A complex absorbing potential electron propagator approach to resonance states of metastable anions

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Abstract. An earlier developed electron propagator method for the treatment of electron attachment to molecules within the non-Dyson algebraic-diagrammatic construction framework (EA-ADC) is extended by inclusion of the complex absorbing potential (CAP). The resulting method allows for the investigation of resonance states of metastable anions. Approximation schemes up to third-order perturbation theory for the electron propagator (EA-ADC(3)) are implemented. The CAP operator is treated up to second-order using the intermediate state representation formalism (ISR(2)) and the subspace projection technique. The CAP/EA-ADC(3) method is tested in first applications to the resonances in CO and N₂ molecules associated with electron attachment to their low-lying π*-orbitals. The results of the calculations agree well with the available experimental and theoretical data and demonstrate the CAP-augmented EA-ADC modeling can become a useful tool for theoretical studies of metastable electron-attached states.

1. Introduction

Electron attachment to molecules can yield metastable states which have a short, but finite, lifetime [1, 2]. Such states, also referred to as resonances, lie in energy above the parent N-electron states and decay by electron emission. Despite their limited lifetime, metastable electron-attached (EA) states are responsible for many important physical and chemical processes [3, 4]. In particular, formation of temporary anions [1, 2] is considered as one of the cause of DNA damage following dissociative attachment [5].

Since resonances describe discrete (N+1)-electron states, that are embedded into the continuum of unbound states, their position, \( E_R \), and width, \( \Gamma \), can be determined only from theoretical approaches, that can treat the continuum nature of the wavefunction as well as the strong electron correlation effects, typical for such systems. The former makes the wavefunctions not \( L^2 \)-integrable, which is a rather undesirable feature for standard quantum chemical calculations usually exploiting \( L^2 \)-type basis sets. In order to enable the treatment of resonances within the \( L^2 \)-quantum chemical framework, several approaches have been
developed [6], such as stabilization techniques [7-9], complex scaling techniques [10-15] and complex absorbing potential (CAP) methods [16-19].

In recent years, CAP methods have been developing particularly dynamically, and a number of computational schemes combining the CAP formalism with various electronic structure approaches for the treatment of electron attachment processes were proposed. Ehara and Sommerfeld have introduced a CAP into the symmetry-adapted cluster-configuration interaction (SAC-CI) method [20-22]. Successful efforts of obtaining the CAP-augmented equation-of-motion (EOM) coupled-cluster (CC) methods were reported by the group of Pal [23-25]. A similar strategy was pursued by the group of Krylov [26-29], which led to the development of the CAP/EOM-EA-CC family of methods for the treatment of metastable electron-attached states. Recently, Bravaya and co-workers [30] proposed a new method combining the extended multiconfigurational quasidegenerate perturbation theory with complex absorbing potential technique (CAP-XMCQDPT2).

The characteristics of EA processes can directly be evaluated within the framework of the one-particle Green's function (or electron propagator) theory [31, 32]. Here, one of the most useful schemes is the third-order algebraic-diagrammatic construction approximation (ADC(3)) exploiting the Dyson equation [33, 34]. Although the CAP version of this method was developed and tested [18, 35, 36], it did not become a practical tool for calculations of resonances owing to difficulties in an efficient implementation, caused by the coupling of the $(N+1)$- and $(N−1)$-parts of the one-particle Green's function due to the Dyson equation.

Subsequently, the ADC approach with the decoupled $(N+1)$- and $(N−1)$-parts of the Green's function was proposed within the so-called non-Dyson (nD) framework, giving rise to separate EA-ADC and IP (ionization potential)-ADC schemes [37]. As is presently well known, the nD-ADC methods can be derived using both algebraic-diagrammatic [37] and various purely algebraic approaches [38-41], including the intermediate state representation (ISR) formalism [38]. The latter formalism is particularly useful in the present context, since it offers also an elegant way of introducing additional one-particle operators into the nD-ADC schemes, like, e.g., the CAP operator. Whereas the EA-ADC(3) method was earlier implemented [40-42], no CAP extension for it was available so far. In this work, we report the first implementation of several such CAP/EA-ADC computational schemes and evaluate their performance in comparison with experimental data and some other theoretical results using the low-lying resonances of the $N_2^−$ and $CO^−$ anions as example.

2. Theory
As follows from theory of resonances [15, 43], a resonance state can be treated as a bound state with the complex Siegert energy

$$E = E_R − i \frac{Γ}{2}$$

(1)

where $E_R$ denotes the resonance position and $Γ$ characterizes the width of the resonance (or its lifetime, $τ = h/Γ$). The energy form of Eq. (1) implies that resonances decay with time, which can be also seen from the expression describing time-dependence of the wavefunction

$$Ψ(r, t) = e^{−i(E_R)t} e^{−(Γ/2)t}Ψ(r)$$

(2)

When this type of formalism is employed, the Siegert energies are found as eigenvalues of specific non-Hermitian Hamiltonians [15, 43]. In CAP methods, such Hamiltonians are constructed by inclusion of an appropriate one-particle CAP operators $−iW$ into the original Hamiltonians $H$, which absorb the diverging part of the wavefunctions, making them $L^2$-integrable.
\[
\hat{H}' = \hat{H} - i\eta \hat{W}
\]  
(3)

Here, the quantity \( \eta \) is referred to as CAP strength parameter. Most often (and in the present work), the potential \( \hat{W} \) is chosen in such a way that it is zero within the domain where the principle part of the molecular wavefunction resides, but grows quadratically beginning at some offset \( d_\alpha \) beyond this region

\[
\hat{W} = \sum_{\alpha=x,y,z} \hat{W}_\alpha, \quad \hat{W}_\alpha = \begin{cases} 
0, & |r_\alpha| \leq d_\alpha \\
(|r_\alpha| - d_\alpha)^2, & |r_\alpha| > d_\alpha
\end{cases}
\]  
(4)

In theory, the resonance energy is obtained in the limit \( \eta \to 0 \). In practice, the conventional way of identifying \( E_R \) and \( \Gamma \), however, is based on the analysis of \( \eta \)-trajectories of the \( \hat{H}'(\eta) \) eigenvalues, \( E(\eta) \) [17]. Here, it is exploited that the energy of the resonance state stabilizes as the optimal \( \eta \)-value is approached. In this region, the trajectories slow down, and its logarithmic velocity, \( v(\eta) = \eta dE(\eta)/d\eta \), has a minimum. The best approximation for the resonance energy is \( E(\eta) \) at this minimum [17, 20].

In the EA-ADC method, the electron attachment energies are obtained as the solutions of the Hermitian secular equation

\[
\mathbf{MY} = \mathbf{Y}\Omega, \quad \mathbf{Y}^\dagger\mathbf{Y} = \mathbf{1}
\]  
(5)

The vertical EA energies are elements of the diagonal eigenvalue matrix \( \Omega \). The “effective interaction” matrix \( \mathbf{M} \) in Eq. (5) is most easily explained using the ISR extension [38, 39] of the ADC formalism [37]. In the ISR approach, the \( \mathbf{M} \) matrix is defined as a representation of the shifted Hamiltonian operator \( (\hat{H} - E_0^N) \) within the basis of the \((N+1)\)-electron intermediate states (IS), \( |\tilde{\Psi}_1^{N+1}\rangle \)

\[
M_{IJ} = \langle \tilde{\Psi}_I^{N+1} | (\hat{H} - E_0^N) | \tilde{\Psi}_J^{N+1}\rangle
\]  
(6)

where \( E_0^N \) denotes the \( N \)-electron ground-state energy.

The IS in Eq. (6) are specifically constructed \((N+1)\)-electron states, that allow for a hierarchy of systematic approximations to be formulated (ranged by the order of perturbation theory treating the residual electronic interaction beyond the Hartree-Fock model). The IS are obtained by means of Gram-Schmidt orthogonalization of the correlated excited states (CES)

\[
|\Psi_0^{N+1}\rangle = \tilde{C}_J |\Psi_0^N\rangle
\]  
(7)

More specifically, various CES classes (comprising one-particle \((1p)\), two-particle-one-hole \((2p-1h)\), ... states) are generated by acting with an excitation operator \( \tilde{C}_J \) on the \( N \)-electron ground state \( |\Psi_0^N\rangle \), and then orthogonalized with respect to each other to obtain the IS.

In order to incorporate the CAP operator into the EA-ADC approach, the Hamiltonian \( \hat{H}' \) of Eq. (3) has to be substituted for the Hamiltonian \( \hat{H} \) in Eq. (6). This yields modified matrix \( \mathbf{M}' \), defined according to

\[
M_{IJ}' = \langle \tilde{\Psi}_I^{N+1} | (\hat{H} - i\eta \hat{W} - E_0^N) | \tilde{\Psi}_J^{N+1}\rangle = M_{IJ} - i\eta \langle \tilde{\Psi}_I^{N+1} | \hat{W} | \tilde{\Psi}_J^{N+1}\rangle
\]  
(8)

The modified matrix \( \mathbf{M}' \) includes the CAP in the form of the matrix element.
\[ W_{ij} = \langle \hat{\Psi}^{N+1}_i | \hat{W} | \hat{\Psi}^{N+1}_j \rangle \]  

(9)

where the one-particle operator \( \hat{W} \) is represented with respect to the IS.

In the CAP/EA-ADC approach, the additional matrix quantity \( W \) defined by Eq. (9) has to be evaluated and added to the original EA-ADC secular matrix \( \mathbf{M} \) (\( \mathbf{M} = \mathbf{M} - i\eta \mathbf{W} \)). As a result, the Hermitian eigenvalue problem, given by Eq. (5), transforms to a non-Hermitian eigenvalue problem for the complex matrix \( \mathbf{M}' \). The latter represents a technically challenging step in view of its typically very large dimension and that special versions of the Davidson and Lanczos algorithms have to be used for the diagonalization of these large complex matrices.

A computationally more attractive approach in such situations consists in resorting to the subspace projection technique [18]. In this method, the matrix \( \mathbf{M}' \) is projected onto the subspace of selected eigenvectors \( \{ \mathbf{Y}_n \} \) of the matrix \( \mathbf{M} \). If the CAP operator is considered as perturbation, the described technique is similar to a first-order perturbative approach to the perturbed eigenvalue problem of \( \mathbf{M}' \). The projected \( \mathbf{M}' \) matrix takes on the following form

\[ \mathbf{\tilde{M}}' = \mathbf{Y}^\dagger \mathbf{M}' \mathbf{Y} = \Omega - i\eta \mathbf{Y}^\dagger \mathbf{W} \mathbf{Y} \]  

(10)

where \( \Omega \) denotes the diagonal eigenvalue matrix associated with the unperturbed EA-ADC approach.

The formation of \( \mathbf{\tilde{M}}' \) requires only modest computational effort, provided the set \( \{ \mathbf{Y}_n \} \) is not too large. In addition, the latter is well justified, since the previous experience with similar problems [18] indicated that a relatively small number of eigenvectors is sufficient for obtaining results that are well converged with respect to the solutions of the unprojected problem. The resulting dimension of the \( \mathbf{\tilde{M}}' \) matrix can therefore be kept relatively small, so that the matrix can be diagonalized in the RAM memory of a computer still using standard well-optimized routines for diagonalization of complex matrices. This circumstance is especially important in view of the necessity for repeated construction and diagonalization of \( \mathbf{\tilde{M}}' \) in course of the computation of the \( \eta \)-trajectories. The eigenvalues \( \Omega' \) obtained at each \( \eta \) point from the solution of the projected equation

\[ \mathbf{\tilde{M}}' \mathbf{Z} = \Omega' \mathbf{Z} \]  

(11)

have the meaning of the complex Siegert energies (Eq. (1)) of electron-attached states minus the energy of the \( N \)-electron ground state.

The approximate EA-ADC schemes, also referred to as EA-ADC(\( n \)) methods, are obtained by expanding \( E_0^N \) and \( |\hat{\Psi}^N_0\rangle \) in Eqs. (6) and (7) in series through order \( n \) of the ground-state Møller-Plesset perturbation theory (PT). The space of the IS for the representation of \( \mathbf{M} \) is then truncated in such a way that only a minimal number of excitation classes required for a consistent \( n \)-th order treatment of the single-electron attached states is retained. The perturbative treatment of the elements within the blocks of \( \mathbf{M} \) between various IS classes is also adjusted accordingly, so that in each block only the minimal required PT order is employed. Such a construction procedure provides the most compact IS expansion spaces for \( \mathbf{M} \) and the minimal possible scaling of the computational effort required for consistent \( n \)-th order treatment of EA properties within the lowest excitation class. Besides this so-called compactness property, the IS-based computational ADC schemes possess also such desirable properties for quantum chemical calculations like regularity and size consistency [31, 38, 39].

The most accurate computational scheme used in the present work, EA-ADC(3) [37], involves the \( p \) and \( 2p-1h \) classes of IS and is characterized by computational efforts that scale as \( n^5 \) with the number of the molecular orbitals \( n \). This is the best ratio between PT-theoretical
accuracy and computational effort available for electronic structure methods presently used for studies of EA processes.

ISR approximation schemes for the treatment of the one-particle operators (Eq. (9)), also referred to as ISR(0) methods, are obtained in a closely analogous way to the one described above using the IS-framework. In the present work, the ISR(2) equations [39] were rederived and implemented [42] for use in the CAP/EA-ADC calculations. The best level of theory presently available, EA-ADC(3)/ISR(2), treats CAP consistently through second order of PT, which implies a consistent second-order treatment of the resulting Siegert energies. The computational effort in the EA-ADC(3)/ISR(2) scheme scales as \( n^5 \) for a single step along the \( \eta \) -trajectory.

3. Computational details of the CAP/EA-ADC calculations

The calculations of the \( ^3I_g \) resonance of \( \text{N}_2^- \) and the \( ^3I \) resonance of \( \text{CO}^- \) were performed using the same geometrical parameters as in the CAP/EOM-CCSD calculations of these systems [26], where the equilibrium ground-state bond lengths of the neutral \( \text{N}_2 \) and \( \text{CO} \) molecules (1.0975 and 1.128Å, respectively) [44] were adopted. The aug-cc-pVDZ and aug-cc-pVTZ basis sets were used in the calculations [45-47], augmented by three diffuse \( s \) and \( p \) functions with the same exponents as in Ref. [26]. Cartesian representation of the \( d \) basis functions was employed. The \( d_x, d_y \), and \( d_z \) parameters in Eq. (4), defining the “CAP box”, were chosen to be 2.5, 2.5, and 3.5 a.u., respectively, in the case of \( \text{N}_2^- \), and 2.0, 2.0, and 5.0 a.u., respectively, in the case of \( \text{CO}^- \). The dimension of the projection subspace was 200. This dimension was found to be sufficient for obtaining convergent results for the problems considered in the present work, based on the series of preliminary calculation. The \( \eta \) parameter varied from \( 10^{-8} \) to \( 10^{-1} \) a.u. in exponentially increasing steps. All calculations were performed using the original EA-ADC/ISR code interfaced to the GAMESS program [48]. The code was developed independently from and in parallel with the local Q-Chem [49] implementation of the same method [42], and the two implementations were verified against each other. In all calculations the CAP was treated at the (presently maximal) ISR(2) level theory, whereas the ADC schemes [37, 39] of the strict second order, extended second order, and third order (EA-ADC(2), EA-ADC(2)x, and EA-ADC(3), respectively) were employed.

| Method       | \( \text{EA}_R \) (eV) | \( \Gamma \) (eV) | \( \eta_{\text{opt}} \) (a.u.) |
|--------------|------------------------|----------------|---------------------------------|
| CAP/EA-ADC(2)| 2.78                   | 0.41           | 0.0050                          |
| CAP/EA-ADC(2)x| 2.37                   | 0.36           | 0.0038                          |
| CAP/EA-ADC(3)| 2.54                   | 0.40           | 0.0042                          |
| Expt.\(^a\) | 2.32                   | 0.41           |                                 |

\(^a\) Experimental data [50] as cited in Ref. [26].

4. Results and discussions

The low-lying \( \eta \)\(^*\) resonances of \( \text{N}_2^- \) and \( \text{CO}^- \) belong to the most well-studied metastable anionic states. This makes them convenient test systems for the evaluation of any new electronic structure method for computations of resonances [27]. Our CAP/EA-ADC results for the \( ^3I_g \) resonance of \( \text{N}_2^- \) are shown in tables 1 and 2. The results for the \( ^3I \) resonance of \( \text{CO}^- \) are given in table 3. In figure 1, exemplary \( \eta \)-trajectories are presented. The complex resonance energies
are discussed in terms of the resonance positions represented by the EA energies, $E_{A_R}$, and widths, $\Gamma$, as obtained from the eigenvalues of Eq. (11), $\Omega'_{nn} = (E_{A_R} - i \Gamma/2)_n$.

As mentioned above, it can be expected that the level of the electronic structure treatment (account of the electron correlation effects) is one of the most important factors for obtaining reliable results for systems with an excess electron. In this regard, we study the dependence of the calculated resonance parameters on the level of the EA-ADC scheme using the $^2\Pi_g$ resonance of $N_2^-$ as an example in Table 1. More specifically, the EA-ADC(2), EA-ADC(2)x, and EA-ADC(3) schemes are compared. The experimental data [26, 50] serves as reference. The $\eta$-trajectories obtained at each of the compared CAP/EA-ADC levels of theory are shown in Figure 1a.

![Figure 1](image.png)

**Figure 1.** $\eta$-trajectories of the $^2\Pi_g$ resonance of $N_2^-$ calculated using CAP/EA-ADC(2), CAP/EA-ADC(2)x, and CAP/EA-ADC(3) schemes (shown in green, blue, and red color, respectively) with the aug-cc-pVDZ+3s3p basis set (a); $\eta$-trajectory of the $^2\Pi$ resonance of CO$^-$ calculated using CAP/EA-ADC(3) scheme with the aug-cc-pVTZ+3s3p basis set (b).

As can be seen from the presented data, good agreement with experiment is achieved at the level of the CAP/EA-ADC(3) and CAP/EA-ADC(2)x schemes with respect to resonance positions and widths. Nearly excellent agreement with experiment is obtained at the EA-ADC(2)x level for the resonance position. While this result is of course somewhat fortuitous, the deviation from the experimental value of $\sim 0.2$ eV observed at the level of the EA-ADC(3) scheme looks more realistic. The resonance width appears to be much less dependent on the level of the EA-ADC scheme and in all cases agrees very well with the experimental value.

In Table 2 the CAP/EA-ADC(3) results for the two basis sets, aug-cc-pVDZ+3s3p and aug-cc-pVTZ+3s3p, are compared. As can be seen, the basis set extension from the double-zeta to triple-zeta level considerably improves the resonance position, but has nearly no influence on the resonance width. Since both basis sets are augmented by reasonably large diffuse parts, the widths could be already sufficiently converged and do no longer respond to an improvement of the basis.

Table 2 shows also the results of the CAP/EOM-EA-CCSD calculations [26] performed with the cc-pVTZ+3s3p basis set. This calculation yields a somewhat less accurate estimate for the
resonance position but virtually the same resonance width as in our calculations. Here it has to be noted that the CAP/EOM-EA-CCSD results [26] shown in table 2 are obtained using the same set of CAP parameters and refer to the same (logarithmic velocity-based) approach for the identification of the resonance energy. The results obtained in Ref. [26] using first-order corrections and corrected trajectories are not shown, since they would make our comparison less strict. On the other hand, a rigorous comparison of the two sets of results is highly desirable in the present context, since we compare here two theoretically similar methods (EA-ADC(3) and EOM-EA-CCSD) and expect that their results would show pronounced similarities. This is indeed the case, as is well demonstrated by the data in table 2.

Table 2. Resonance positions $E_R$ (eV) and widths $\Gamma$ (eV) as well as the optimal CAP strength parameter $\eta_{opt}$ (a.u.) for the $^3\Pi_g$ resonance of N$_2^+$ computed using the CAP/EA-ADC(3) method with the aug-cc-pVDZ+3s3p and aug-cc-pVTZ+3s3p basis sets in comparison with CAP/EOM-EA-CCSD/aug-cc-pVTZ+3s3p and experimental data.

| Method                        | $E_R$   | $\Gamma$ | $\eta_{opt}$ |
|-------------------------------|---------|----------|--------------|
| CAP/EA-ADC(3)/aug-cc-pVDZ+3s3p| 2.54    | 0.40     | 0.0042       |
| CAP/EA-ADC(3)/aug-cc-pVTZ+3s3p| 2.35    | 0.35     | 0.0034       |
| CAP/EOM-EA-CCSD/aug-cc-pVTZ+3s3p | 2.61 | 0.40     | 0.0040       |
| Expt.                        | 2.32    | 0.41     |              |

$^a$ Uncorrected result evaluated from the original $\eta$-trajectory [26].

$^b$ Experimental data [50] as cited in Ref. [26].

Table 3. Resonance positions $E_R$ (eV) and widths $\Gamma$ (eV) as well as the optimal CAP strength parameter $\eta_{opt}$ (a.u.) for the $^2\Pi$ resonance of CO$^+$ computed using CAP/EA-ADC(3) method in comparison with the CAP/EOM-EA-CCSD and experimental data. All theoretical results are obtained using aug-cc-pVTZ+3s3p basis set.

| Method                        | $E_R$   | $\Gamma$ | $\eta_{opt}$ |
|-------------------------------|---------|----------|--------------|
| CAP/EA-ADC(3)                | 1.95    | 0.63     | 0.0020       |
| CAP/EOM-EA-CCSD              | 2.14    | 0.69     |              |
| Expt.                        | 1.50$^b$| 0.40$^b$, 0.75$^c$, 0.80$^d$ | 0.0020 |

$^a$ Uncorrected result evaluated from the original $\eta$-trajectory [26].

$^b$ Experimental data [51] as cited in Refs. [26, 27].

$^c$ Experimental data [52] as cited in Ref. [53].

$^d$ Experimental data [54] as cited in Ref. [53].

In the case of the $^2\Pi$ resonance of CO$^+$ (table 3) the CAP/EA-ADC(3) results obtained with the aug-cc-pVTZ+3s3p basis set differ from the experimental data somewhat stronger than in the case of the $^3\Pi_g$ resonance of N$_2^+$. Our calculations predict the resonance position at 1.95 eV, which overestimates the experimental result by ~0.45 eV. Similar problems can be seen in the CAP/EOM-EA-CCSD calculations, which predict an $E_R$ value of 2.14 eV. Both theoretical methods predict similar resonance widths (0.63 and 0.69 eV, respectively), which belong to the range of the reported experimental estimates 0.40-0.80 eV [49-52], but do not agree well enough with any of the individual values (table 3). Since the situation does not improve considerably in the corrected CAP/EOM-EA-CCSD calculations which use also larger basis sets [27], the actual problem may be on the side of the experiment, since the derivation of resonance characteristics from molecular measurements is a challenging task, complicated in particular by nuclear dynamics [27].
5. Conclusions

The non-Dyson algebraic-diagrammatic construction approach [37] for the treatment of electron attachment processes (EA-ADC) is extended to include complex absorbing potentials (CAP) [16-19]. The resulting CAP/EA-ADC methods allow metastable (resonances) states with an attached electron to be studied on the same footing as the bound states using $L^2$-integrable basis sets.

The implemented CAP/EA-ADC approximations comprise second- and third-order schemes (EA-ADC(2), EA-ADC(2)x, and EA-ADC(3)). The CAP operator is incorporated into the EA-ADC Hamiltonian using the intermediate state representation (ISR) formalism [38] and is treated at the level of the second-order perturbation theory (ISR(2)) [39]. Whereas the EA-ADC secular equations are solved for the required number of eigenstates using a conventional large-matrix diagonalization approach, the CAP/EA-ADC eigenvalue problem is projected onto the subspace of selected EA-ADC eigenvectors to facilitate solution and evaluation of the $\eta$ -trajectories. The standard approach [17, 20] to resonance energies, based on the location of a minimum of the logarithmic velocity, $v(\eta) = [\eta dE(\eta)/d\eta]$, has been employed.

The implemented CAP/EA-ADC methods were evaluated in first applications to the low-lying $\pi^*$ resonances of CO and N$_2$ molecules, which serve de facto as mandatory test systems for all new electronic structure methods for metastable states. The results of the calculations demonstrate – though yet without sufficient statistics – that fully functional computational schemes have been obtained. The computed resonance characteristics are in reasonable agreement with available experimental data. Moreover, as expected, the present CAP/EA-ADC(3) results agree with the results of the CAP/EOM-EA-CCSD method which represents a closely related approach of an approximately similar theoretical level. The CAP/EA-ADC results are seen to improve as the level of the theoretical treatment is increased and as the basis set is extended.

Thus, a rather satisfactory and consistent picture characterizing the performance of the CAP/EA-ADC schemes was obtained indicating that the CAP-augmented EA-ADC modeling has clear prospects to become a useful tool for theoretical studies of metastable electron-attached states. Further development of the EA-ADC approach directed to the improvement of its numerical performance is under way. Particular efforts are also made in the directions, previously pursued in Refs. [26, 27], of making CAP calculations a robust black-box type methodology, accessible to a wide audience and routinely applicable in practical quantum chemical calculations.

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