ij}^{ab} = \frac{\sum_{kc} \langle \Phi_{ij}^{ab} | [\tilde{H}, \{c^\dagger k\}] | \Phi_0 \rangle r_k^c}{\omega - \Delta_{ij}^{ab}} = \frac{\overline{\langle \hat{a} \hat{b} | [\hat{i} \hat{j}] \rangle}}{\omega + \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (24)$$

where an additional set of modified electron-repulsion integrals has been introduced as

$$\overline{\langle \hat{a} \hat{b} | [\hat{i} \hat{j}] \rangle} = \sum_{kc} r_k^c d\Omega_{ij}^{ab}/dt_k^c = \sum_c \left[r_i^c \langle \hat{a} \hat{b} | [\hat{c} \hat{j}] \rangle + r_j^c \langle \hat{a} \hat{b} | [\hat{i} \hat{c}] \rangle \right] - \sum_k \left[r_k^a \langle \hat{k} \hat{b} | [\hat{i} \hat{j}] \rangle + r_k^b \langle \hat{a} \hat{k} | [\hat{i} \hat{j}] \rangle \right] . \quad (25)$$

Substituting Eq. (24) into the first row of Eq. (22) yields a pseudoeigenvalue equation in the space of single excitations that reads

$$\mathbf{A}^{\text{eff}}(\omega) r_{\text{S}} = \omega r_{\text{S}} \quad (26)$$

with the elements of $\mathbf{A}^{\text{eff}}(\omega)$ given by

$$\begin{aligned}
\sigma_i^a &= (\mathbf{A}^{\text{eff}} \cdot r)_i^a = \sum_{kc} \langle \Phi_i^a | [\tilde{H} + [\tilde{H}, T_2], \{c^\dagger k\}] | \Phi_0 \rangle r_k^c \\
&+ \sum_{klcd} \langle \Phi_i^a | [\tilde{H}, \{c^\dagger k d^\dagger l\}] | \Phi_0 \rangle \frac{\sum_{me} \langle \Phi_{kl}^{cd} | [\tilde{H}, \{e^\dagger m\}] | \Phi_0 \rangle}{\omega - \Delta_{kl}^{cd}} r_m^e \\
&= \frac{1}{2} \sum_{kcd} r_{ik}^{cd} \langle \hat{a} k || cd \rangle - \frac{1}{2} \sum_{klc} r_{kl}^{ac} \langle kl || \hat{i} c \rangle + \sum_{kc} r_{ik}^{ac} \tilde{F}_c^k + \sum_{kc} t_{ik}^{ac} \bar{F}_c^k \\
&- \frac{1}{2} \sum_{bckl} r_l^a t_{ik}^{cd} \langle lk || cd \rangle - \frac{1}{2} \sum_{bckl} r_i^b t_{kl}^{ac} \langle kl || bc \rangle + \sum_b r_i^b \tilde{F}_b^a - \sum_j r_j^a \tilde{F}_i^j + \bar{F}_i^a \quad (27)
\end{aligned}$$

Similar to Eq. (18) for the reference state, Eq. (26) can be solved without the need to store the double amplitudes r_{ij}^{ab} . In addition, the electron-repulsion integrals in Eqs. (24) and (27) can be decomposed using the RI approximation according to Eq. (19). The quantities $\bar{F}_a^i$ and $\bar{F}_i^a$ are defined as

$$\bar{F}_i^a = \sum_{ck} r_k^c \langle ik || ac \rangle, \quad \bar{F}_a^i = \sum_{ck} r_k^c \langle ak || \hat{i} c \rangle. \quad (28)$$

F. Computation of electron-attachment and ionization energies with the EOM-EA-CC2 and EOM-IP-CC2 methods

An advantage of the EOM-CC approach is that it provides access not only to excited states, but also to ionized, electron-attached, and spin-flipped states. Ionized and electron-attached states can be generated using the operators

$$R^{\text{IP}} = R_1 + R_2 = \sum_i r_i i + \frac{1}{2} \sum_{aij} r_{ij}^a a^\dagger i j, \quad (29)$$

$$R^{\text{EA}} = R_1 + R_2 = \sum_a r_a a^\dagger + \frac{1}{2} \sum_{abi} r_i^{ab} a^\dagger i b^\dagger \quad (30)$$

that have the same form in EOM-CC2 and EOM-CCSD theory.

The EOM-EA-CC2 working equations can be derived from Eqs. (24) and (27) by replacing r_i^a by r^a and r_{ij}^{ab} by r_j^{ab} . This yields

$$r_j^{ab} = \frac{\sum_c r^c \langle \hat{a} \hat{b} || c \hat{j} \rangle}{\omega + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad (31)$$

$$\sigma^a = (\mathbf{A}^{\text{eff}} \cdot r)^a = \frac{1}{2} \sum_{kcd} r_k^{cd} \langle \hat{a} k || cd \rangle + \sum_{kc} r_k^{ac} \tilde{F}_c^k - \frac{1}{2} \sum_{bckl} r^b t_{kl}^{ac} \langle kl || bc \rangle + \sum_b r^b \tilde{F}_b^a. \quad (32)$$

Likewise, the EOM-IP-CC2 working equations can be derived from Eqs. (24) and (27) by replacing r_i^a by r_i and r_{ij}^{ab} by r_{ij}^b . This yields

$$r_{ij}^b = -\frac{\sum_k r_k \langle k\hat{b}|\hat{i}\hat{j}\rangle}{\omega + \varepsilon_i + \varepsilon_j - \varepsilon_b}, \quad (33)$$

$$\sigma_i = (\mathbf{A}^{\text{eff}} \cdot \mathbf{r})_i = -\frac{1}{2} \sum_{klc} r_{kl}^c \langle kl|\hat{i}c\rangle + \sum_{kc} r_{ik}^c \tilde{F}_c^k - \frac{1}{2} \sum_{bckl} r_l t_{ik}^{cd} \langle lk|cd\rangle - \sum_j r_j \tilde{F}_i^j. \quad (34)$$

G. Spin scaling

Spin scaling was initially used to improve the accuracy of the MP2 energy[77, 78] and later extended to CC2 theory.[79] If $|\Phi_0\rangle$ is a closed-shell wave function, the spin-scaled CC2 energy can be expressed as

$$\begin{aligned} E_{\text{CC2}}^{\text{scaled}} = & \sum_{iJaB} (ia|JB) [t_i^a t_J^B + c_{\text{os}} t_{iJ}^{aB}] \\ & + \frac{1}{4} \sum_{ijab} [(ia|jb) - (ib|ja)] [t_i^a t_j^b - t_i^b t_j^a + c_{\text{ss}} t_{ij}^{ab}] \\ & + \frac{1}{4} \sum_{IJAB} [(IA|JB) - (IB|JA)] [t_I^A t_J^B - t_I^B t_J^A + c_{\text{ss}} t_{IJ}^{AB}] \end{aligned} \quad (35)$$

where uppercase and lowercase letters are used to distinguish α and β spin orbitals. The constants c_{os} and c_{ss} are chosen as 6/5 and 1/3 in the SCS-CC2 method and as 1.3 and 0 in the SOS-CC2 method. The same scaling factors c_{os} and c_{ss} are applied in a similar fashion to Eqs. (18), (27), (32), and (34) wherever the double amplitudes t_{ij}^{ab} and r_{ij}^{ab} , r_j^{ab} , r_{ij}^a appear.

H. Modifications for complex-energy CC2 methods

All equations presented in Sections IID to IIG remain valid if CC2 theory is built on a reference wave function $|\Phi_0\rangle$ that includes a CAP or is represented in a basis set including complex-scaled functions. However, it is necessary to apply the c-product[25] to all expressions so that the bra state is not complex conjugated. With these modifications, the eigenvalues of the CC2 Jacobian (Eq. (26)) become complex-valued and can be interpreted in terms of Eq. (1).

In the case of CAP calculations, all integrals over atomic orbitals (AOs) are real-valued and remain unchanged compared to the CAP-free case. The molecular orbital (MO) coefficients

and all other wave function parameters, are, however complex-valued. In the case of CBF calculations, the AO integrals are complex-valued, but it is possible to use purely real-valued auxiliary basis sets without compromising accuracy so that J_{PQ} from Eq. (19) is real-valued.[62]

III. IMPLEMENTATION

A. Code structure

We added two independent implementations of real-energy RI-CC2 including the EOM-EE, EOM-EA, EOM-IP, and EOM-SF variants and complex-energy RI-CC2 including the EOM-EE and EOM-EA variants to the modules CCMAN2 and GMBPT of the Q-Chem software.[73, 80, 105, 106]. These two implementations differ in their handling of the double excitation amplitudes and the electron-repulsion integrals, which has implications for the operation count and the memory requirements.

In the CCMAN2 module, which was originally developed for CCSD and EOM-CCSD calculations and uses the libtensor library for the handling of all tensors,[107] we implemented the RI-CC2 method in the form of Eqs. (13) and (17), i.e., by removing terms from the RI-CCSD equations. Likewise, the working equations for the RI-EOM-CC2 methods are obtained from the corresponding RI-EOM-CCSD equations.[47, 108] All equations are coded in spin-orbital form and the different spin cases are handled by libtensor. The EOM-CC2 eigenvalue equations are solved using the single-root or multiroot Davidson algorithms[109] that were implemented previously for EOM-CCSD calculations.

The double amplitudes t_{ij}^{ab} and r_{ij}^{ab} are stored on disk in this CC2 implementation entailing $\mathcal{O}(N^4)$ memory requirements. Their contraction with the electron-repulsion integrals leads to an operation count of $\mathcal{O}(N^6)$, which means that the technical requirements are comparable to those of EOM-CCSD, limiting the range of application. However, this implementation supports point-group symmetry, resulting in computational savings for molecules that belong to higher point groups than C_1 , and the EOM calculations can be directed towards the desired solution using all functionalities that were implemented previously for EOM-CCSD, such as user-defined guesses, root following, eigenvalue shifts, and pre-converging the single amplitude equations.

Our second implementation uses the GMBPT module, which was originally developed for RI-MP2 calculations.[110] This implementation is more memory efficient and based on Eqs. (15) and (18), partially transformed to the AO basis.[65] Likewise, the implementation of the EOM methods in GMBPT is based on Eqs. (27), (32), and (34), transformed to the AO basis. The $\hat{t}_{ij}^{ab}$ and $\hat{r}_{ij}^{ab}$ amplitudes are not stored; instead their contributions to the single amplitude equations are computed on the fly.

This approach results in a scaling of the operation count as $\mathcal{O}(N^5)$ and memory requirements scaling as $\mathcal{O}(N^3)$ as no four-index quantity needs to be stored. Standard linear algebra operations are handled in the GMBPT module by the Armadillo library,[111] and the different spin cases are treated explicitly. This code structure makes it straightforward to apply scaling factors as discussed in Section II G. A difference between the two implementations lies in the treatment of complex-valued integrals. In CCMAN2, the real and imaginary parts are handled separately as real-valued objects, whereas in GMBPT, all integrals are treated directly as *std::complex* objects. Moreover, in CCMAN2 the three-index electron-repulsion integrals arising from the RI approximation are precomputed and stored in memory, while they are recomputed and transformed by t_i^a or r_i^a in each CC or EOM-CC iteration in GMBPT.

The pseudoeigenvalue equation from Eq. (26) is solved with a modified Davidson algorithm, which is discussed further in Section III B. For real-valued calculations in GMBPT, the convergence of the solution of Eq. (26) is accelerated by extrapolation using direct inversion in the iterative subspace (DIIS)[112] after the residual error in the Davidson algorithm has dropped below some threshold, typically 10^{-5} . [65, 106] In the complex-valued case, we observed faster convergence when this step is omitted and the solutions of Eq. (26) are determined using solely using the algorithm from Section III B.

Also, we implemented user-defined guesses, root following, and eigenvalue shifts. However, the implementation in the GMBPT module currently does not exploit point-group symmetry, meaning all calculations are performed in the C_1 point group. In practice, we have found user-defined guesses to be more effective for calculations with GMBPT and eigenvalue shifts more useful for calculations with CCMAN2. If multiple roots are sought, they can be computed in GMBPT either sequentially or together using a multiroot algorithm similar to the implementation in CCMAN2.

Targeting a specific resonance state requires some prior knowledge of the resonance position

or the character of the state. In this work, we found it useful to inspect the complex orbital energies from a CAP-HF or CBF-HF calculation to form suitable initial guesses for EA-CC2 calculations on temporary anions. Specifically, we usually selected orbitals with small imaginary energy for that purpose. If the choice of orbital was ambiguous, we resorted to the multiroot algorithm.

Further technical details concerning the implementation in the GMBPT module have been provided in Ref. [106]. We finally note that our code was used to re-implement the CC2 method with a stochastic RI approximation into the Q-Chem software.[113–115]

B. Solution of the CC2 pseudoeigenvalue equation for excitation, attachment, or ionization energies

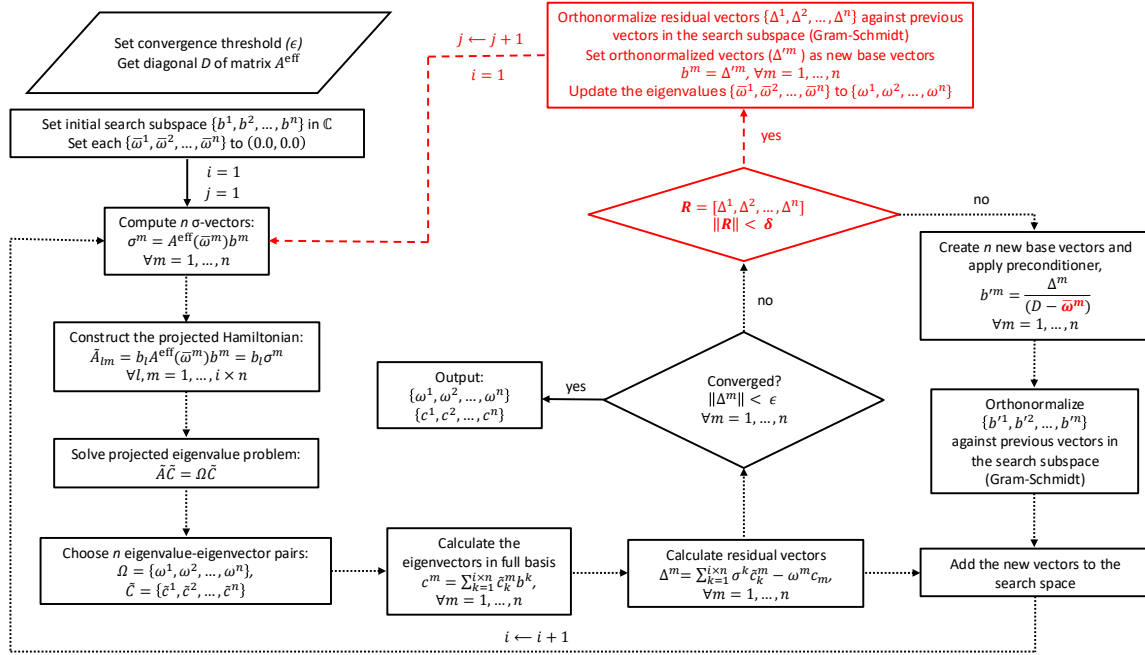


FIG. 1. Algorithm for solving the CC2 pseudoeigenvalue equation (Eq. (26)). Macro iterations follow the dashed lines and micro iterations follow the dotted lines. Different from the standard Davidson algorithm are indicated in red.

The algorithm by Davidson[109] is commonly used to find a few solutions to the large-scale eigenvalue equations $\mathbf{A}C = \omega C$ occurring, for example, in EOM-CC, ADC, and CI theories, where a complete diagonalization is prohibitively expensive. A low-dimensional

search subspace is constructed in an iterative manner and the original large matrix $\mathbf{A}$ is projected onto this subspace in each iteration. The projected eigenvalue equation $\tilde{\mathbf{A}}\tilde{\mathbf{C}} = \tilde{\omega}\tilde{\mathbf{C}}$ can be solved explicitly and an approximate eigenvalue $\tilde{\omega}$ and eigenvector $\tilde{\mathbf{C}}$ are obtained. The quality of these approximate quantities is assessed by computing the residual vector Δ for the original large-scale eigenvalue equation. If the residual norm is sufficiently small, convergence is achieved. Otherwise, the subspace is expanded by an additional vector that is constructed from the residual using the zeroth-order Hamiltonian as preconditioner and orthogonalized against all current vectors.

However, the CC2 pseudoeigenvalue equation (Eq. (26)) is not a true eigenvalue equation because the Jacobian $\mathbf{A}^{\text{eff}}$ depends on the excitation energy ω . To address this, we follow Ref. [65] and employ an algorithm that accounts for this energy dependence as shown in Fig. 1. The key idea is to use two nested loops. In the inner loop, referred to as “micro iterations” in Ref. [65] and denoted by dotted lines in Fig. 1, $\mathbf{A}^{\text{eff}}$ is held fixed, which renders Eq. (26) a true eigenvalue equation. As soon as the residual has dropped below the threshold δ , which is determined by comparing the current value for ω with that used to construct $\mathbf{A}^{\text{eff}}$, the inner loop is exited and $\mathbf{A}^{\text{eff}}$ is re-evaluated with the updated value for ω . In the multiroot version of the algorithm, the elements of the projected Jacobian $\tilde{\mathbf{A}}$ are updated with the different approximate eigenvalues. At the start of each of these “macro iterations”, denoted by dashed lines in Fig. 1, the subspace is constructed anew, starting from the current best solution and discarding all previous subspace vectors. The macro iterations are continued until the residual has dropped below the convergence threshold ϵ .

IV. COMPUTATIONAL DETAILS

The equilibrium geometries for the temporary anions C_2H_4^- , CH_2O^- and HCOOH^- were taken from Ref.[49] to enable a direct comparison with CAP-EOM-EA-CCSD results. For N_2^- , the bond length was set to 1.098Å. In the case of uracil, naphthalene, and the two cyanonaphthalene isomers, we used the structures from Ref. [86] to match the projected CAP-EOM-EA-CCSD reference data. The geometry of pyrene was optimized at the MP2/cc-pVTZ level. All structures are available in the supplementary material. We used the same equilibrium geometries for both CAP and CBF calculations to ensure consistency. The frozen core approximation was applied to uracil, naphthalene, the cyanonaphthalene

isomers, and pyrene.

The CAP-RI-CC2 calculations were performed using basis sets consistent with those applied in Refs. [49, 86]. For N_2^- , C_2H_4^- , CH_2O^- and HCOOH^- , we used the aug-cc-pVDZ basis set augmented by three additional diffuse s- and p-shells on each non-hydrogen atom, denoted as aug-cc-pVDZ+3s3p. All calculations were also carried out with the aug-cc-pVTZ basis set, augmented with three additional s-, p-, and d-shells on each non-hydrogen atom. This basis is denoted as aug-cc-pVTZ+3s3p3d. The exponents of the additional shells are even tempered, wherein each exponent is obtained by dividing the preceding exponent by 2. For the larger molecules naphthalene, cyanonaphthalene, and pyrene, we only used the cc-pVDZ basis set, augmented by 2s, 5p, and 2d diffuse shells, resulting in cc-pVDZ+2s5p2d. This choice of basis was motivated by Ref. [36], where the exponents for the s- and d-shells were obtained using a scaling factor of 2, and those for the p-shells were obtained using a scaling factor of 1.5. This same basis set was used for the CAP calculations on pyrene to ensure consistency.

We used a quadratic box potential in all CAP-RI-CC2 calculations. CAP onsets were taken from Ref. [49] for C_2H_4^- , CH_2O^- , and HCOOH^- and from Ref. [86] for N_2^- , naphthalene, and the cyanonaphthalene isomers. For pyrene, the CAP onset along each Cartesian coordinate was taken as the square root of the second moment of the electron density of the ground state, $\sqrt{\langle \alpha^2 \rangle}$ ($\alpha = x, y, z$) computed at the CCSD/cc-pVDZ level. All CAP onset values are given in the supplementary material. The orientation of the molecules is displayed in Fig. 2. CBF-RI-CC2 calculations were carried out using the aug-cc-pVDZ+2s3p2d and aug-cc-pVTZ+3s3p3d basis sets. In these calculations, complex scaling was applied to the most diffuse Gaussian shells: one s- and d-, and two p-shells in the double- ζ basis; two shells of each angular momentum in the triple- ζ basis. We denote these basis sets as aug-cc-pVDZ+1s1p1d+*1s2p1d* and aug-cc-pVTZ+1s1p1d+*2s2p2d*, where the italicized part indicates the complex-scaled shells.

The auxiliary basis was aug-cc-pVDZ-RIFIT or aug-cc-pVTZ-RIFIT, depending on the orbital basis set, for CAP and CBF calculations. No complex scaling was applied to the auxiliary basis functions, as previous RI-MP2 calculations have shown that this has a negligible effect on the results.[62]

An important computational advantage of the CBF approach is the similarity of the optimal complex scaling angles θ_{opt} at the EA-CC2 and EOM-EA-CCSD levels of theory. As

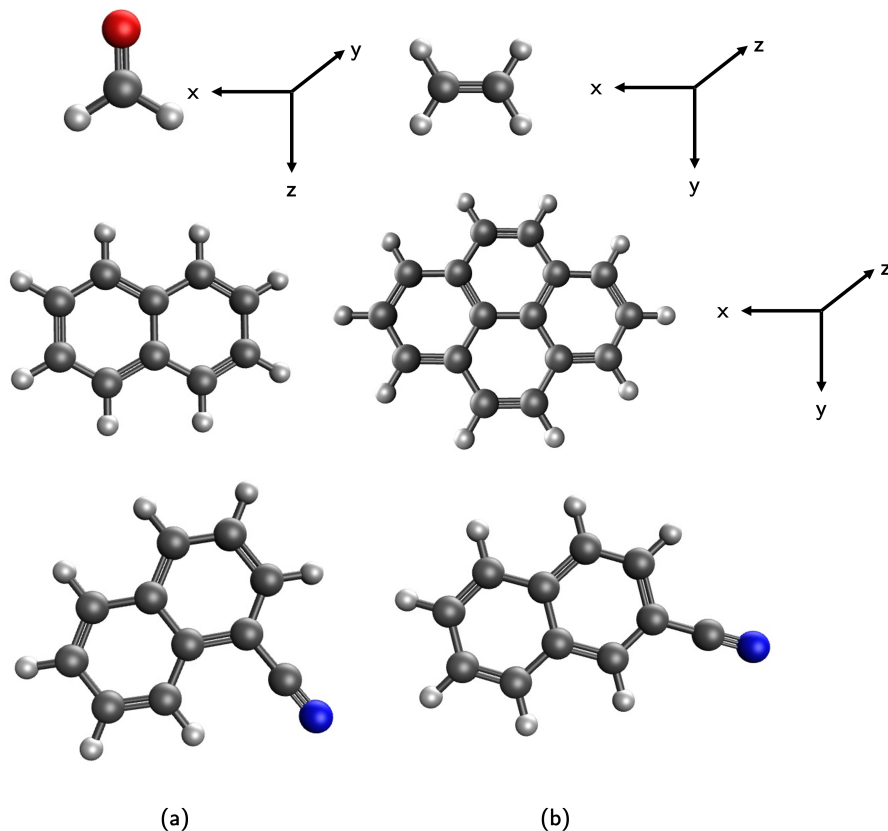


FIG. 2. Orientation of the molecules in our calculations. From top left to bottom right: formaldehyde, ethylene, naphthalene, pyrene, 1-cyanonaphthalene, and 2-cyanonaphthalene.

illustrated in the supplementary material, the energy and width remain stable with deviations of the order of 1 meV even if θ_{opt} can vary by $2\text{--}3^\circ$. This suggests that the θ_{opt} value determined at the EA-CC2 level of theory can be used in EOM-EA-CCSD calculations, reducing the computational cost significantly. Notably, a similar trend does not apply to CAP calculations. Here, the optimal CAP strength η_{opt} changes substantially when going from EA-CC2 to EOM-EA-CCSD, so that it is necessary to recalculate the full η -trajectory for each method.

It is important to clarify how the irreducible representations were assigned to the anionic states of ethylene, formaldehyde, naphthalene, and pyrene. The CH_2O^- molecule belongs to the C_{2v} point group, whereas the other molecules belong to the D_{2h} point group. For both of these point groups, the irreducible representations depend on the chosen molecular orientation. Throughout this work, all irreducible representations refer to the orientation

shown in Fig. 2, which was used in all calculations.

V. RESULTS AND DISCUSSION

A. Temporary anions of dinitrogen, ethylene, formaldehyde, and formic acid

To investigate the performance of complex-energy RI-EA-CC2, we first applied the new methods to a set of well-characterized temporary anions, N_2^- , C_2H_4^- , CH_2O^{2-} , HCOOH^- . These anions are small enough to enable a comparison to EOM-EA-CCSD. The vertical electron affinities and resonance widths computed with CAP and CBF versions of RI-EA-CC2 and EOM-EA-CCSD are shown in Table I. The corresponding optimal CAP strengths and complex-scaling angles are reported in the SI.

As shown in Table I, CAP-EA-CC2 and CBF-EA-CC2 both yield electron affinities that are about 0.1–0.2 eV smaller in magnitude than the corresponding EOM-EA-CCSD values, meaning that EA-CC2 places the temporary anions at absolute energies that are somewhat too low. This is consistent with the trend observed for bound anions of small molecules, which EA-CC2 also places at absolute energies that are too low by 0.1–0.2 eV, resulting in too big electron affinities.[75] Notably, the deviations between EA-CC2 and EOM-EA-CCSD observed for bound anions of larger molecules are substantially higher, typically amounting to 0.4–0.5 eV.[80, 81] We note that EA-CC2 agrees better with the experimental reference values for C_2H_4^- , CH_2O^- , and HCOOH^- than EOM-EA-CCSD does, which we interpret as a fortuitous error cancellation.

A conspicuous exception to the general trend in Table I is N_2^- ; here the EA-CC2 and EOM-EA-CCSD electron affinities deviate by no more than 0.02 eV. To check the validity of this result, we performed additional calculations for the $^2\Pi$ temporary anion state of CO^- , which is isoelectronic to N_2^- . CAP-EOM-EA-CCSD and CAP-EA-CC2 yield vertical electron affinities of –2.06 eV and –2.02 eV, respectively, in the aug-cc-pVTZ+3s3p3d basis set, which suggests that the different performance may be related to the electronic structure of these resonances.

The spin-scaled EA-CC2 methods both yield larger negative electron affinities than unmodified EA-CC2, the SCS variant leads to an increase of 0.3–0.4 eV and the SOS variant to an increase of about 0.5 eV. As a result, spin scaling does not improve the accuracy of EA-CC2

TABLE I. Vertical electron affinities of N_2 , C_2H_4 , CH_2O , and HCOOH and resonance widths of the corresponding temporary anions computed with RI-EA-CC2 and EOM-EA-CCSD combined with CAP or CBFs. All values in eV.

Method	Basis set	$\text{N}_2^- (^2\Pi_g)$	$\text{C}_2\text{H}_4^- (^2\text{B}_{2g})$	$\text{CH}_2\text{O}^- (^2\text{B}_1)$	$\text{HCOOH}^- (^2\text{A}')$
Vertical electron affinities computed with CAP					
RI-EA-CC2	aDZ+33	-2.633	-2.039	-1.241	-2.203
EOM-EA-CCSD	aDZ+33	-2.616	-2.228 ^[49]	-1.372 ^[49]	-2.325 ^[49]
RI-EA-CC2	aTZ+333	-2.514	-1.755	-1.044	-1.981
SCS-RI-EA-CC2	aTZ+333	-2.803	-2.042	-1.425	-2.319
SOS-RI-EA-CC2	aTZ+333	-2.949	-2.209	-1.589	-2.482
EOM-EA-CCSD	aTZ+333	-2.524 ^[86]	-1.911	-1.275	-1.989
Vertical electron affinities computed with CBFs					
RI-EA-CC2	aTZ+333*	-2.542	-1.759	-0.932	-1.959
SCS-RI-EA-CC2	aTZ+333*	-2.849	-2.091	-1.281	-2.312
SOS-RI-EA-CC2	aTZ+333*	-3.006	-2.262	-1.461	-2.491
EOM-EA-CCSD	aTZ+333*	-2.552	-1.993	-1.106	-2.151
Reference value		-2.32 ^[116]	-1.76 ^[117]	-0.86 ^[118]	-1.73 ^[119]
Resonance widths computed with CAP					
RI-EA-CC2	aDZ+33	0.589	0.376	0.304	0.219
EOM-EA-CCSD	aDZ+33	0.565	0.450 ^[49]	0.353 ^[49]	0.252 ^[49]
RI-EA-CC2	aTZ+333	0.489	0.351	0.285	0.234
SCS-RI-EA-CC2	aTZ+333	0.589	0.491	0.376	0.293
SOS-RI-EA-CC2	aTZ+333	0.642	0.591	0.421	0.344
EOM-EA-CCSD	aTZ+333	0.494 ^[86]	0.434	0.355	0.246
Resonance widths computed with CBFs					
RI-EA-CC2	aTZ+333*	0.566	0.536	0.465	0.372
SCS-RI-EA-CC2	aTZ+333*	0.674	0.718	0.658	0.470
SOS-RI-EA-CC2	aTZ+333*	0.729	0.812	0.771	0.527
EOM-EA-CCSD	aTZ+333*	0.559	0.705	0.568	0.456
Reference value		0.41 ^[116]	0.3–0.7 ^[117]	0.2–0.4 ^[118]	—

aDZ+33 = aug-cc-pVDZ+3s3p; auxiliary basis for RI calculations is aug-cc-pVDZ-RIFIT.

aTZ+333 = aug-cc-pVTZ+3s3p3d; auxiliary basis for RI calculations is aug-cc-pVTZ-RIFIT.

aTZ+333* = aug-cc-pVTZ+1s1p1d+2s2p2d; auxiliary basis for RI calculations is

aug-cc-pVTZ-RIFIT.

for the temporary anions in Table I, but places the anions at too high absolute energies. This is different from bound valence anions of larger molecules for which electron affinities computed with SCS-EA-CC2 deviate by only 0.07 eV from EOM-EA-CCSD.[80] We note that spin-scaling also does not improve the electron affinities of dipole-bound anions for which unmodified EA-CC2 yields very accurate results.[80]

The resonance widths computed with CAP-EA-CC2 and CBF-EA-CC2 exhibit smaller deviations of less than 0.1 eV from EOM-EA-CCSD. EA-CC2 consistently underestimates the resonance width, which we relate to a more severe underestimation at the HF level,[31] where electron correlation is neglected completely. The spin-scaled EA-CC2 methods yield widths that are broader by 0.1–0.3 eV and again do not represent a clear improvement. N_2^- is again a notable exception for which the widths computed with EA-CC2 and EOM-EA-CCSD differ by no more than 0.025 eV. We also computed widths for CO^- , which yielded values of 0.87 eV and 0.88 eV with CAP-EOM-EA-CCSD and CAP-EA-CC2, respectively, confirming the trend observed for N_2^- .

B. Temporary anions of uracil

As a first example of a somewhat larger molecule, we investigated the two lowest-lying π^* temporary anion states of uracil ($\text{C}_4\text{H}_4\text{N}_2\text{O}_2$), both of which belong to the A'' representation of the C_s point group. These results are shown in Table II. Here, we used only the CBF technique combined with EA-CC2 and EOM-EA-CCSD; projected CAP-EOM-EA-CCSD and CAP-SAC-CI results have been taken from Refs. [86] and [120], respectively.

Table II illustrates that the electron affinities computed with EA-CC2 are less negative by about 0.4 eV than the EOM-EA-CCSD values, which is a bigger deviation than that observed for the smaller molecules in Table I. Spin scaling improves the agreement of EA-CC2 with EOM-EA-CCSD significantly, with the SCS variant deviating by no more than 0.03 eV, which is in contrast with Table I. The resonance widths computed with EA-CC2 are narrower than the EOM-EA-CCSD widths by about 0.05 eV, which is similar to the results from Table I. Spin scaling improves the agreement, which is again in contrast to Table I.

Projected CAP-EOM-EA-CCSD is in very good agreement with CBF-EOM-EA-CCSD; the only significant deviation occurs for the resonance width of the π_2^* state, which is about 0.1 eV narrower when computed with CAP as compared to the CBF result. Notably, the

TABLE II. Vertical electron affinities (EA) of uracil and resonance widths Γ of the corresponding temporary anion states (π_1^* , π_2^*) computed with different methods. All values in eV.

Method	Basis set	EA		Γ	
		π_1^*	π_2^*	π_1^*	π_2^*
CBF-RI-EA-CC2	aDZ+232*	-0.326	-1.906	0.025	0.290
CBF-SCS-RI-EA-CC2	aDZ+232*	-0.758	-2.353	0.045	0.307
CBF-SOS-RI-EA-CC2	aDZ+232*	-0.960	-2.577	0.055	0.313
CBF-RI-EOM-EA-CCSD	aDZ+232*	-0.745	-2.329	0.053	0.332
CBF-RI-EA-CC2	aTZ+333*	-0.146	-1.667	0.019	0.240
CBF-SCS-RI-EA-CC2	aTZ+333*	-0.558	-2.131	0.042	0.270
CBF-SOS-RI-EA-CC2	aTZ+333*	-0.767	2.364	0.050	0.281
CBF-RI-EOM-EA-CCSD ^a	aTZ+333*	-0.583	-2.176	0.054	0.301
CAP-EOM-EA-CCSD (zero-order) ^b	DZ+252	-0.731	-2.284	0.05	0.232
CAP-EOM-EA-CCSD (first-order) ^b	DZ+252	-0.726	-2.258	0.042	0.17
CAP-SAC-CI (first-order) ^c	DZ+252	-0.57	-2.21	0.05	0.10
R-Matrix ^d		-0.12	-1.94	0.003	0.17
Experiment ^e		-0.22	-1.58	—	—

DZ+252 = cc-pVDZ+2s5p2d.

aDZ+232* = aug-cc-pVDZ+1s1p1d+1s2p1d and aug-cc-pVDZ-RIFIT as auxiliary basis.

aTZ+333* = aug-cc-pVTZ+1s1p1d+2s2p2d and aug-cc-pVTZ-RIFIT as auxiliary basis.

^a Complex scaling angle not optimized, instead taken from RI-EA-CC2 calculation. ^b From Ref.

[86]. ^c From Ref. [120]. ^d From Ref. [121]. ^e From Ref. [122]

electron affinity computed with CAP-SAC-CI deviates more substantially from this value, which must be caused by different CAP parameters or a different basis set used for the calculation, as the EOM-CCSD and SAC-CI Jacobian matrices have identical eigenvalues.

Similar to the results in Table I, the EA-CC2 results for the electron affinities of both anion states of uracil are in better agreement with the experimental reference values than the EOM-EA-CCSD results. In the triple- ζ basis, the deviation of EA-CC2 from the experimental values amounts to less than 0.1 eV.

C. Anions of naphthalene and cyanonaphthalene

Next, we investigated the lowest three π^* anion states of naphthalene (C_{10}H_8) as well as 1- and 2-cyanonaphthalene (C_{11}NH_7). These states belong to the B_{2g} , B_{3g} , and B_{1u} representations, respectively, of the D_{2h} point group for naphthalene and to the A'' representation of the C_s point group for the cyanonaphthalenes. Notably, the lowest-lying state is bound for the cyanonaphthalenes, while unsubstituted naphthalene does not support a bound anion. This can be related to the electron-withdrawing character of the cyano group. The cyanonaphthalene molecules were recently detected in the Taurus Molecular Cloud-1,[123] which motivates the renewed interest in the temporary anion states of these molecules.

The anions of cyanonaphthalene are at the current practical limit for a computational characterization using complex-energy EOM-EA-CCSD in appropriately large basis sets. The projected CAP approach offers a possible solution in this regard, but the application of CBFs is challenging. This motivates using EA-CC2 for the present study.

Our results for naphthalene and the cyanonaphthalenes are shown in Tables III and IV, respectively. We first computed the vertical electron affinities and resonance widths of naphthalene and its cyano derivatives using CAP-EA-CC2 and compared them to the CAP-EOM-EA-CCSD results from Ref. [86], employing the same double- ζ basis set. Since the results from Ref. [86] were obtained with a projected smooth Voronoi CAP, we recomputed the CAP-EOM-EA-CCSD energy of unsubstituted naphthalene using a box CAP. As Table III illustrates, the form of the CAP does not affect the results significantly, which is consistent with previous findings.[124, 125]

We then computed the resonances energies and widths with the CBF approach, employing double- ζ and triple- ζ basis sets. While we used CBF-EA-CC2 in both basis sets, we used CBF-EOM-EA-CCSD only in the double- ζ basis set. In addition, a CBF-EOM-EA-CCSD calculation was carried out for naphthalene in the triple- ζ basis using the optimal complex scaling angle θ_{opt} from the corresponding CBF-EA-CC2 calculation. This is possible because θ_{opt} values from EA-CC2 and EOM-EA-CCSD calculations are very similar as discussed in Section IV. For example, for the π_2^* state of naphthalene, θ_{opt} values from CBF-EA-CC2 and CBF-EOM-EA-CCSD calculations differ by 4° in the double- ζ basis. If the CBF-EOM-EA-CCSD energy is evaluated at the θ_{opt} from CBF-EA-CC2, the result changes by less than 1 meV for both the real and the imaginary part. This approach saves a lot of compute

time: One CBF-RI-EOM-EA-CCSD calculation in the aug-cc-pVTZ+1s1p1d+2s2p2d basis set (734 functions) took approximately 120 hours using 16 threads of an Intel(R) Xeon(R) Gold 6334 processor (3.6 GHz), while the corresponding CBF-RI-EA-CC2 calculation only took 4 hours on the same machine.

TABLE III. Vertical electron affinities of naphthalene and resonance widths of the corresponding temporary anion states computed with RI-EA-CC2 and EOM-EA-CCSD combined with CAP or CBFs. All values in eV.

Method	Basis set	Vertical electron affinity			Resonance width		
		π_1^*	π_2^*	π_3^*	π_1^*	π_2^*	π_3^*
CAP-RI-EA-CC2 ^a	DZ+252	-0.252	-0.934	-1.687	0.004	0.032	0.443
CAP-EOM-EA-CCSD ^a	DZ+252	-0.673	-1.327	-2.120	0.014	0.067	0.442
CAP-EOM-EA-CCSD ^b	DZ+252	-0.680	-1.343	-2.198	0.029	0.059	0.499
CBF-RI-EA-CC2	aDZ+232*	-0.265	-0.962	-1.669	0.003	0.038	0.449
CBF-SCS-RI-EA-CC2	aDZ+232*	-0.594	-1.229	-2.021	0.013	0.049	0.522
CBF-SOS-RI-EA-CC2	aDZ+232*	-0.761	-1.356	-2.201	0.021	0.053	0.569
CBF-RI-EOM-EA-CCSD	aDZ+232*	-0.683	-1.353	-2.187	0.022	0.062	0.662
CBF-RI-EA-CC2	aTZ+333*	-0.074	-0.756	-1.487	-0.001	0.028	0.379
CBF-SCS-RI-EA-CC2	aTZ+333*	-0.414	-1.040	-1.847	0.007	0.041	0.468
CBF-SOS-RI-EA-CC2 ^c	aTZ+333*	-0.583	-1.181	-2.032	0.013	0.042	0.515
CBF-RI-EOM-EA-CCSD ^c	aTZ+333*	-0.536	-1.203	-2.051	0.013	0.053	0.622
Experiment ^d		-0.19	-0.90	-1.67	—	—	—

DZ+252 = cc-pVDZ+2s5p2d and cc-pVDZ-RIFIT as auxiliary basis set.

aDZ+232* = aug-cc-pVDZ+1s1p1d+1s2p1d and aug-cc-pVDZ-RIFIT as auxiliary basis set.

aTZ+333* = aug-cc-pVTZ+1s1p1d+2s2p2d and aug-cc-pVTZ-RIFIT as auxiliary basis set.

^a Computed using box CAP. ^b From Ref. [86], computed using projected smooth Voronoi CAP. ^c Complex scaling angle not optimized, instead taken from RI-EA-CC2 calculation. ^d From Ref. [126].

At the EA-CC2 level of theory, the anions are on average 0.4–0.6 eV lower in energy than at the EOM-EA-CCSD level, with the π_3^* state exhibiting the largest deviations. The CAP calculations in the double- ζ basis for the π_3^* state of 2-cyanonaphthalene stand out with the largest deviation of 0.8 eV between EA-CC2 and EOM-EA-CCSD. Spin scaling raises the EA-CC2 energies of the anion states by about 0.3–0.6 eV and brings them closer to

TABLE IV. Vertical electron affinities of cyanonaphthalene and resonance widths of the corresponding temporary anion states computed with RI-EA-CC2 and EOM-EA-CCSD combined with CAP or CBFs. All values in eV.

Method	Basis set	Vertical electron affinity			Resonance width	
		π_1^*	π_2^*	π_3^*	π_2^*	π_3^*
1-Cyanonaphthalene						
CAP-RI-EA-CC2 ^a	DZ+252	0.678	−0.315	−0.835	0.005	0.137
CAP-EOM-EA-CCSD ^b	DZ+252	0.226	−0.760	−1.398	0.033	0.226
CBF-RI-EA-CC2	aDZ+232*	0.654	−0.337	−0.895	0.005	0.137
CBF-SCS-RI-EA-CC2	aDZ+232*	0.305	−0.620	−1.254	0.011	0.177
CBF-SOS-RI-EA-CC2	aDZ+232*	0.128	−0.762	−1.436	0.022	0.203
CBF-RI-EOM-EA-CCSD	aDZ+232*	0.207	−0.962	−1.669	0.038	0.449
CBF-RI-EA-CC2	aTZ+333*	0.859	−0.129	−0.701	0.002	0.106
CBF-SCS-RI-EA-CC2 ^c	aTZ+333*	0.497	−0.425	−1.074	0.007	0.146
CBF-SOS-RI-EA-CC2 ^c	aTZ+333*	0.313	−0.574	−1.263	0.015	0.169
Experiment ^d	0.68 ± 0.10					
2-Cyanonaphthalene						
CAP-RI-EA-CC2 ^a	DZ+252	0.602	−0.068	−0.788	0.003	0.379
CAP-EOM-EA-CCSD ^b	DZ+252	0.146	−0.502	−1.582	0.028	0.376
CBF-RI-EA-CC2	aDZ+232*	0.577	−0.089	−1.030	−0.004	0.316
CBF-SCS-RI-EA-CC2	aDZ+232*	0.233	−0.384	−1.385	0.013	0.385
CBF-SOS-RI-EA-CC2	aDZ+232*	0.058	−0.535	−1.568	0.019	0.425
CBF-RI-EOM-EA-CCSD	aDZ+232*	0.127	−0.512	−1.569	0.024	0.499
CBF-RI-EA-CC2	aTZ+333*	0.785	−0.132	−0.840	0.079	0.280
CBF-SCS-RI-EA-CC2 ^c	aTZ+333*	0.427	−0.138	−1.213	0.084	0.332
CBF-SOS-RI-EA-CC2 ^c	aTZ+333*	0.246	−0.141	−1.400	0.088	0.368
Experiment ^d	0.65 ± 0.10					

DZ+252 = cc-pVDZ+2s5p2d and cc-pVDZ-RIFIT as auxiliary basis set.

aDZ+232* = aug-cc-pVDZ+1s1p1d+1s2p1d and aug-cc-pVDZ-RIFIT as auxiliary basis set.

aTZ+333* = aug-cc-pVTZ+1s1p1d+2s2p2d and aug-cc-pVTZ-RIFIT as auxiliary basis set.

^a Computed using box CAP. ^b From Ref. [86], computed using projected smooth Voronoi CAP. ^c

Complex scaling angle not optimized, instead taken from RI-EA-CC2 calculation. ^d From Ref.

[127], adiabatic value.

the EOM-EA-CCSD values. In general, the SOS approach leads to bigger shifts and better agreement with EOM-EA-CCSD, deviating by more than 0.1 eV only in two cases, the π_2^* and π_3^* states of 1-cyanonaphthalene. Notably, we observed a somewhat better performance of the SCS approach instead in our earlier study on bound valence anions.[80]

Table IV shows that all computational methods agree with the experimental result that 1-cyanonaphthalene has a somewhat larger electron affinity than 2-cyanonaphthalene. However, Tables III and IV also demonstrate that the EA-CC2 energies for the π^* resonances of naphthalene and for the bound anions of the cyanonaphthalenes are in considerably better agreement with experiment than the EOM-EA-CCSD energies. We emphasize that the electron affinities of the cyanonaphthalenes obtained from gas-phase ion-molecule equilibrium constants should be interpreted as adiabatic values.[127] Likewise, the data from electron transmission spectroscopy for the naphthalene temporary anions have been interpreted as adiabatic electron affinities as well,[128] even though they were originally presumed to be vertical values.[126] This ambiguity complicates the comparison with our computed vertical electron affinities.

As concerns the resonance width, we find that EA-CC2 yields lower values than EOM-EA-CCSD, which is partially corrected by spin scaling, similar to what we discussed in Sections V A and V B. The deviations between the methods are small for the narrow π_1^* and π_2^* resonances but can amount to more than 0.2 eV for the broader π_3^* resonances. It is also worth noting that the CBF-EA-CC2 method struggles with the very narrow resonance widths of the π_1^* state of naphthalene and the π_2^* state of 2-cyanonaphthalene, where it yields unphysical positive imaginary energies, i.e., negative decay widths in some basis sets. This may be caused by the RI approximation similar to what we found in previous investigations of autoionizing Rydberg states,[47] but it may also indicate that a higher-level treatment of correlation is needed to describe the decaying character of these states. Notably, the spin-scaled EA-CC2 methods do not exhibit this problem.

The comparison between CAP and CBF methods illustrates very good agreement with deviations below 0.1 eV for the electron affinities and even lower deviation for the resonance widths in most cases. We note that, with both techniques, the resonance states can in some cases not be identified from their energy alone. Rather, it is necessary to analyze the EOM-CC eigenvectors: While resonance states show significant contributions from attachment to different orbitals, this is not the case for pseudocontinuum states, which are usually

dominated to >99% by attachment to one single orbital. Also, the determination of θ_{opt} was ambiguous in some CBF calculations as there were two minima in $|dE/d\theta|$. However, the corresponding energies and widths in Tables III and IV would change by less than 0.002 eV if they were evaluated at the respective other θ -values.

D. Anions of pyrene

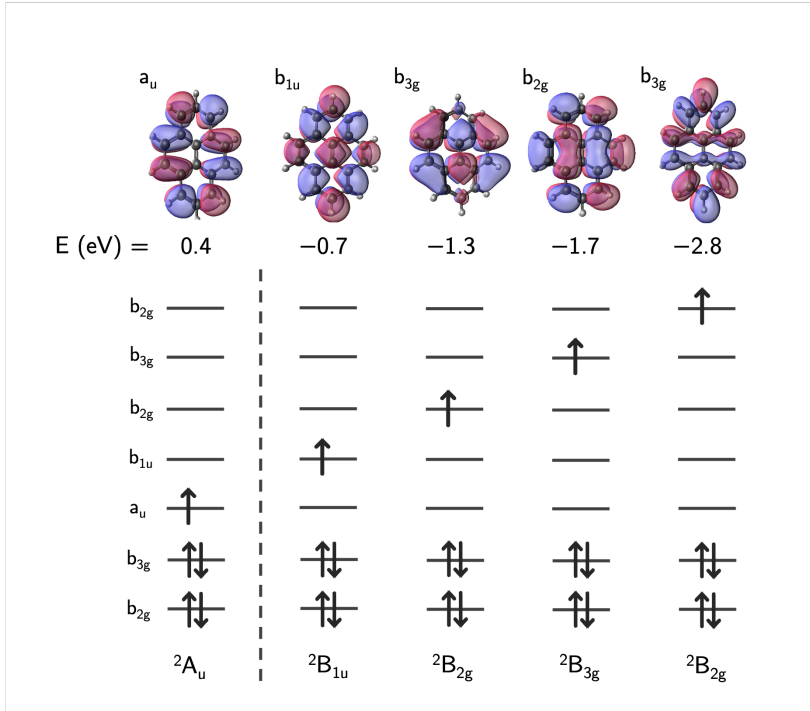


FIG. 3. Electronic configurations of the low-lying anion states of pyrene and corresponding Hartree-Fock orbitals computed in the cc-pVTZ basis without f-shells on carbon atoms and d-shells on hydrogen atoms. Electron affinities were extracted from 2D photoelectron spectroscopy. Figure adapted from Ref. [129] with permission.

As a final example, we investigated anion states of pyrene ($C_{16}H_{10}$), which can be viewed as a larger homologue of naphthalene. This planar, fully π -conjugated molecule supports one bound anionic state (2A_u). Pyrene offers an ideal test case due to the availability of recent experimental data from photodetachment spectroscopy.[129] To elucidate the spectrum, EOM-EA-CCSD calculations in the cc-pVTZ basis set were carried out in Ref. [129]. These calculations neglect the continuum and give no information on the decay width, but they

TABLE V. Vertical electron affinities of pyrene and resonance widths of the corresponding temporary anion states computed with RI-EA-CC2 and EOM-EA-CCSD combined with CAP or CBFs. Results from R matrix calculations and experimental values from photodetachment spectroscopy are also shown. All values in eV.

Method	Vertical electron affinity					Resonance width			
	2A_u	$^2B_{1u}$	$^2B_{2g}$	$^2B_{3g}$	$^2B_{2g}$	$^2B_{1u}$	$^2B_{2g}$	$^2B_{3g}$	$^2B_{2g}$
CAP-RI-EA-CC2 ^a	0.501	-0.239	-0.592	-0.878	-2.583	0.003	0.016	0.203	0.052
CBF-RI-EA-CC2 ^b	0.678	-0.057	-0.427	-0.870	-2.389	0.003	0.019	0.289	0.095
CBF-SCS-RI-EA-CC2 ^b	0.333	-0.335	-0.840	-1.276	-2.728	0.011	0.056	0.388	0.113
CBF-SOS-RI-EA-CC2 ^b	0.156	-0.507	-1.052	-1.481	-2.898	0.014	0.072	0.414	0.121
EOM-EA-CCSD ^c	0.17	-0.83	-1.43	-1.93	-3.23	—	—	—	—
R-Matrix ^d	—	-0.5	-1.1	-1.6	-3.1	0.06	0.28	0.63	0.14
Experiment ^e	0.4	-0.7	-1.3	-1.7	-2.8	—	—	—	—

^a Basis set: cc-pVDZ+2s5p2d, auxiliary basis set: cc-pVDZ-RIFIT.

^b Basis set: aug-cc-pVTZ+1s1p1d+2s2p2d, auxiliary basis set: aug-cc-pVTZ-RIFIT.

^c From Ref. [129]. Computed in the cc-pVTZ-f/d basis set.

^d From Ref. [130]. Results shifted by 1.0 eV as motivated in Ref. [129].

^e From Ref. [129]. Adiabatic value obtained from two-dimensional photoelectron spectroscopy.

provide a qualitative picture of the electronic structure of the four low-lying π^* shape resonances of pyrene as shown in Fig. 3. The energies computed with EOM-EA-CCSD/cc-pVTZ agree within 0.1–0.4 eV with the photodetachment spectrum. Part of this disagreement can be ascribed to structural relaxation, which in Ref. [129] was estimated to account for less than 0.2 eV for the bound anion state.

Our complex-energy EA-CC2 results are reported in Table V and show a consistent pattern for all electronic states and methods. All EA-CC2 variants qualitatively agree on the order and the energetic spacing of the states. R-matrix results agree on the order and spacing as well,[130] but these calculations fail to identify a bound anion state and the energies of the unbound states need to be lowered by 1.0 eV to align with the experimental data.[129]

Spin-scaling lowers the EA-CC2 energies of the bound and temporary anion states alike and the SOS-EA-CC2 result for the bound 2A_u state is in very good agreement with the EOM-EA-CCSD energy from Ref. [129]. Based on the results from Sections V A to V C, we

consider the SOS-EA-CC2 results to be our best estimates of the vertical electron affinities of the anion states. Indeed, SOS-EA-CC2 provides the closest estimates of the experimental values for the energies of the unbound states. For the bound anion state, this is not the case, but we note that the experimental value of 0.4 eV represents an adiabatic electron affinity, while our results refer to vertical energy differences.

As concerns the resonance widths, all EA-CC2 variants yield a narrow width of less than 15 meV for the lowest resonance state ($^2B_{1u}$), corresponding to a lifetime of more than 40 fs. For the two next higher resonances ($^2B_{2g}$ and $^2B_{3g}$), the width grows progressively, but the fourth resonance ($^2B_{2g}$) is considerably narrower again. This somewhat unusual pattern is consistent with results from R-matrix calculations.[130] Also, we note that CBF-EA-CC2 consistently yields larger widths than CAP-EA-CC2, while the R-matrix method delivers even larger widths.

VI. SUMMARY AND CONCLUSIONS

We have presented two independent implementations of the RI-EA-CC2 and RI-EE-CC2 methods for complex-valued Siegert energies. Our implementations can use complex absorbing potentials or, alternatively, complex basis functions and include spin-scaled CC2 variants as well. In addition, the EE, EA, IP, and SF variants of RI-CC2 have been implemented for real-valued energies. Our first implementation is based on the corresponding EOM-CCSD codes,[45, 47] whereas our second implementation avoids the storage of all double excitation amplitudes,[65] making it considerably more efficient in terms of memory and operation count.

We benchmarked the performance of the new complex-energy EA-CC2 methods in appropriately augmented double- ζ and triple- ζ basis sets for a test set of 18 temporary anion states in molecules of varying size, including 4 states of pyrene ($C_{16}H_{10}$) as largest example. We find that EA-CC2 in general places the anion states at lower energies than EOM-EA-CCSD, i.e., EA-CC2 yields electron affinities that are less negative. The deviation between the methods does not exceed 0.04 eV for the smallest examples in our test set (N_2^- and CO^-), but amounts to about 0.5 eV for larger molecules. Spin scaling raises the anion energies so that the agreement with EOM-EA-CCSD becomes significantly better for the anions of the larger molecules. Notably, all these trends are in agreement with previous findings for

bound anions.[75, 80, 81]

We observe a seemingly better agreement of experimental resonance energies with EA-CC2 results than with EOM-EA-CCSD results. However, this comparison with experiment should be treated with caution as it is not always clear whether the available data refer to vertical or adiabatic electron affinities. For the bound anions of pyrene and cyanonaphthalene, for which it is clear that the experimental values are adiabatic, it is obvious that the good performance of EA-CC2 is at least partially due to a cancelation with the reorganization energy caused by structural relaxation. For the resonance width, EA-CC2 consistently yields lower values than EOM-EA-CCSD, which agrees with previous findings that HF theory yields even narrower widths. Also for the width, spin scaling improves the agreement with EOM-EA-CCSD.

In general, CAP and CBF calculations are in very good agreement for resonance energies and widths. However, an advantage of the CBF approach is that the optimal value for the complex scaling angle is very similar at the EA-CC2 and EOM-EA-CCSD levels of theory, which makes it possible to determine it with EA-CC2 and then run a single EOM-EA-CCSD calculation at this value.

Our work illustrates that EA-CC2 can be readily applied to temporary anion states that are too big for a complex-energy EOM-EA-CCSD treatment such as those of pyrene. Also, for cases for which EOM-EA-CCSD calculations are still feasible, EA-CC2 offers a drastic speedup. For example, an EOM-EA-CCSD calculation on naphthalene in a triple- ζ basis took 120 hours, but the corresponding EA-CC2 calculation could be completed within 4 hours and delivered, when spin scaling was applied, the same energy and width within less than 0.1 eV. Therefore, we expect that our implementation will be useful for the investigation of temporary anions in larger molecules.

To enable a more comprehensive characterization of temporary anions beyond energies and widths, we consider it worthwhile to extend the complex-energy EA-CC2 methods to molecular properties and analytic gradients similar to what was done for EOM-EA-CCSD.[48–51] Also, we consider it promising to apply complex-valued CC2 methods to other resonances besides temporary anions. Specifically, this includes IP-CC2 calculations for Auger decay of core-ionized states or intermolecular Coulombic decay of ionized clusters, and EE-CC2 calculations for autoionization of superexcited Rydberg states.

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