

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/272134743>

Complex Absorbing Potential Equation-of-Motion Coupled-Cluster Method Yields Smooth and Internally Consistent Potential Energy Surfaces and Lifetimes for Molecular Resonances

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · SEPTEMBER 2014

Impact Factor: 7.46 · DOI: 10.1021/jz501515j

CITATIONS

4

READS

31

2 AUTHORS, INCLUDING:



Anna I Krylov

University of Southern California

179 PUBLICATIONS 7,033 CITATIONS

SEE PROFILE

Complex Absorbing Potential Equation-of-Motion Coupled-Cluster Method Yields Smooth and Internally Consistent Potential Energy Surfaces and Lifetimes for Molecular Resonances

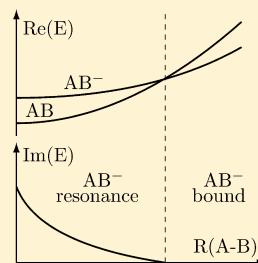
Thomas-C. Jagau* and Anna I. Krylov

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, United States

S Supporting Information

ABSTRACT: The recently developed equation-of-motion electron-attachment coupled-cluster singles and doubles (EOM-EA-CCSD) method augmented by a complex absorbing potential (CAP) is applied to the $^2\Pi_g$ resonance of N_2^- and the $^2\Sigma_u^+$ resonance of H_2^- at various internuclear distances. The results illustrate the advantages of EOM-CC for treating resonance states over state-specific approaches. CAP-EOM-EA-CCSD produces smoothly varying potential energy curves and lifetimes for both Σ and Π resonances. The computed lifetimes and energy differences between the neutral and electron-attached states are internally consistent, that is, the resonance width becomes zero at the same internuclear distance where the energy of the electron-attached state drops below that of the neutral state. Such smooth and internally consistent behavior is only achieved when the perturbation due to the CAP is removed using the first-order deperturbative correction that we introduced earlier; the evaluation of resonance positions and widths from raw (uncorrected) energies leads to unphysical discontinuities and fails to correctly describe the conversion of a resonance to a bound state at large internuclear distances.

SECTION: Spectroscopy, Photochemistry, and Excited States



Transient anions¹ formed by electron attachment to a neutral closed-shell molecule with negative electron affinity play an important role in multiple areas, including plasma physics, atmospheric chemistry, and biology. The resulting electronic states have finite lifetimes and are called resonances. These states belong to the continuum part of the spectrum; therefore, their wave functions are not L^2 -integrable.^{2,3} Using the Siegert (imposing outgoing wave boundary conditions) or Feshbach (a bound state diabatically coupled to the continuum) formalisms, a resonance can be described similar to a bound state but with a complex energy that gives rise to an exponential decay in time

$$\psi(r, t) = e^{-iEt} \Psi_{\text{res}}(r) = e^{-(\Gamma/2)t} e^{-iE_R t} \Psi_{\text{res}}(r) \quad (1)$$

In this formulation, the resonance position E_R and width Γ are obtained from the real and imaginary parts of the energy eigenvalue of the time-independent Schrödinger equation.^{2–4}

In order to avoid working with continuum functions or dealing with boundary conditions, a number of approaches that treat resonances using L^2 methods have been developed.⁵ These include stabilization techniques,^{6,7} using small bases⁸ and artificial real stabilizing potentials,^{9–11} complex scaling,^{3,4,12,13} and complex absorbing potential (CAP) methods.^{14–18} Complex scaling where one scales all coordinates in the Hamiltonian by a complex number has rigorous theoretical foundation,¹³ but is plagued by an extreme basis set dependence^{19–22} and conceptual difficulties in describing molecular resonances^{23–26} and, especially, potential energy surfaces (PESs). In contrast, CAP methods do not suffer from

such problems and can be easily implemented within standard quantum-chemical methods.

In CAP methods, the molecular Hamiltonian H_0 is augmented by an artificial imaginary potential W that absorbs the diverging tail of the resonance wave function, converting it into an L^2 -integrable form

$$H(\eta) = H_0 - i\eta W \quad (2)$$

$$W = W_x + W_y + W_z \quad W_\alpha = \begin{cases} 0 & \text{if } |r_\alpha| < r_\alpha^0 \\ (r_\alpha - r_\alpha^0)^2 & \text{if } |r_\alpha| > r_\alpha^0 \end{cases} \quad (3)$$

Here, α denotes the three Cartesian coordinates, r_α^0 is the onset of the CAP, and η is the CAP's strength. In a complete basis set, the exact resonance position and width are obtained in the limit $\eta \rightarrow 0$.^{14,15} Unfortunately, this limit cannot be achieved in practical calculations employing finite basis sets. Consequently, one needs to deal with so-called reflections (i.e., perturbations) due to the finite basis set and the finite-strength CAP. Reflection-free CAPs have been proposed,^{15,27} but are far from routine application. Instead, a CAP of the simple form in eq 3 is usually employed, and the optimal value of η is determined from the condition

Received: July 18, 2014

Accepted: August 20, 2014

$$\eta \cdot \frac{dE}{d\eta} = \min \quad (4)$$

which entails calculations of η -trajectories $E(\eta)$. This criterion is based on a perturbative analysis of the energy¹⁴

$$E(\eta) = E_0 + a_1\eta + a_2\eta^2 + \dots \quad (5)$$

where one defines the n th order corrected energy as

$$E^{(n)} = E_0 + \sum_{j=1}^n \frac{-\eta^j}{j!} \frac{d^j E(\eta)}{d\eta^j} \quad (6)$$

Minimization of the first-order term in eq 6 leads to eq 4 for the zeroth-order energy.

CAPs have been implemented within density functional theory,²⁸ multireference configuration-interaction (MRCI),^{29,30} Fock-space coupled-cluster theory,³¹ and equation-of-motion electron-attachment coupled-cluster singles and doubles (EOM-EA-CCSD).^{32–35}

A straightforward application of CAPs, along with the criterion from eq 4, leads to a strong dependence of the resulting resonance positions and lifetimes on the CAP onset and the one-electron basis set. Furthermore, since finite (and often rather large) values of η_{opt} are obtained by applying eq 4, the results are always perturbed by the CAP, despite the above minimization based on perturbative arguments. Thus, a superior approach is to explicitly remove the leading first-order term in eq 5 instead of minimizing it. Recently, we introduced a deperturbative first-order correction³⁵ that is applied to the computed raw energies to remove the perturbation due to the CAP. The resulting first-order corrected values exhibit much more stable behavior than the values obtained by the standard approach.^{33,35} The deperturbative correction from ref 35 is derived by analyzing the energy expression and, as explained below, is computed by using the one-particle density matrix of the resonance wave function and the CAP matrix. Interestingly, a very similar (and, under certain conditions,³³ identical) result can be obtained by extrapolation (using Padé approximants) of the stabilized complex energy to the zero η limit, as advocated by Moiseyev and co-workers.^{36,37}

The physical reason for using a finite-strength CAP that leads to undesirable perturbations of the resonance states is that Gaussian basis sets span a finite space; they decay rapidly outside of the molecular core. Thus, the CAP is represented only within the domain spanned by the basis functions. Using an orthonormal set, $\{\phi_p(\mathbf{r})\}$, the value of the CAP represented in that basis set at point \mathbf{r} is

$$W(\mathbf{r}) = \sum_{pq} |\phi_p(\mathbf{r})\rangle \langle \phi_p | \hat{W} | \phi_q \rangle \langle \phi_q(\mathbf{r})| = \sum_{pq} |\phi_p(\mathbf{r})\rangle W_{pq} \langle \phi_q(\mathbf{r})| \quad (7)$$

and not $(\mathbf{r} - \mathbf{r}_0)^2$ as given by eq 3. Thus, instead of going to infinity at large \mathbf{r} , the CAP eventually drops to zero, following the decay of the most diffuse basis function. Consequently, one needs to use a sufficiently large η to create a “barrier” that is high enough to contain the resonance. (The barrier height is related to the energy of the resonance, making the optimal CAP strength state and geometry dependent.) The incompleteness of the CAP representation is nicely illustrated by the strong basis-set dependence of the Frobenius norm of W discussed in refs 33 and 35. Using large η leads to perturbation of resonance (and bound) states; however, the deperturbative correction removes the CAP contribution to the energy (in first order),

thus allowing one to obtain accurate results with standard quantum-chemical methods.³³

In CAP-EOM-EA-CCSD,³³ the wave function of the resonance state is written as

$$|\Psi_{\text{res}}\rangle = R e^T |\Phi_0\rangle \quad (8)$$

where the operators R and T are defined as

$$T = \sum_{ai} t_i^a a^\dagger i + \frac{1}{4} \sum_{abij} t_{ij}^{ab} a^\dagger i b^\dagger j \quad (9)$$

$$R = \sum_a r^a a^\dagger + \frac{1}{2} \sum_{abi} r_i^{ab} a^\dagger i b^\dagger \quad (10)$$

The wave function amplitudes t and r as well as the complex energy of the resonance are obtained by solving the CC and EOM-CC equations^{38–41}

$$(\Phi_\mu | e^{-T} H(\eta) e^T | \Phi_0) = 0 \quad \forall \mu \quad (11)$$

$$(\Phi_\mu | e^{-T} H(\eta) e^T R | \Phi_0) = r_\mu E \quad \forall \mu \quad (12)$$

In these equations, Φ_0 and Φ_μ denote the Hartree–Fock (HF) determinant and the singly and doubly excited determinants, respectively, whereas a , b , i , and j are creation and annihilation operators. In our implementation, the CAP is added at the HF stage so that the usual expressions from CC/EOM-CC theory need not be modified and the complex Koopmans’ theorem holds.³³ In all expressions, it is, however, necessary to replace the standard scalar product by the c -product because the CAP-augmented Hamiltonian is no longer Hermitian but complex symmetric.^{12,14,42} We indicate the c -product by using parentheses instead of the usual chevrons in eqs 8, 11, 12, and below.

In a previous paper,³⁵ we demonstrated that the dependence of resonance positions and widths on the CAP onset is mitigated when the explicit dependence on the CAP is removed from the energy. This led to the first-order corrected energy U , which is defined as

$$\text{Re}(U) = \text{Re}(E) - \eta \text{Tr}[\text{Im}(\gamma)W] \quad (13)$$

$$\text{Im}(U) = \text{Im}(E) + \eta \text{Tr}[\text{Re}(\gamma)W] \quad (14)$$

with γ denoting the one-particle density matrix

$$\gamma_{pq} = (\Phi_0 | L e^{-T} \{p^\dagger q\} e^T R | \Phi_0) \quad (15)$$

Following the terminology from refs 35 and 33, we refer to E (raw uncorrected energies) and U (deperturbed energies) as zero- and first-order values, respectively. To evaluate the first-order correction, the left EOM-CC eigenvalue equation needs to be solved

$$L = \sum_a l_a a + \frac{1}{2} \sum_{abi} l_{ab}^i a i^\dagger b \quad (16)$$

$$(\Phi_0 | L e^{-T} H(\eta) e^T | \Phi_\mu) = l_\mu E \quad \forall \mu \quad (17)$$

In ref 35, we illustrated that the first-order corrected energy becomes near stationary when some critical CAP strength is reached because the resonance wave function does not change anymore. In this region of stability, which may be different for the real part and the imaginary part, we evaluate the resonance position and width from $\text{Re}(U)$ and $\text{Im}(U)$, respectively. We add that U from eqs 13 and 14 is identical to $E^{(1)}$ from eq 6

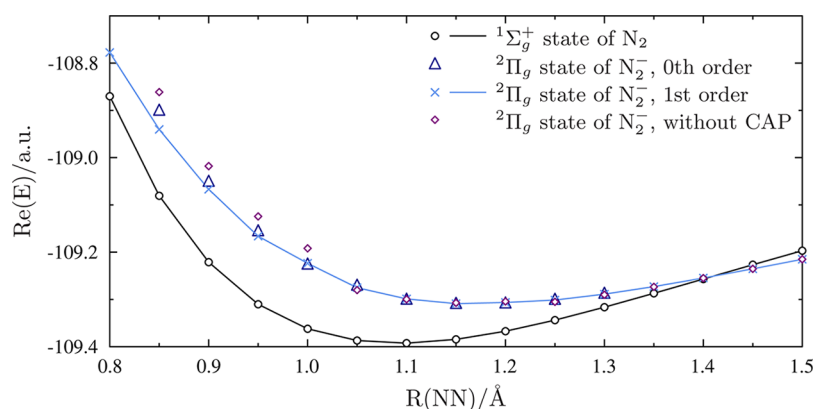


Figure 1. Potential energy curves of the $1\Sigma_g^+$ ground state of N_2 and the $2\Pi_g$ ground state of N_2^- at internuclear distances from 0.8 to 1.5 Å. Values for the $1\Sigma_g^+$ state of N_2 were computed by CCSD/aug-cc-pVTZ+3s3p3d(C); values for the $2\Pi_g$ state of N_2^- were computed by CAP-EOM-EA-CCSD/aug-cc-pVTZ+3s3p3d(C).

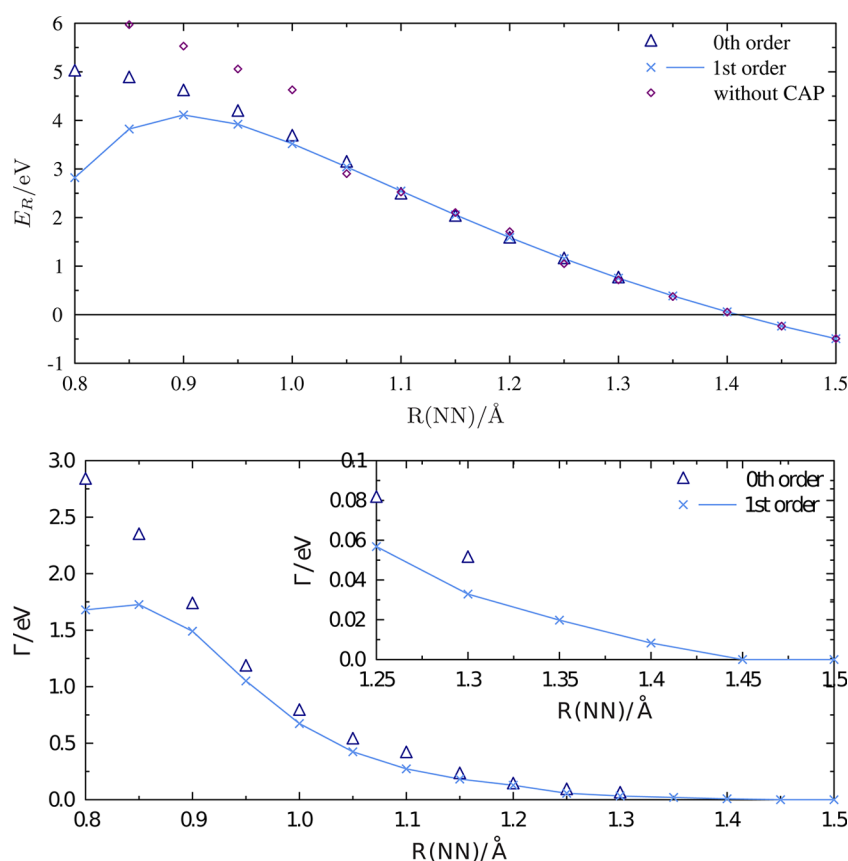


Figure 2. Resonance position (top) and width (bottom) of the $2\Pi_g$ state of N_2^- as a function of the NN distance computed by CAP-EOM-EA-CCSD/aug-cc-pVTZ+3s3p3d(C).

since $dE/d\eta = -i\text{Tr}[\gamma W]$ according to the Hellmann–Feynman theorem. Our deperturbative correction can thus be interpreted as removal of the first-order term in eq 5.

In our previous paper,³³ we presented a protocol for determining resonance positions and widths in a black-box manner and benchmarked the performance of CAP-EOM-EA-CCSD for small- to medium-size molecules. We illustrated that when used with the deperturbative correction, CAP-EOM-EA-CCSD yields resonance positions and widths that are in good agreement with those from experiment and with other theoretical estimates.

In this Letter, we explore whether CAP-EOM-EA-CCSD is suitable for the characterization of PESs of resonance states. The ability to compute PESs is critically important for a complete theoretical description of resonances. Often, in order to interpret findings from scattering experiments, structural changes of the temporary anion need to be taken into account. Electron attachment can induce chemical transformations including dissociation and bond breaking (see, for example, ref 43); the description of such processes also requires PESs. In addition to these practical considerations, molecules with stretched bonds provide a nice test case for theory. Since the bond length acts as a parameter that tunes the resonance width,

one can study how the performance of a method depends on the width of the resonance state without the need to consider other changes in the electronic structure of the system.

Since the CAP is an artificial potential and its optimal strength according to eq 4 is different at different geometries, it is not guaranteed a priori that smooth PESs can be produced by CAP methods. An even more important issue is internal consistency of the computed resonance energies and lifetimes, that is, the resonance width should become zero at exactly the same geometry where the energy of the electron-attached resonance state drops below the energy of the parent neutral state and the resonance becomes bound. A number of previous studies have found that the conversion from a resonance to a bound state is not correctly described by various CAP methods, that is, the resonance width was calculated to be zero even though the resonance state of the anion was located above the ground state of the neutral molecule.^{44–47} Such internal inconsistency is expected for state-specific approaches like HF or MRCI because in these methods, the model Hamiltonians of the N - and $(N+1)$ -electron systems are different;⁴⁴ consequently, the respective wave functions are not described on an equal footing. In contrast, EOM-CC is a multistate method in which N - and $(N\pm 1)$ -electron states are obtained by diagonalization of the same model Hamiltonian \bar{H} (constructed using the same reference orbitals and T amplitudes). Consequently, the energies of these states are consistent with each other; for example, the onsets of ionization continua in EOM-EE-CCSD calculations are exactly equal to the corresponding EOM-IP-CCSD ionization energies. Thus, in EOM-EA-CC, the wave functions and the energies of the N -electron state and the $(N+1)$ -electron state are described on an equal footing and are consistent with each other.

As benchmark systems, we chose N_2^- ($^2\Pi_g$ state) and H_2^- ($^2\Sigma_u^+$ state) representing Π and Σ resonances, respectively. We used the same protocol as in ref 33. The closed-shell neutral states were described by CCSD, whereas the attached states were described by EOM-EA-CCSD. The aug-cc-pVTZ+3s3p3d(C) basis set from ref 33 was used in all calculations. Calculations were performed using the Q-Chem electronic structure package.^{48,49}

On the basis of benchmark studies in refs 35 and 33, the CAP onset should be equal to (or slightly larger than) the spatial extent (i.e., $\langle X^2 \rangle$, $\langle Y^2 \rangle$, $\langle Z^2 \rangle$) of the reference wave function. Thus, in principle, the onset should be different at different geometries, i.e., the CAP should move with the molecule. In calculations of H_2^- , which is a Σ resonance, the onset parameters were recomputed at each bond length. However, in N_2^- , which is a Π resonance that is not sensitive to the CAP onset along the molecular axis,³³ it is possible to use a fixed CAP onset computed at the N_2 equilibrium structure.

We note that a multireference method is needed for computing the entire potential energy curve of N_2 as single-reference methods fail to correctly describe the dissociation into two nitrogen atoms in their quartet ground states. However, at the moderately stretched bond distances that are of interest here, CCSD recovers MRCI results.^{50,51}

Figure 1 displays potential energy curves for the $^1\Sigma_g^+$ ground state of neutral N_2 and the $^2\Pi_g$ state of N_2^- . The resonance positions derived from these curves as well as the corresponding resonance widths are shown in Figure 2 as a function of bond distance. All relevant raw data as well as optimal values for the CAP strength are compiled in Table S1 in the Supporting Information (SI). The CAP onset parameters

were chosen as the expectation values of the spatial extent of the CCSD wave function of N_2 at $R(NN) = 1.1$ Å ($r_x^0 = r_y^0 = 2.76$ bohr, $r_z^0 = 4.88$ bohr, with the molecule oriented along the z -axis) for calculations at all distances. To further validate using a frozen CAP onset for Π resonances, we carried out an exemplary calculation at $R(NN) = 0.9$ Å, in which we adjusted the CAP onset to the spatial extent of the N_2 wave function at this bond length ($r_x^0 = r_y^0 = 2.67$ bohr and $r_z^0 = 4.33$ bohr). This yielded values for the resonance position and width larger by just 0.022 and 0.050 eV, respectively, than those shown in Figure 2.

Figure 1 shows that CAP-EOM-EA-CCSD yields a smooth potential energy curve for the $^2\Pi_g$ state of N_2^- . A shallow minimum is found around 1.15 Å, i.e., at a distance a little larger than the equilibrium bond length of the neutral N_2 , which agrees qualitatively with results from most previous studies^{44,45,52–54} and with molecular orbital considerations (electron attachment to an antibonding orbital). Only complex-scaled MRCI yielded the minimum of N_2^- at a distance similar to that of N_2 .^{21,46}

The crossing of the curves of N_2 and N_2^- , i.e., the conversion of the resonance into a bound state, occurs around 1.4 Å, which confirms an earlier CC study⁵⁰ on the bound part of the N_2^- potential energy curve. Figure 1 also demonstrates that standard EOM-EA-CCSD calculations without CAP produce a similarly shaped potential energy curve for N_2^- . We emphasize that this is an artifact due to using a finite basis set; in the complete basis-set limit a CAP-free calculation of N_2^- should yield a potential energy curve identical to that of N_2 because such calculations would converge to the neutral molecule plus a free electron. Furthermore, the resonance width cannot be obtained from CAP-free calculations and the resonance state can only be identified among the continuum states by its different dependence on the CAP strength when using reasonably large basis sets. That is, the curve for standard EOM-EA-CCSD in Figure 1 could be constructed only after the calculations with finite CAP had been performed. Moreover, without CAP, a kink was obtained between 1.0 and 1.05 Å that is paralleled by a sudden change of the eigenvalue of the valence LUMO. Similar behavior was observed in calculations using stabilization techniques and was attributed to avoided crossings between the resonance and discretized continuum states.⁵⁴

Figure 2 illustrates that zeroth-order (uncorrected) and first-order (deperturbed) values for the resonance position and width differ by less than 0.1 eV for bond distances larger than 1.0 Å. In this region, we observe an almost linear increase of the resonance position and a superlinear increase of the resonance width with decreasing bond length, in agreement with earlier EOM-CC studies using CAPs⁴⁵ and stabilization techniques.⁵⁴ At shorter distances, the deviation between zeroth-order and first-order values rapidly increases, which can be attributed to the greater importance of higher-order terms in eq 5 for larger resonance widths. First-order corrected CAP-EOM-EA-CCSD yields a maximum for the resonance position near 0.9 Å and for the resonance width near 0.85 Å, whereas zeroth-order values monotonically increase as the bond length shrinks.

At distances larger than 1.3 Å where the resonance becomes very narrow, no optimal CAP strength could be determined using the criterion from eq 4. This means that the resonance cannot be uncovered because it is perturbed too strongly by the CAP. However, upon application of the first-order correction that removes the perturbation due to the CAP, the potential

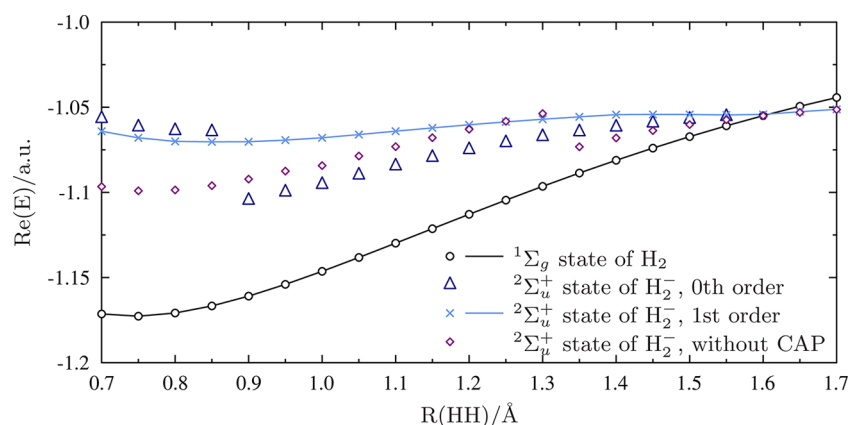


Figure 3. Potential energy curves of the $1\Sigma_g^+$ ground state of H_2 and the $2\Sigma_g^+$ ground state of H_2^- at internuclear distances from 0.7 to 1.7 Å. Values for the $1\Sigma_g^+$ state of H_2 were computed by CCSD/aug-cc-pVTZ+3s3p3d(C); values for the $2\Sigma_g^+$ state of H_2^- were computed by CAP-EOM-EA-CCSD/aug-cc-pVTZ+3s3p3d(C).

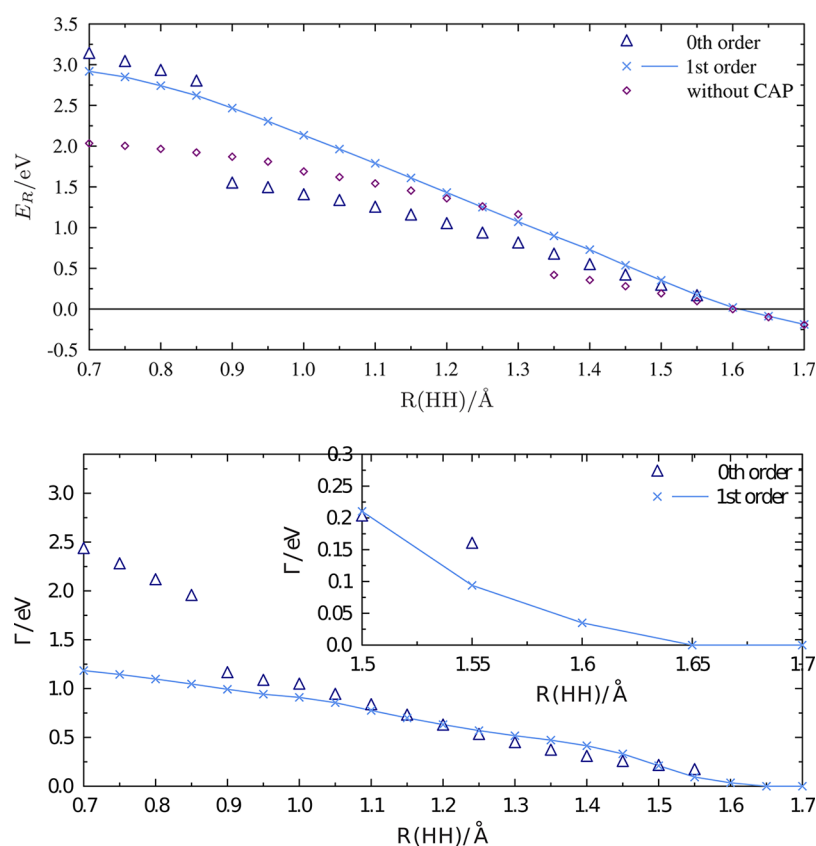


Figure 4. Resonance position (top) and width (bottom) of the $1\Sigma_u^+$ state of H_2^- as a function of the HH distance computed by CAP-EOM-EA-CCSD/aug-cc-pVTZ+3s3p3d(C).

energy curve can be continued beyond 1.3 Å and even beyond the crossing point with the N_2 curve. In the latter region, the N_2^- anion is stable, which means that the CAP acts as a pure perturbation. This is indeed confirmed by our results, which show that the CAP-free EOM-EA-CCSD values for the resonance position are recovered within 0.002 eV by first-order CAP-EOM-EA-CCSD in the bound region. We also see from Figure 2 that the conversion of the resonance to a bound state is correctly described by first-order corrected CAP-EOM-EA-CCSD as the resonance width becomes zero at the same distance where the resonance position changes its sign. This is different from previous studies^{44–46} and constitutes an

important advantage of CAP-EOM-CC methods for the study of resonances.

As a potential alternative to the correction for the CAP perturbation, one might consider increasing the CAP onset in the crossing region to mitigate the perturbation by the CAP. However, such a change of the CAP onset would most likely result in a kink in the potential energy curve. We also note that a gradual increase of the onset along the molecular axis depending on the bond length will not help as one has to increase the onset perpendicular to the molecular axis owing to the Π character of the resonance.

As a second example, we studied the $^2\Sigma_u^+$ resonance of H_2^- . Potential energy curves for this resonance are shown in Figure 3, along with the $^1\Sigma_g^+$ ground state of neutral H_2 . The corresponding resonance positions and widths are displayed in Figure 4. All relevant raw data as well as optimal values for the CAP strength are compiled in Table S2 in the SI. Since the H_2^- resonance is of Σ character, we employed a flexible CAP onset chosen as the expectation value of the spatial extent of the H_2 wave function at the respective bond distance plus 1 bohr (see Table S2, SI).

Figure 3 illustrates that the potential energy curve of the H_2^- resonance is flat over a long range of bond distances. A very shallow minimum is found near 0.85 Å, while the crossing with the potential energy curve of neutral H_2 occurs near 1.6 Å, which roughly agrees with previous studies.^{47,55–60} Unlike for N_2^- , first-order, zeroth-order, and CAP-free results differ considerably and a smooth potential energy curve is only obtained when using the deperturbative correction (first-order values). The zeroth-order curve exhibits a pronounced kink around the minimum that is paralleled by a sudden change of the optimal CAP strength (see Table S2, SI). A similar kink is obtained near 1.3 Å in the CAP-free curve.

Figure 4 shows that not only the zeroth-order resonance position but also the resonance width undergoes a sudden change around 0.85 Å. In contrast, the first-order corrected calculations yield an almost linear increase of the resonance position and width with shrinking bond length. For bond lengths larger than 1.0 Å, zeroth-order and first-order resonance widths differ by less than 0.1 eV, while resonance positions differ by up to 1 eV in the same region. It is also noteworthy that our results for the resonance width qualitatively agree with those from an MRCI study,⁶⁰ whereas complex SCF⁴⁷ and the static-exchange approximation⁵⁹ yielded much higher values. This confirms the conclusion from our previous paper³³ that electron correlation reduces the resonance width considerably.

As in the N_2^- case, an optimal CAP strength according to eq 4 could not be determined beyond 1.55 Å since the resonance becomes too narrow here. Yet, upon application of the deperturbative correction, the potential energy curve of H_2^- can be continued to and past the crossing with the curve of neutral H_2 . In the bound region, first-order corrected CAP-EOM-EA-CCSD and regular EOM-EA-CCSD agree within 0.01 eV, which illustrates that the perturbation due to the CAP was indeed successfully removed by the correction (thus, 0.01 eV gives a measure of the remaining perturbation). We emphasize that we observe again the physically correct conversion of the resonance to a bound state, i.e., the resonance width becomes zero at the same distance where the resonance position changes its sign.

In conclusion, we have demonstrated that CAP-EOM-EA-CCSD is well suited for the study of PESs (both energies and lifetimes) of resonance states. A smooth dependence of resonance positions and widths on bond lengths is obtained when the CAP contribution to the complex energies is removed by applying our first-order deperturbative correction.³⁵ In contrast, smooth and internally consistent behavior is not guaranteed when the results are not corrected for the CAP perturbation because the optimal CAP strength is different at different geometries, leading to kinks and discontinuities in resonance positions and widths. CAP-free calculations also fail to produce smooth curves because of the variable mixing of the resonance with pseudocontinuum states. Moreover, in regions where the resonance is narrow, the perturbation by the CAP is

too strong for the resonance to be uncovered so that only the first-order approach yields valid results. Most importantly, our approach—first-order corrected CAP-EOM-EA-CCSD—yields internally consistent resonance positions and widths; the sign change of the resonance position relative to the neutral state occurs at the same bond length where the resonance width becomes zero for both N_2^- and H_2^- . In other words, first-order corrected CAP-EOM-EA-CCSD correctly describes the conversion of resonances to bound states, unlike state-specific approaches.

■ ASSOCIATED CONTENT

§ Supporting Information

Raw data for Figures 1–4 and additional results, including absolute energies, resonance positions and widths, as well as optimal CAP strengths. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been supported by the Army Research Office through the W911NF-12-1-0543 grant. We also acknowledge support from the Humboldt Research Foundation (Bessel Award to A.I.K. and Feodor Lynen fellowship to T.C.J.). We thank Prof. Nimrod Moiseyev for helpful feedback on the manuscript.

■ REFERENCES

- (1) Simons, J. Theoretical study of negative molecular ions. *Annu. Rev. Phys. Chem.* **2011**, 62, 107–128.
- (2) Klaiman, S.; Gilary, I. On resonance: A first glance into the behavior of unstable states. *Adv. Quantum Chem.* **2012**, 63, 1–31.
- (3) Reinhardt, W. P. Complex coordinates in the theory of atomic and molecular structure and dynamics. *Annu. Rev. Phys. Chem.* **1982**, 33, 223–255.
- (4) Moiseyev, N. *Non-Hermitian quantum mechanics*; Cambridge University Press: Cambridge, U.K., 2011.
- (5) Jordan, K. D.; Voora, V. K.; Simons, J. Negative electron affinities from conventional electronic structure methods. *Theor. Chem. Acc.* **2014**, 133, 1445.
- (6) Hazi, A. U.; Taylor, H. S. Stabilization method of calculating resonance energies: Model problem. *Phys. Rev. A* **1970**, 1, 1109–1120.
- (7) Taylor, H. S.; Hazi, A. U. Comment on the stabilization method: Variational calculation of the resonance width. *Phys. Rev. A* **1976**, 14, 2071–2074.
- (8) Simons, J.; Jordan, K. D. Ab initio electronic structure of anions. *Chem. Rev.* **1987**, 87, 535–555.
- (9) DeRose, E.; Gislason, E. A.; Sabelli, N. H. A new method for computing properties of negative ion resonances with application to $^2\Sigma_u^+$ states of H_2^- . *J. Chem. Phys.* **1985**, 82, 4577–4584.
- (10) Izmaylov, S. F.; Adamson, S. O.; Zaitsevskii, A. Multipartitioning many-body perturbation theory calculations on temporary anions: Applications to N_2^- and CO^- . *J. Phys. B* **2004**, 37, 2321–2329.
- (11) Sajeev, Y. Real-valued continuum remover potential: An improved L^2 -stabilization method for the chemistry of electronic resonance states. *Chem. Phys. Lett.* **2013**, 587, 105–112.
- (12) Moiseyev, N. Quantum theory of resonances: Calculating energies, widths and cross-sections by complex scaling. *Phys. Rep.* **1998**, 302, 212–293.
- (13) Aguilar, J.; Combes, J. M. A class of analytic perturbations for one-body Schrödinger Hamiltonians. *Commun. Math. Phys.* **1971**, 22, 269–279.

- (14) Riss, U. V.; Meyer, H.-D. Calculation of resonance energies and widths using the complex absorbing potential method. *J. Phys. B* **1993**, *26*, 4503–4536.
- (15) Riss, U. V.; Meyer, H.-D. Reflection-free complex absorbing potentials. *J. Phys. B* **1995**, *28*, 1475–1493.
- (16) Riss, U. V.; Meyer, H.-D. The transformative complex absorbing potential method: A bridge between complex absorbing potentials and smooth exterior scaling. *J. Phys. B* **1998**, *31*, 2279–2304.
- (17) Santra, R.; Cederbaum, L. S. Non-Hermitian electronic theory and applications to clusters. *Phys. Rep.* **2002**, *368*, 1–117.
- (18) Muga, J. G.; Palao, J. P.; Navarro, B.; Egusquiza, I. L. Complex absorbing potentials. *Phys. Rep.* **2004**, *395*, 357–426.
- (19) Rescigno, T. N.; McCurdy, C. W.; Orel, A. E. Extensions of the complex-coordinate method to the study of resonances in many-electron systems. *Phys. Rev. A* **1978**, *17*, 1931–1938.
- (20) Chuljian, D. T.; Simons, J. Coordinate rotation studies of H^- , He^- , Be^- , Mg^- resonances: Basis set and configuration list dependence. *Int. J. Quantum Chem.* **1983**, *23*, 1723–1738.
- (21) Honigmann, M.; Bunker, R. J.; Liebermann, H.-P. Complex self-consistent field and multireference single- and double-excitation configuration interaction calculations for the $^2\Pi_g$ resonance state of N_2^- . *J. Chem. Phys.* **2006**, *125*, 234304.
- (22) Bravaya, K. B.; Zuev, D.; Epifanovsky, E.; Krylov, A. I. Complex-scaled equation-of-motion coupled-cluster method with single and double substitutions for autoionizing excited states: Theory, implementation, and examples. *J. Chem. Phys.* **2013**, *138*, 124106.
- (23) McCurdy, C. W.; Rescigno, T. N. Extension of the method of complex basis functions to molecular resonances. *Phys. Rev. Lett.* **1978**, *41*, 1364–1368.
- (24) McCurdy, C. W. Complex-coordinate calculation of matrix elements of the resolvent of the Born–Oppenheimer Hamiltonian. *Phys. Rev. A* **1980**, *21*, 464–470.
- (25) McCurdy, C. W.; Rescigno, T. N. Complex-basis-function calculations of resolvent matrix elements: Molecular photoionization. *Phys. Rev. A* **1980**, *21*, 1499–1505.
- (26) Balanarayan, P.; Sajeev, Y.; Moiseyev, N. Ab initio complex molecular potential energy surfaces by back-rotation transformation method. *Chem. Phys. Lett.* **2012**, *524*, 84–89.
- (27) Moiseyev, N. Derivations of universal exact complex absorption potentials by the generalized complex coordinate method. *J. Phys. B* **1998**, *31*, 1431–1441.
- (28) Zhou, Y.; Ernzerhof, M. Calculating the lifetimes of metastable states with complex density functional theory. *J. Phys. Chem. Lett.* **2012**, *3*, 1916–1920.
- (29) Sommerfeld, T.; Riss, U. V.; Meyer, H.-D.; Cederbaum, L. S.; Engels, B.; Suter, H. U. Temporary anions — Calculation of energy and lifetime by absorbing potentials: The N_2^- $^2\Pi_g$ resonance. *J. Phys. B* **1998**, *31*, 4107–4122.
- (30) Sommerfeld, T.; Santra, R. Efficient method to perform CAP/CI calculations for temporary anions. *Int. J. Quantum Chem.* **2001**, *82*, 218–226.
- (31) Sajeev, Y.; Santra, R.; Pal, S. Analytically continued Fock-space multireference coupled-cluster theory: Application to the $^2\Pi_g$ shape resonance in $e-N_2$ scattering. *J. Chem. Phys.* **2005**, *122*, 234320.
- (32) Ehara, M.; Sommerfeld, T. CAP/SAC-CI method for calculating resonance states of metastable anions. *Chem. Phys. Lett.* **2012**, *537*, 107–112.
- (33) Zuev, D.; Jagau, T.-C.; Bravaya, K. B.; Epifanovsky, E.; Shao, Y.; Sundstrom, E.; Head-Gordon, M.; Krylov, A. I. Complex absorbing potentials within EOM-CC family of methods: Theory, implementation, and benchmarks. *J. Chem. Phys.* **2014**, *141*, 024102.
- (34) Ghosh, A.; Vaval, N.; Pal, S. Equation-of-motion coupled-cluster method for the study of shape resonances. *J. Chem. Phys.* **2012**, *136*, 234110.
- (35) Jagau, T.-C.; Zuev, D.; Bravaya, K. B.; Epifanovsky, E.; Krylov, A. I. A fresh look at resonances and complex absorbing potentials: Density matrix based approach. *J. Phys. Chem. Lett.* **2014**, *5*, 310–315.
- (36) Lefebvre, R.; Sindelka, M.; Moiseyev, N. Resonance positions and lifetimes for flexible complex absorbing potentials. *Phys. Rev. A* **2005**, *72*, 052704.
- (37) Lefebvre, R.; Moiseyev, N. Localization of exceptional points with Padé approximants. *J. Phys. B* **2010**, *43*, 095401.
- (38) Sekino, H.; Bartlett, R. J. A linear response, coupled-cluster theory for excitation energy. *Int. J. Quantum Chem.* **1984**, *26*, 255–265.
- (39) Stanton, J. F.; Bartlett, R. J. The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. *J. Chem. Phys.* **1993**, *98*, 7029–7039.
- (40) Krylov, A. I. Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchhiker's guide to Fock space. *Annu. Rev. Phys. Chem.* **2008**, *59*, 433–462.
- (41) Shavitt, I.; Bartlett, R. J. *Many-body methods in chemistry and physics: MBPT and coupled-cluster theory*; Cambridge University Press: Cambridge, U.K., 2009.
- (42) Moiseyev, N.; Certain, P. R.; Weinhold, F. Resonance properties of complex-rotated Hamiltonians. *Mol. Phys.* **1978**, *36*, 1613–1630.
- (43) Simons, J. How do low-energy (0.1–2 eV) electrons cause DNA-strand breaks? *Acc. Chem. Res.* **2006**, *39*, 772–779.
- (44) Lauderdale, J. G.; McCurdy, C. W.; Hazi, A. U. Conversion of bound states to resonances with changing internuclear distance in molecular anions. *J. Chem. Phys.* **1983**, *79*, 2200–2205.
- (45) Ghosh, A.; Karne, A.; Pal, S.; Vaval, N. CAP/EOM-CCSD method for the study of potential curves of resonant states. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17915–17921.
- (46) Honigmann, M.; Bunker, R. J.; Liebermann, H.-P. Complex multireference configuration interaction calculations employing a coupled diabatic representation for the $^2\Pi_g$ resonance states of N_2^- . *J. Chem. Phys.* **2009**, *131*, 034303.
- (47) McCurdy, C. W.; Mowrey, R. C. Complex potential-energy function for the $^2\Sigma_u^+$ shape resonance state of H_2^- at the self-consistent-field level. *Phys. Rev. A* **1982**, *25*, 2529–2538.
- (48) Krylov, A. I.; Gill, P. M. W. Q-Chem: An engine for innovation. *WIREs Comput. Mol. Sci.* **2013**, *3*, 317–326.
- (49) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; et al. Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. *Mol. Phys.* **2014**, DOI: 10.1080/00268976.2014.952696.
- (50) Gutsev, G. L.; Rozyczko, P. B.; Bartlett, R. J.; Weatherford, C. A. Does N_2^- exist? A coupled-cluster study. *J. Chem. Phys.* **1999**, *110*, 5137–5139.
- (51) Bartlett, R. J.; Stanton, J. F. Applications of Post-Hartree-Fock Methods: A Tutorial. In *Reviews in Computational Chemistry*; John Wiley & Sons, Inc.: New York, 1994; p 65.
- (52) Birtwistle, D. T.; Herzenberg, A. Vibrational excitation of N_2 by resonance scattering of electrons. *J. Phys. B* **1971**, *4*, 53–70.
- (53) Nestmann, B. M.; Peyerimhoff, S. D. CI method for determining the location and width of resonances in electron–molecule collision processes. *J. Phys. B* **1985**, *18*, 4309–4319.
- (54) Falcetta, M. F.; Di Falco, L. A.; Ackerman, D. S.; Barlow, J. C.; Jordan, K. D. Assessment of various electronic structure methods for characterizing temporary anion states: Application to the ground state anions of N_2 , C_2H_2 , C_2H_4 , and C_6H_6 . *J. Phys. Chem. A* **2014**, DOI: 10.1021/jp5003287.
- (55) Bardsley, J. N.; Herzenberg, A.; Mandl, F. Electron resonances of the H_2^- ion. *Proc. Phys. Soc.* **1966**, *89*, 305–319.
- (56) Eliezer, I.; Taylor, H. S.; Williams, J. K. Resonant states of H_2^- . *J. Chem. Phys.* **1967**, *47*, 2165–2177.
- (57) Moiseyev, N.; Corcoran, C. Autoionizing states of H_2 and H_2^- using the complex-scaling method. *Phys. Rev. A* **1979**, *20*, 814–817.
- (58) DeRose, E.; Gislason, E. A.; Sabelli, N. H. A new method for computing properties of negative ion resonances with application to $^2\Sigma_u^+$ states of H_2^- . *J. Chem. Phys.* **1985**, *82*, 4577–4584.
- (59) Domcke, W.; Berman, M.; Mündel, C.; Meyer, H.-D. Direct calculation of complex resonance poles using separable expansions of

the potential: Application to the $^2\Sigma_u^+$ shape resonance in electron- H_2 scattering. *Phys. Rev. A* **1986**, 33, 222–232.

(60) DeRose, E.; Gislason, E. A.; Sabelli, N. H.; Sluis, K. M. A theoretical investigation of $^2\Sigma_u^+$ resonance states of H_2^- . *J. Chem. Phys.* **1988**, 88, 4878–4883.