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Communication: Analytic gradients for the complex absorbing potential equation-of-motion coupled-cluster method

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The general theory of analytic energy gradients is presented for the complex absorbing potential equation-of-motion coupled-cluster (CAP-EOM-CC) method together with an implementation within the singles and doubles approximation. Expressions for the CAP-EOM-CC energy gradient are derived based on a Lagrangian formalism with a special focus on the extra terms arising from the presence of the CAP. Our implementation allows for locating minima on high-dimensional complex-valued potential energy surfaces and thus enables geometry optimizations of resonance states of polyatomic molecules. The applicability of our CAP-EOM-CC gradients is illustrated by computations of the equilibrium structures and adiabatic electron affinities of the temporary anions of formaldehyde, formic acid, and ethylene. The results are compared to those obtained from standard EOM-CC calculations and the advantages of CAP methods are emphasized. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4974094]

Electron attachment to molecules with negative vertical electron affinity (VEA) leads to the formation of temporary anions that can decay through autodetachment and often exhibit distinctly different properties and reactivity patterns than the parent neutral molecules.[1,2] The so opened uncommon reaction channels play a role in unwanted processes such as radiative DNA damage[3,4] but can also be exploited productively, for example, in electron-induced reactions.[5–7] These phenomena and the underlying physical mechanisms such as dissociative electron attachment[1,8] or interatomic Coulombic decay[9] cannot be understood in a fixed-nuclei picture but require to take into account the coupling between electronic and nuclear degrees of freedom. The importance of nuclear motion for the understanding of temporary anions is also evident in photodetachment,[10,11] electron transmission,[12,13] and electron-impact spectra[14–16] that feature vibrational structure and thereby allow for the determination of adiabatic electron affinities (AEAs).

The theoretical treatment of temporary anions is challenging because they belong to the continuum and cannot be associated with discrete eigenstates in the Hermitian domain of the molecular Hamiltonian.[17] By means of the Siegert formalism,[17–19] it is, however, possible to associate temporary anions with adiabatic resonance states with complex energy. This allows for a characterization in analogy to bound states and, in particular, the construction of complex-valued potential energy surfaces (CPESs)[20] by invoking the Born-Oppenheimer approximation. The real part of a CPES can be interpreted similarly to the PES of a bound state, whereas the imaginary part yields the local decay rate as a function of molecular structure.[20–22]

CPESs of several diatomic and triatomic temporary anions, such as N_2^-,[23–29] H_2O^-,[30] and CO_2^-,[31] have been studied previously, but little is known about the CPESs of polyatomic species. This is because the efficient determination of minima, transition states, conical intersections, etc. on

high-dimensional CPES is feasible only by means of analytical gradients, which have not been available so far for any method for resonance states. Since analytical gradients have been derived and implemented for numerous bound-state electronic-structure methods, including Hartree-Fock (HF),[32] coupled-cluster (CC),[33,34] and equation-of-motion (EOM)-CC theory,[35] a possible solution is to apply these methods to resonances. This has been done, for example, for the benzene radical anion[36] and the cyclooctatetraene dianion[37] but is not satisfying as the metastable nature of the resonance state is neglected entirely.

In this Communication, we present the theory of analytic gradients for the complex absorbing potential (CAP)-EOM-CC method,[38–41] which enables the determination of equilibrium structures of polyatomic temporary anions. While Siegert energies can be obtained using different techniques such as straight complex scaling (CS),[42–44] exterior scaling (ES),[45] complex basis functions (CBF),[46,47] stabilization methods,[48,49] and CAPs[50,51] that can be further combined with different electronic-structure methods, CAP-EOM-CC holds several distinct advantages: First, and in contrast to ES and CBF approaches, evaluation of the energy gradient does not require non-standard two-electron integral derivatives. Second, the wave functions of a temporary anion and its parent neutral state are obtained as eigenfunctions of the same Hamiltonian in CAP-EOM-CC, which ensures that the imaginary part of a CPES is zero if and only if its real part is below the PES of the parent neutral state.[29] EOM-CC also offers further advantages such as an unbiased description of the target states by taking account of dynamical and non-dynamical electron correlation at once.

In CAP methods, a purely imaginary potential is added to the usual molecular Hamiltonian $\mathcal{H}$, which leads to a non-Hermitian Hamiltonian,

$$\mathcal{H}(\eta) = \mathcal{H} - i\eta W. \tag{1}$$

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Here, η is the CAP strength parameter and W is in the following chosen to be of the form:

$$W = \sum_\alpha W_\alpha, \qquad \alpha = x, y, z, \qquad (2)$$

$$W_\alpha = \begin{cases} 0 & \text{if } |r_\alpha - o_\alpha| \le r_\alpha^0, \\ (|r_\alpha - o_\alpha| - r_\alpha^0)^2 & \text{if } |r_\alpha - o_\alpha| > r_\alpha^0, \end{cases} \qquad (3)$$

with r_α^0 as the box size parameters and the vector $o = (o_x, o_y, o_z)$ as the origin of the CAP. In our computational protocol, we choose r_α^0 as the spatial extent of the wave function of the neutral molecule ($\sqrt{\langle \alpha^2 \rangle}$)[40] and o as the center of nuclear charges, that is,

$$o_\alpha = \frac{\sum_k R_{k,\alpha} Z_k}{\sum_k Z_k}, \qquad (4)$$

where $R_{k,\alpha}$ and Z_k are the nuclear coordinates and nuclear charges, respectively. By this choice of o we ensure that the molecule is not displaced relative to the CAP during a geometry optimization, which could happen otherwise if o was defined independently of the nuclear coordinates. Note that the molecule can still rotate relative to the CAP unless this would break spatial symmetry.[52]

Inserting Eq. (1) into the Schrödinger equation leads to a non-Hermitian eigenvalue problem, from whose complex eigenvalues $E = E_R - i\Gamma/2$ the resonance positions E_R and widths Γ are obtained. In CAP-EOM-CC, the resonance wave function is parametrized as $|\Psi\rangle = R\,e^T |\Phi_{\text{HF}}\rangle$, where $|\Phi_{\text{HF}}\rangle$ is the CAP-HF wave function of the reference state that we choose as the ground state of the neutral molecule, T is the cluster operator, and R creates the target states. For temporary anions, the CAP-EOM-EA-CC variant is employed, where R describes the attachment of an electron to the neutral molecule. T and R are defined and determined in analogy to standard EOM-CC theory,[53–55] but we use parentheses instead of chevrons to indicate the c-product.[56,57] When $|\Psi\rangle$ is represented in a complete basis, the energy calculated with the CAP corresponds to the exact resonance energy in the limit $\eta \to 0$.[51] In a finite basis set, however, an optimal finite η_{opt} exists that minimizes the error introduced by the CAP. η_{opt} is usually determined based on perturbation theory by minimizing the expression $|\eta\, dE/d\eta|$.[51]

To derive an expression that allows for the efficient evaluation of the CAP-EOM-CC energy gradient, we employ the Lagrangian technique.[58,59] Following the same steps as in standard CC gradient theory, we finally arrive at the following expression for the Lagrangian in the atomic-orbital (AO) basis that is valid for any CAP-CC or CAP-EOM-CC model in which the CAP is introduced at the HF level:

$$\mathcal{L} = \sum_{\mu\nu} D_{\mu\nu}^{\text{HF}} (h_{\mu\nu} - i\eta\, W_{\mu\nu}) + \frac{1}{2} \sum_{\mu\nu\sigma\rho} D_{\mu\nu}^{\text{HF}} D_{\sigma\rho}^{\text{HF}} \langle \mu\sigma || \nu\rho \rangle + \sum_{\mu\nu} I_{\mu\nu}^{\text{HF}} S_{\mu\nu}$$
$$+ \sum_{\mu\nu} D_{\mu\nu}^{\text{CC}} (f_{\mu\nu} - i\eta\, W_{\mu\nu}) + \sum_{\mu\nu\sigma\rho} \Gamma_{\mu\sigma\nu\rho}^{\text{CC}} \langle \mu\sigma || \nu\rho \rangle + \sum_{\mu\nu} I_{\mu\nu}^{\text{CC}} S_{\mu\nu} + \sum_\alpha \lambda_\alpha \left(\frac{\sum_k R_{k,\alpha} Z_k}{\sum_k Z_k} - o_\alpha \right) + V_{\text{nuc}}. \qquad (5)$$

Here, $h_{\mu\nu}$, $f_{\mu\nu}$, and $S_{\mu\nu}$ are the elements of the one-electron Hamiltonian, the Fock matrix, and the overlap matrix, $\langle \mu\sigma || \nu\rho \rangle$ denotes antisymmetrized two-electron integrals,[60] and V_{nuc} is the nuclear repulsion energy. Whereas all these quantities are real-valued, the effective one-electron, two-electron, and generalized energy-weighted density matrices D, Γ,[61] and I are complex-valued. Quantities labeled with superscripts "HF" and "CC" refer to contributions due to the response of the CAP-HF and the CAP-CC/CAP-EOM-CC wave function, respectively. The expressions for the latter quantities depend on the employed CC/EOM-CC model with no modifications required due to the CAP.[34,35] We note that the CAP-HF Lagrangian is obtained from Eq. (5) by setting all "CC" quantities to zero.

Eq. (5) includes two kinds of extra terms compared to the regular CC/EOM-CC Lagrangian: The contribution of the CAP to the energy ($-i\eta \sum_{\mu\nu}(D_{\mu\nu}^{\text{HF}} + D_{\mu\nu}^{\text{CC}})W_{\mu\nu}$) and an extra constraint to account for the dependence of the CAP origin on the nuclear coordinates. To obtain this latter term, Eq. (4) is rearranged and multiplied with Lagrange multipliers λ_α. By requiring $\mathcal{L}$ to be stationary with respect to o, we obtain

$$\lambda_\alpha = -i\eta \sum_{\mu\nu} \left(D_{\mu\nu}^{\text{HF}} + D_{\mu\nu}^{\text{CC}} \right) \left(\frac{\partial W_\alpha}{\partial o_\alpha} \right)_{\mu\nu}, \qquad (6)$$

$$\frac{\partial W_\alpha}{\partial o_\alpha} = \begin{cases} 0, & \text{if } |r_\alpha - o_\alpha| \le r_\alpha^0, \\ -2(r_\alpha - o_\alpha - r_\alpha^0), & \text{if } (r_\alpha - o_\alpha) > r_\alpha^0, \\ 2(-r_\alpha + o_\alpha - r_\alpha^0), & \text{if } (r_\alpha - o_\alpha) < -r_\alpha^0, \end{cases} \qquad (7)$$

where we exploit that only the terms containing the CAP or the CAP origin depend explicitly on o in Eq. (5).

In addition to the CAP origin, $\mathcal{L}$ also depends on the box size parameters and the CAP strength. Since η_{opt} and r_α^0 in turn depend on the nuclear coordinates, further constraints should be included in $\mathcal{L}$ in principle. However, in our current computational protocol, which is described further below, we keep η_{opt} and r_α^0 constant while optimizing the geometry so that there is no need for additional constraints.

An element of the gradient vector $dE/dR_{n,\alpha}$ corresponding to nucleus n and $\alpha = x, y, z$ can then be obtained by taking the derivative of Eq. (5) and bearing in mind the $2n+1$ and $2n+2$ rules.[62] For locating minima on the real part of a CPES, only the real part of the gradient is needed. Since all integral derivatives are real-valued, this yields the following general expression for the various CAP-CC and CAP-EOM-CC methods:

$$\mathrm{Re}\left(\frac{dE}{dR_{n,\alpha}}\right) = \sum_{\mu\nu}\left[\mathrm{Re}(D_{\mu\nu}^{\mathrm{HF}}) + \mathrm{Re}(D_{\mu\nu}^{\mathrm{CC}})\right]\frac{\partial h_{\mu\nu}}{\partial R_{n,\alpha}} + \eta\sum_{\mu\nu}\left[\mathrm{Im}(D_{\mu\nu}^{\mathrm{HF}}) + \mathrm{Im}(D_{\mu\nu}^{\mathrm{CC}})\right]\left[\frac{\partial W_{\mu\nu}}{\partial R_{n,\alpha}} + \frac{Z_n}{\sum_k Z_k}\left(\frac{\partial W_\alpha}{\partial o_\alpha}\right)_{\mu\nu}\right]$$

$$+ \sum_{\mu\nu\sigma\rho}\left[\frac{1}{2}\mathrm{Re}(D_{\mu\nu}^{\mathrm{HF}})\mathrm{Re}(D_{\sigma\rho}^{\mathrm{HF}}) - \frac{1}{2}\mathrm{Im}(D_{\mu\nu}^{\mathrm{HF}})\mathrm{Im}(D_{\sigma\rho}^{\mathrm{HF}}) + \mathrm{Re}(D_{\mu\nu}^{\mathrm{CC}})\mathrm{Re}(D_{\sigma\rho}^{\mathrm{HF}}) - \mathrm{Im}(D_{\mu\nu}^{\mathrm{CC}})\mathrm{Im}(D_{\sigma\rho}^{\mathrm{HF}})\right.$$

$$\left. + \mathrm{Re}(\Gamma_{\mu\sigma\nu\rho}^{\mathrm{CC}})\right]\frac{\partial\langle\mu\sigma||\nu\rho\rangle}{\partial R_{n,\alpha}} + \sum_{\mu\nu}\left[\mathrm{Re}(I_{\mu\nu}^{\mathrm{HF}}) + \mathrm{Re}(I_{\mu\nu}^{\mathrm{CC}})\right]\frac{\partial S_{\mu\nu}}{\partial R_{n,\alpha}} + \frac{\partial V_{\mathrm{nuc}}}{\partial R_{n,\alpha}} \qquad (8)$$

where the derivative of the Fock matrix element $f_{\mu\nu}$ = $h_{\mu\nu} + \sum_{\sigma\rho} D_{\sigma\rho}^{\mathrm{HF}}\langle\mu\sigma||\nu\rho\rangle$ has been split into a one-electron and a two-electron contribution. The corresponding CAP-HF expression is again obtained by setting all "CC" quantities to zero. Note that even though only the real part of the two-electron density matrix Γ^{CC} is needed, this quantity is calculated using complex algebra in the molecular orbital (MO) basis and then back-transformed to the AO basis using complex MO coefficients. This increases the cost of CAP-CC/CAP-EOM-CC gradients considerably compared to the CAP-free case. However, the formal scaling of every CAP method is the same as that of the corresponding real-valued method.

Eq. (8) illustrates that the computation of the energy gradient for CAP methods requires the evaluation of two additional derivatives compared to standard gradient theory: $\partial W_{\mu\nu}/\partial R_{n,\alpha}$ and $(\partial W_\alpha/\partial o_\alpha)_{\mu\nu}$. Explicit expressions for the latter term are given in Eq. (7), while the former term becomes

$$\frac{\partial W_{\mu\nu}}{\partial R_{n,\alpha}} = \frac{\partial(W_x)_{\mu\nu}}{\partial R_{n,\alpha}} + \frac{\partial(W_y)_{\mu\nu}}{\partial R_{n,\alpha}} + \frac{\partial(W_z)_{\mu\nu}}{\partial R_{n,\alpha}}, \qquad (9)$$

$$\frac{\partial(W_x)_{\mu\nu}}{\partial R_{n,\alpha}} = \left\langle\frac{\partial\chi_\mu}{\partial R_{n,\alpha}}\Big|W_x\Big|\chi_\nu\right\rangle + \left\langle\chi_\mu\Big|W_x\Big|\frac{\partial\chi_\nu}{\partial R_{n,\alpha}}\right\rangle \qquad (10)$$

with χ_μ, χ_ν as standard Gaussian basis functions.[60] Eqs. (7) and (10) are evaluated numerically in our implementation in the same way as detailed in Ref. 40 for $W_{\mu\nu}$.

CAP-CC and CAP-EOM-EA-CC gradients have been implemented within the singles and doubles (SD) approximation into the Q-Chem program package.[63] In addition, our implementation allows for the evaluation of restricted and unrestricted CAP-HF gradients. Spatial symmetry is exploited and the libtensor library[64] is used for operations on high-dimensional tensors. The implementation has been verified by means of numerical differentiation. Currently, the implicit dependence of E on $R_{n,\alpha}$ through η_{opt} and r_α^0 is not considered in the expression for the gradient (Eq. (8)), instead we use the following procedure for geometry optimizations:

1. Determine $\sqrt{\langle\alpha^2\rangle}$ of the neutral molecule.
2. Find η_{opt} for $r_\alpha^0 = \sqrt{\langle\alpha^2\rangle}$.
3. Optimize the geometry while leaving $\eta = \eta_{opt}$ and r_α^0 unchanged.
4. Go to 1 until $\sqrt{\langle\alpha^2\rangle}$ and η_{opt} are converged.

Updating the box size parameters is especially important if the molecule rotates in the box during geometry optimization. If this is not the case, re-optimizing the geometry with updated CAP parameters typically entails only small structural changes.

In the following, we apply the CAP-EOM-EA-CCSD method for geometry optimizations of the anionic resonance states of CH_2O, HCOOH, and C_2H_4 and determine the corresponding AEAs and resonance widths. The aug-cc-pVDZ+3s3p(A) basis set[65] from Ref. 40 is used in all calculations. This basis is diffuse enough to represent the coupling of the resonance to the continuum and hence sufficient to illustrate the differences between CAP-including and CAP-free gradient calculations, which is the focus of our Communication. A quantitative comparison to experimental values would demand the use of a triple-ζ or quadruple-ζ basis as will be discussed in more detail further below. Values for the parameters r_α^0 and η_{opt} are compiled in the supplementary material.

Changes in the box size are related to structural differences between the neutral molecule and the anion. In the case of CH_2O, the C=O bond length differs significantly between the neutral and anionic equilibrium structures (1.215 Å vs. 1.286 Å), whereas the differences in the remaining geometrical parameters are negligible (see the supplementary material). This is reflected in the large change in r_z^0 compared to the changes in r_x^0 and r_y^0. The geometrical change can be explained qualitatively by the π^* character of the corresponding Dyson orbital[66,67] depicted in Figure 1(a). Note that the anionic equilibrium structure is planar and belongs to the C_{2v} point group, i.e., electron attachment does not induce a lowering of the molecular symmetry.

In the cases of HCOOH and C_2H_4, non-planar distortion of the molecule is observed upon electron attachment in addition to lengthening of the C–O and C–C bonds. For formic acid, the C–O bond lengths change from 1.208 Å and 1.354 Å to 1.276 Å and 1.451 Å, while for ethylene, the C–C bond length changes from 1.348 Å to 1.439 Å, which can again be explained by the π^* character of the corresponding Dyson orbitals (Figures 1(b) and 1(c)). The differences in the other bond lengths are very small (see the supplementary material). The equilibrium structure of HCOOH⁻ is of C_1 symmetry compared to C_s for the neutral molecule, while

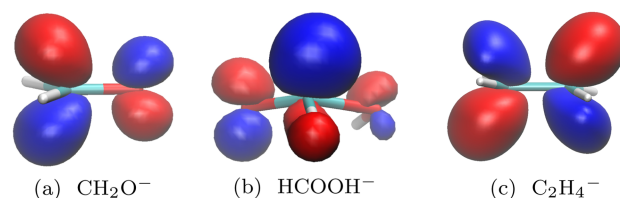(a) CH_2O^- (b) HCOOH⁻   (c) $C_2H_4^-$

FIG. 1. Real parts of CAP-EOM-EA-CCSD Dyson orbitals for electron attachment to CH_2O, HCOOH, and C_2H_4. Computed with the aug-cc-pVDZ+3s3p(A) basis set at the equilibrium structures of the respective resonant anions.

TABLE I. Theoretical and experimental values for the vertical and adiabatic electron affinities (VEA and AEA), vertical detachment energies (VDE), and resonance widths (Γ) of formaldehyde, formic acid, ethylene, and the corresponding anions. Γ_0 is the resonance width at the neutral equilibrium structure and Γ_{res} is that at the resonance equilibrium structure. The CAP-EOM-EA-CCSD/aug-cc-pVDZ+3s3p(A) method was employed in all calculations. All values are given in eV.

		VEA	VDE	AEA	Γ_0	Γ_{res}
CH_2O^-	Calc.	−1.372	−0.837	−1.019	0.353	0.213
	Expt.	−0.86[69]	⋯	−0.65[69]	0.2–0.4[69]	
$HCOOH^-$	Calc.	−2.325	−0.482	−1.481	0.252	0.126
	Expt.	−1.73[70]	⋯	−1.3[71]	⋯	
$C_2H_4^-$	Calc.	−2.228	−1.654	−2.039	0.450	0.307
	Expt.	−1.76[72]	⋯	−1.55[73]	0.3–0.7[72]	

that of $C_2H_4^-$ belongs to the C_{2h} point group compared to D_{2h} for the neutral molecule. For the anion of ethylene, symmetry lowering from D_{2h} to C_{2h} has also been predicted by HF calculations using very small bases and was rationalized in terms of σ^*-π^* mixing.[68] η_{opt} values for CH_2O^- and $HCOOH^-$ are significantly smaller at the equilibrium structure of the resonance than at that of the neutral molecule, while this decrease is less pronounced for $C_2H_4^-$.

The calculated VEAs and AEAs and vertical detachment energies (VDE) along with the resonance widths at the neutral equilibrium (Γ_0) and at the resonance equilibrium structure (Γ_{res}) are listed in Table I. For all molecules, AEA is significantly lower than VEA in terms of absolute values; the effect of structural relaxation amounts to 0.85 eV for $HCOOH^-$, 0.35 eV for CH_2O^-, and 0.19 eV for $C_2H_4^-$. Remarkably, experimental results[69–73] also suggest a larger relaxation energy for $HCOOH^-$ than for the other two anions.

The quantitative comparison to experiment is difficult due to the incomplete basis set, the perturbation due to the CAP, the truncation of the CC expansion, and the neglect of the zero-point vibrational energy. Also, the experimental determination of VEA is problematic.[13] The calculated absolute values for VEA are typically 0.5 eV higher than the corresponding experimental values. This discrepancy can be largely attributed to the first two effects: CAP-EOM-EA-CCSD calculations for $C_2H_4^-$ using the aug-cc-pVQZ+3s3p3d(C) basis set yielded VEA values 0.24 eV lower than aug-cc-pVDZ+3s3p(A) and a first-order correction for the CAP perturbation lowered the

energy further by 0.08 eV.[40] Similar effects can be anticipated for the AEA values as well.

Table I shows that Γ_{res} is smaller than Γ_0 for all three molecules. This is a general feature of temporary anions because VDE is always smaller than VEA. When the energy difference between an anionic resonance and the parent neutral state becomes smaller, the resonance width has to decrease and, if the two PES cross, it has to become zero as the resonance turns into a stable state.[29]

To demonstrate the advantages of a geometry optimization including a CAP over an approach that treats the resonance as a bound state, we carried out CAP-free EOM-EA-CCSD calculations for $C_2H_4^-$ using a variety of basis sets. This is documented in Table II.

Using the cc-pVDZ basis set, the lowest EOM-EA-CCSD root resembles the resonance state and a bent equilibrium structure of C_{2h} symmetry is obtained for the anion. However, the AEA is overestimated by 0.9 eV. As we enlarge the basis set, more and more continuum states appear in the spectrum, making it harder to associate a single state with the resonance.[74,75] Already for aug-cc-pVDZ, the lowest root has continuum character describing $C_2H_4 + e^-$ rather than $C_2H_4^-$, which is reflected in the optimized geometrical parameters R(CC) = 1.351 Å and ∠(HCCH) = 180.0°. As Table II shows, it is still possible to identify resonance-like higher-lying roots in the larger bases, but even so, their equilibrium structures differ qualitatively from that obtained in the presence of the CAP: regular EOM-EA-CCSD predicts a planar equilibrium structure and a too short C—C bond length using the aug-cc-pVDZ and aug-cc-pVDZ+3s3p(A) basis sets.

This clearly shows that although states with properties similar to the resonance can be found with bound-state approaches, this is an artifact of discretizing the continuum by means of small basis sets and valid results are not guaranteed. In contrast, in the presence of a CAP, the resonance state is usually one of the lowest-lying roots also in larger bases and the determination of the equilibrium structure and the AEA is straightforward.

In sum, we have derived and implemented analytic gradients for CAP-HF, CAP-CCSD, and various CAP-EOM-CCSD methods and proposed a procedure for the geometry optimization of temporary anions. Equilibrium structures and adiabatic electron affinities of the anions of formaldehyde, formic acid, and ethylene have been determined for the first time using CAP methods, and the advantages

TABLE II. Equilibrium structures for neutral C_2H_4 (0) computed with CCSD and the resonant anion $C_2H_4^-$ (res) computed with regular and CAP-augmented EOM-EA-CCSD using different basis sets. AEAs and the followed root (of A_g symmetry in the C_{2h} point group) in the EOM-EA-CCSD eigenvalue equation are also listed.

Basis	R(CC)/Å		∠(HCCH)/deg		AEA/eV	Root
	0	Res	0	Res		
cc-pVDZ[a]	1.345	1.456	0.0	48.7	−2.941	1
aug-cc-pVDZ[a]	1.348	1.418	0.0	0.0	−1.923	2
aug-cc-pVDZ+3s3p(A)[a]	1.348	1.405	0.0	0.1	−1.983	7
aug-cc-pVDZ+3s3p(A)[b]	1.348	1.439	0.0	26.6	−2.039	2

[a]Without CAP.
[b]Including CAP.

over applying bound-state methods have been illustrated. The present work represents a key step towards modeling nuclear motion in processes involving electronic resonances. We plan to generalize our current implementation to other types of resonances and different electronic-structure methods.

See supplementary material for the coordinates of all optimized molecular structures in Z-matrix format, CAP box sizes, and optimal CAP strengths.

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