Extending Quantum Chemistry of Bound States to Electronic Resonances

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Abstract

Electronic resonances are metastable states with finite lifetime embedded in the ionization or detachment continuum. They are ubiquitous in chemistry, physics, and biology. Resonances play a central role in processes as diverse as DNA radiolysis, plasmonic catalysis, and attosecond spectroscopy. This review describes novel equation-of-motion coupled-cluster (EOM-CC) methods designed to treat resonances and bound states on an equal footing. Built on complex-variable techniques such as complex scaling and complex absorbing potentials that allow resonances to be associated with a single eigenstate of the molecular Hamiltonian rather than several continuum eigenstates, these methods extend electronic-structure tools developed for bound states to electronic resonances. Selected examples emphasize the formal advantages as well as the numerical accuracy of EOM-CC in the treatment of electronic resonances. Connections to experimental observables such as spectra and cross sections, as well as practical aspects of implementing complex-valued approaches, are also discussed.

Keywords

metastable states, temporary anions, complex scaling, complex absorbing potentials, equation-of-motion coupled-cluster
1. INTRODUCTION: WHAT IS A RESONANCE?

Resonances are nonstationary states of systems that have sufficient energy to break up into subsystems and sufficiently long lifetimes to be characterized experimentally (1–3), which implies that the decay process is long compared to the timescale of an observation. Depending on the nature of the resonance, timescales vary from femtoseconds (autoionization) to billions of years (radioactive nuclear decay). In the context of chemical dynamics, picosecond lifetimes are most common (molecular predissociation, predesorption from surfaces, etc). The focus of this review is on electronic resonances—metastable electronic states embedded in the ionization or electron-detachment continua (see Figure 1).

Electronic resonances play important roles in nature, science, and technology. They are common in energetic environments, such as plasma, which is generated in electric arcs, supersonic combustion, fusion reactors and stars, plasma displays, extremely hot flames, lightning, polar aurorae, etc. Dissociative recombination via autoionizing states is important in interstellar chemistry (4). Resonances are also involved in condensed-phase processes, e.g., in radiolysis and damage to DNA by slow electrons (5, 6), single-molecule electronics (7), and plasmonic catalysis (8, 9) (see the sidebar titled Plasmonic Catalysis). A new wave of interest in autoionizing states has been

![Figure 1](image_url)

**Figure 1**

Resonances are metastable states with finite lifetimes embedded in the continuum. Different types of electronic resonances include temporary anions (species with negative electron affinity) (a), high-lying excited electronic states (b), and core-ionized states (c).

PLASMONIC CATALYSIS

A temporary electron capture into a metastable electronic state can initiate diverse and complex chemistry in isolated molecules and in condensed phase. This phenomenon provides a basis for plasmonic photocatalysis (8, 9), photocatalytic conversions on the surface of plasmonic metal nanoparticles. Owing to their collective excitation nature, plasmons have large cross sections for light absorption and act as antennas. The subsequent relaxation of surface plasmon resonance can release energy by producing ballistic or hot electrons, which can be trapped by molecules absorbed on the surface. The resulting transient negative ions can further decay via electron ejection into the vacuum and into the metal, or undergo chemical transformations. As electron attachment changes the bonding pattern of a molecule, it opens up new reaction pathways, which can be exploited in catalytic applications. Depending on the topology of the potential energy surface of the transient negative ion and its lifetime, reactions can be initiated by one electron transfer (linear regime) or via multiple electron transfer-recombination events (super-linear regime) (8).
Figure 2
Excitation ($S_1$) and detachment ($D_0$, $D_n$) energies in eV for model chromophores of the photoactive yellow protein (PYP) in the phenolate and carboxylate forms (14). (a) The excited state of the phenolate form is a shape resonance. Electron detachment from $S_1$ to the lowest detachment continuum is a Koopmans-allowed one-electron transition: $\pi^1(\pi^*)^1 \rightarrow \pi^1(\pi^*)^0 + e^-$. (b) The excited state of the carboxylate form, in which electron detachment from $S_1$ to $D_0$ is a Koopmans-forbidden two-electron process $[n^2\pi^1(\pi^*)^1 \rightarrow n^1\pi^1(\pi^*)^0 + e^-]$, is a Feshbach resonance. Figure adapted from Reference 15 with permission. Copyright 2013 AIP.

Metastable electronic states can be classified as either shape or Feshbach resonances (see Figure 2). Shape resonances decay by a one-electron process (16). Examples include radical anions such as electron-attached states of $N_2$, $CO$, and $CO_2$, as well as some excited states of closed-shell species. Autoionization of the electronically excited phenolate form of the photoactive yellow protein (PYP) chromophore shown in Figure 2a illustrates the behavior of a shape resonance. In contrast, Feshbach resonances decay to the continuum via two-electron transitions. Consider, for example, the decay of the carboxylate form of the PYP chromophore (see Figure 2b): This is a Koopmans-forbidden process governed by electron correlation. Polyatomic molecules often feature both types of resonances, as illustrated in a recent theoretical study of the $p$-benzoquinone anion (17). Core-ionized states are Feshbach resonances; their Auger decay, in which one electron relaxes to fill the core hole while another is ejected from a higher molecular orbital, is a two-electron process. Yet another group of Feshbach resonances comprises states of high multiplicity such as quartet states of $N_2^-$ (18), whose decay is spin-forbidden. In general, Feshbach resonances are longer-lived than shape resonances.

Resonances belong to the continuum and can be described as nonstationary solutions of the time-dependent Schrödinger equation (19, 20), as stationary exponentially diverging solutions of the time-independent Schrödinger equation (3, 21, 22), or via extrapolation of finite basis set calculations, such as stabilization (23, 24) and Stieltjes–Tchébycheff techniques (25). In Hermitian quantum mechanics, the resonance cannot be associated with a single state; rather, it is manifested by an increased density of states in the continuum. To illustrate this point, consider Dyson orbitals...
Dyson orbitals for the six lowest-lying solutions of $^2\Pi_g$ symmetry in $\text{N}_2 + e^-$ computed by EOM-EA-CCSD/aug-cc-pVTZ+$6s6p6d(C)$ at $R_{NN} = 1.1$ Å and ordered by increasing energy from left to right. To the right of the dashed line, the Dyson orbital of the bound $^2\Pi_g$ state of $\text{N}_2^-$ at $R_{NN} = 1.6$ Å is shown. The orbitals are plotted at an isovalue of 0.004. Figure adapted from Reference 26 with permission. Copyright 2016 AIP.

**Figure 3**

Dyson orbital: orbital concept for correlated many-electron wave functions; characterizes ionization or electron attachment

Analytic continuation: mathematical technique to extend the domain of a function (here, the Hamiltonian) to the complex plane

Complex scaling (CS): transformation of the coordinates by $r \rightarrow re^{i\theta}$, leading to a Hamiltonian with the same bound spectrum, rotated continua, and exposed resonances

Complex absorbing potential (CAP): artificial imaginary potential added to the Hamiltonian to absorb an outgoing wave packet or a diverging tail of the wave function

for $\text{N}_2 + e^-$ computed at the equilibrium bond distance of $\text{N}_2$ using standard quantum chemistry. They are displayed in Figure 3, together with the Dyson orbital of bound $\text{N}_2^-$ with a stretched bond. The orbital at the stretched geometry is a regular $\pi^*$ orbital, whereas the orbitals at the equilibrium structure are pseudocontinuum states in which the excess electron is not bound. When represented in a complete basis, the spectrum of the Hamiltonian becomes continuous, the attachment energy approaches zero, and the orbitals on the left of Figure 3 become plane waves.

In contrast to the Hermitian approach, in non-Hermitian quantum mechanics, resonances can be described as single states and without explicit treatment of the continuum (3). The family of methods grounded in this framework is the focus of this review. How can one describe the transient nature of resonances in the non-Hermitian formulation? The key concept is complex energy. Its meaning is revealed by solving the Schrödinger equation for the standard molecular Hamiltonian with outgoing boundary conditions (2, 3, 22, 27), which gives rise to a non-Hermitian eigenproblem from which the resonance is obtained as a solution with complex eigenvalue

$$E_{\text{res}} = E_R - i\Gamma/2,$$

where $E_R$ is the resonance position and $\Gamma$ is the resonance width. The latter is related to the lifetime $\tau$ through $\Gamma = 1/\tau$ (1, 3, 21, 28). This so-called Siegert representation captures the essential physics of the problem; the resonance is similar to a bound state with $E = E_R$ in the interaction region, i.e., close to the molecular core, but exponentially diverging outside. Owing to the imaginary part of its energy, $-\Gamma/2$, it eventually leaks out of the interaction region. The same physics is revealed by an alternative derivation based on a diabatic representation (29). In this so-called Feshbach formalism, resonances are described as bound states coupled to the continuum. By applying Löwdin’s partitioning technique, one arrives at a non-Hermitian effective Hamiltonian (30) whose solutions are associated with complex eigenvalues as in Equation 1. In addition to its conceptual simplicity, i.e., representation of the resonance as a single state, the non-Hermitian approach provides a simple recipe for extending quantum-chemistry methods developed for bound states to resonances. By analytic continuation of the Hamiltonian to the complex plane via complex scaling (CS) (1, 2, 31–33) or complex absorbing potentials (CAPs) (34, 35), resonances are obtained as square-integrable eigenfunctions of a modified non-Hermitian Hamiltonian without changing boundary conditions, and the corresponding eigenvalues obey Equation 1.

Although the basic ideas behind such complex-valued approaches were introduced long ago (31, 32, 35–39), extensive testing of their performance had been lacking, as these methods had not been implemented within advanced electronic-structure approaches. Only a handful of studies reported high-level results for few-electron systems (e.g., 40). Consequently, prior to very recent
When combined with the complex scaling (CS) or complex absorbing potentials (CAPs) technique, EOM-CC methods can describe resonances as $L^2$-integrable states with complex energies in a basis of standard Gaussian functions. Owing to the versatility of the EOM-CC approach, such complex-valued EOM-CC methods can treat different types of resonances. Clockwise from top right: EOM-EA can tackle electron-attached states, such as temporary anions or excited states of stable anions; EOM-IP and EOM-DIP are appropriate for core-ionized states, whereas EOM-EE can describe highly excited states of closed-shell systems. Importantly, these methods describe resonances and bound states on the same footing and are capable of treating interactions between states of different character.

Developments in this area, it was hard to disentangle the limitations of the complex-variable techniques from the limitations resulting from an insufficient level of correlation treatment or from too-small one-electron basis sets. The choice of the underlying electronic structure method is crucially important for obtaining physically meaningful results for molecular resonances. The central requirement is to locate the continuum onsets correctly and to describe multiple states of different nature on an equal footing. As illustrated in Figure 4 and discussed in Section 2, the equation-of-motion coupled-cluster (EOM-CC) formalism (41–44) satisfies these requirements and provides an excellent platform for treating resonances, whereas many other advanced methods do not, which leads to serious practical limitations.

$L^2$-based theoretical approaches to resonances and earlier computer implementations have been extensively reviewed (1–3, 21, 45–47). CS and CAP techniques have been applied to various ab initio methods, ranging from Hartree–Fock (HF) and multiconfigurational self-consistent field (MCSCF) methods (48–53) to configuration interaction (CI), coupled-cluster (CC), and...
algebraic diagrammatic construction (ADC) approaches (50, 54–58). Recently, a production-level implementation of CS and CAPs within the EOM-CC suite of methods has been presented by us (15, 59–61). In this review, we focus on these complex-valued EOM-CC methods designed to treat resonances and bound states on an equal footing. In addition to discussing formalism and implementation, we also consider practical aspects of calculations with complex-valued methods such as the evaluation of molecular properties, the interpretation of resonance wave functions, and the connection of theoretical results to experiment.

2. REQUIREMENTS FOR ELECTRONIC STRUCTURE METHODS

2.1. Equation-of-Motion Coupled-Cluster Framework: A Versatile Approach for Open-Shell and Electronically Excited Bound States

For bound states, the CC and EOM-CC approaches (42–44) provide a reliable and predictive set of theoretical model chemistries (62). These methods can be systematically improved to approach the exact solution, are size-extensive (or size-intensive for excitation energies), describe dynamical and nondynamical correlation in one computational step, and do not involve system-dependent parameterization. Whereas the CC hierarchy of methods works best for wave functions dominated by a single Slater determinant, the EOM-CC approach extends this single-reference formalism to tackle various open-shell and multiconfigurational cases (41, 42). The EOM-CC wave function for target state \( \ket{k} \) is described by an excitation operator \( \mathcal{R}^k \) acting on the reference-state CC wave function, \( \ket{\Phi_\mu} = \mathcal{R}^k e^T \ket{\Phi_0} \), with \( \Phi_0 \) as the reference Slater determinant usually satisfying the HF equations and \( T \) as the cluster operator. Different choices of \( R \) provide access to different target states (Figure 4). In EOM-EE-CC (EOM-CC for excitation energies), \( R \) is electron- and spin-conserving, thus enabling the description of excited states. Open-shell electron-attached states such as doublet anion radicals can be described by EOM-EA-CC [EOM-CC for electron affinities (EAs)], in which the reference state is again a well-behaved closed-shell state and the operator \( R \) changes the number of electrons. Likewise, ionized states can be described by EOM-IP-CC [EOM-CC for ionization potentials (IPs)], with the operator \( R \) removing an electron. Thus, EOM-CC is a natural choice for extending the many-body methodology to resonances via the CS and CAP approaches.

The working equations for the amplitudes in \( R \) and \( L \) are derived by applying the bivariational principle (42), giving rise to a non-Hermitian eigenproblem:

\[
\mathcal{H} \ket{R^k} = E_k \ket{R^k} \quad \text{and} \quad \bra{L^\dagger} \mathcal{H} = E_k \bra{L^\dagger},
\]

where \( \mathcal{H} \) is the similarity-transformed Hamiltonian, \( \mathcal{H} = e^{-T} H e^T \), and \( \ket{R^k} \equiv R^k \ket{\Phi_0} \) and \( \bra{L^\dagger} \equiv \bra{\Phi_0} L^\dagger \) denote right and left EOM states forming a biorthogonal set (\( \bra{L^\dagger} \ket{R^k} = \delta_{k0} \)). The amplitudes in the operator \( T \) used to construct \( \mathcal{H} \) are usually obtained by solving the CC equations for the reference state \( \ket{\Phi_0} \), \( \bra{\Phi_\mu} \mathcal{H} - E_k \ket{\Phi_0} = 0 \) for all \( \mu \), where \( \Phi_\mu \) denotes the excited determinants. Regardless of the choice of \( T \), \( \mathcal{H} \) has the same spectrum as the original Hamiltonian \( H \) because the similarity transformation is bounded. To avoid factorial scaling of computational costs, it is necessary to truncate the excitation manifold, e.g., \( \mu = 1, 2 \) for the CCSD (coupled-cluster with single and double substitutions) method in which \( T_1 = T_1 + T_2 \). The operators \( R \) and \( L \) are usually subject to the same truncation level as \( T \). As a less computationally expensive alternative to EOM-CCSD, \( T_1 \) amplitudes from a second-order Møller–Plesset (MP2) perturbation theory calculation can be used to construct \( \mathcal{H} \), giving rise to the EOM-MP2 family of methods (63).
Owing to its linear parameterization, the EOM-CC method is capable of describing wave functions that include multiple interacting electronic configurations of different character (e.g., Rydberg and valence, covalent and ionic, etc). No assumptions about their relative weights are made by the user; rather, they are obtained from the well-defined eigenproblem, Equation 2. These equations are solved by using the iterative diagonalization Davidson procedure (64) adapted to nonsymmetric matrices (65, 66). Traditionally, the Davidson method is applied to solve for one or several lowest eigenstates; however, the algorithm can be extended to interior eigenstates (67). For energies, it is sufficient to solve either the right or the left eigenproblem; however, if molecular properties are desired, one needs to solve both.

The availability of property calculations is critically important for applications. The elegant formalism of EOM-CC facilitates the computation of properties, e.g., analytic gradients (68), permanent and transition dipole moments (69), two-photon absorption cross sections (70), spin-orbit couplings (71), and more (44). Owing to electron indistinguishability, only one-electron and two-electron reduced density matrices are needed for the calculation of expectation values and transition matrix elements of typical operators. One-electron properties—for example, the permanent dipole moment $\mu$ and the spatial extent of the wave function $R$—can be computed from the one-electron reduced density matrix $\gamma$ (Equation 2) connecting the two states $\Psi_i$ and $\Psi_F$. The exact expressions for $\gamma$ differ for expectation-value and response-theory approaches (72), but numerical results are often very similar. One-particle transition density matrices contain compact information about the difference between two states; thus, they can be used to analyze the character of the electronic transition and changes in electron distribution (73) upon excitation. Importantly, density-matrix-based analysis of the excited states does not depend on the choice of molecular orbitals and can be applied to any wave function. The norm of $\gamma_{IF}$ is a useful quantity as well: It measures the degree of one-electron character in the $\Psi_i \rightarrow \Psi_F$ transition (74). Also, $\|\gamma\|$ can provide an upper bound for matrix elements by virtue of the Cauchy–Schwarz inequality (74). When dealing with processes in which the number of electrons changes, such as photoionization or photodetachment, Dyson orbitals play a role similar to the one-particle transition densities for electronic transitions, as they enter the expressions for calculating photoionization or photodetachment cross sections (75, 76). Dyson orbitals are defined as overlap between $N$-electron and $(N-1)$-electron states (75, 77–79):

$$\phi_{IF}(1) = \sqrt{N} \int \Psi_{I}^{N}(1, \ldots, n)\Psi_{F}^{N-1}(2, \ldots, n)d2\ldots dn. \quad 3.$$

Efficient implementations of EOM-CC methods exist in several electronic-structure packages (Q-Chem, CFOUR, ACES3, Molpro, etc). For example, the CC/EOM-CC suite of codes based on the Libtensor library for many-body calculations (80) can handle calculations of systems such as the diporphyrin molecule, nucleobase tetramers, and clusters of 20+ water molecules on a single node. Distributed parallel tensor libraries, such as CYCLOPS (81), further extend the scope of applicability of EOM-CC methods.

2.2. Why Equation-of-Motion Coupled-Cluster is the Method of Choice for Metastable States

The choice of the underlying electronic-structure method is very important for obtaining physically meaningful results for molecular resonances. What are the essential requirements? First,
Self-consistent field (SCF): nonlinear equations describing one-electron states (orbitals) in Hartree–Fock and Kohn–Sham DFT.

$\Delta E$: calculations of energy differences (IPs, EAs) by taking the difference of the total energies of the two states computed by a chosen method (AHF, ΔCCSD, etc.).

electron correlation, both static and dynamic, is important. As illustrated in Figure 4, resonance states often have open-shell character. Thus, one should employ an ansatz that includes all the leading configurations, ideally in a spin-complete manner. Even when the resonance is of closed-shell character, dynamic electron correlation is still important. For example, an HF description of a Feshbach resonance, such as the $(2s)^2$ state of He, yields zero width because the wave function does not include terms that couple the resonance to the continuum (82). Second, we seek multistate methods that are capable of describing several electronic states in a single calculation. One reason is merely practical: When no information about the existence of a resonance is available, multistate methods allow one to compute all states in a specified energy range so that a resonance may be identified. However, even if one knows the nature of the target state, so that an appropriate state-specific calculation can be set up, it is still desirable to use a multistate method so that the interaction of this state with other states can be described, e.g., through oscillator strength sharing and through nonadiabatic and spin-orbit couplings. The ability to compute multiple states in the same framework is especially relevant for molecular resonances, as they can drop below the onset of the continuum and become bound at particular geometries. Third, it is crucial for the model Hamiltonian associated with an approximate method to have correct onsets of ionization continua embedded in it and to describe different states on the same footing. For example, in EOM-CC calculations for excited states (EOM-EE), the onsets of the ionization continua correspond to the EOM-IP ionization energies. A hypothetic EOM-EE calculation using a nearly complete basis set saturated with very diffuse functions will yield bound excited states (both valence and Rydberg) as well as ionized states in which one electron is excited to a very diffuse orbital; the energies of these states are exactly equal to those of the EOM-IP states. Thus, the Rydberg states exhibit correct behavior with respect to the convergence to the ionization onsets (83). Likewise, the location of resonances with respect to the bound states can be described correctly and consistently by EOM-CC. Fourth, because resonances are embedded in the continuum, the aufbau principle cannot be used to construct their wave functions. This is a major hurdle for methods that require solving self-consistent field (SCF) equations for the resonance state, such as ΔHF or DFT. Indeed, converging the SCF equations to the correct solution in very diffuse bases is rather cumbersome. In contrast, in EOM-CC calculations of resonances, the SCF equations are solved for a stable reference state where no convergence problems are encountered and the resonance wave functions are constructed according to the EOM ansatz.

Standard considerations such as robustness of the approach and the absence of system-specific parameters also apply (62). The ability to systematically improve the accuracy by including higher excitations in the CC/EOM-CC ansatz is also important. The EOM-CC series converges to the full configuration interaction limit, i.e., EOM-CCSD is exact for two electrons.

3. COMPLEX SCALING AND RELATED METHODS

3.1. Complex Scaling

The CS formalism (1, 2, 31–33, 84) is an elegant and mathematically rigorous way to deal with resonances. By scaling all coordinates in the Hamiltonian $H$ by a complex number $e^{i\theta}$ (dilation transformation), one obtains a non-Hermitian operator $H'$ whose discrete complex eigenvalues can be associated with resonances according to Equation 1. At the same time, thresholds (i.e., ionization and detachment energies) and bound-state energies of $H$ are invariant under complex scaling, and the segments of the continuum are rotated around the respective thresholds into the lower-half complex plane by angle $2\theta$. These spectral changes are illustrated in Figure 5a.
**Figure 5**

(a) The transformation of the spectrum of the Hamiltonian upon complex scaling of all coordinates as described by the Balslev–Combes theorem. Panel a adapted from Reference 15 with permission. Copyright 2013 AIP. (b) $\theta$-trajectory for the $(2s)^2$ resonance of He computed with complex-scaled full configuration interaction using a 30s15p10d even-tempered basis (125 basis functions).

The resonances appear as discrete $L^2$-integrable eigenstates of $H^\theta$ provided that the angle $\theta$ exceeds the critical value (38),

$$\theta_c = \frac{1}{2} \arctan \left( \frac{\Gamma}{2(E_R - E_t)} \right),$$

with $E_t$ as threshold energy. For $\theta > \theta_c$, the resonance energies are independent of $\theta$. The theoretical justification for CS is given by the Balslev–Combes theorem (31–33). Importantly, because CS relies on analytic continuation of the Hamiltonian into the complex plane, it is only applicable to Hamiltonians with dilation analytic potentials, a property that is often nontrivial to determine (31–33).

CS can also be interpreted as a similarity transformation of the Hamiltonian (2, 28, 84):

$$H^\theta = S H S^{-1}, \quad \Psi^\theta = S \Psi, \quad S = e^{i\theta(\delta/\hbar)}.\quad 4.$$

A critical difference from other similarity transformations in bound-state quantum chemistry, such as in EOM-CC, is that $S$ is unbounded. Hence, the spectra of $H$ and $H^\theta$ differ: Some eigenvalues persist (bound-state energies), others are lost (continua on the real axis), and new eigenvalues appear in the complex energy plane. Still, the observation that both are similarity transformations suggests interesting parallels between CS and EOM-CC: CS converts an exponentially diverging solution of the original Schrödinger equation with outgoing boundary conditions into an $L^2$-integrable bound-like wave function $\Psi^\theta$ that belongs to a generalized Hilbert space (3, 38) and is a solution to the modified Schrödinger equation with $H^\theta$. The information about the resonance is compressed into a single spatially compact eigenstate, leaving behind a white continuum with a uniform density of states. In EOM-CC theory, the similarity transformation permits obtaining correlated many-electron energies from expansions of the wave function that are compact in the abstract many-electron space. If up to $N$-electron excitations are included in the operator $T$, the lowest eigenvalue of $\bar{H}$ is the exact ground-state energy and the corresponding eigenstate is just a single Slater determinant. Even in the case of an approximate $T$ that includes only single and double excitations, rather accurate energies and compact wave functions are obtained.

### 3.2. The c-Product

The complex-scaled Hamiltonian $H^\theta$ and the CAP-augmented Hamiltonian discussed in Section 4 are not Hermitian, but complex symmetric, i.e., $(H^\theta)^\dagger = (H^\theta)^*$. Because of this,
regular scalar product needs to be replaced by the symmetric bilinear form (85)

\[
(\Psi_i|\Psi_j) = \int dr \Psi_i \Psi_j,
\]

termed the c-product and denoted by parentheses (round brackets) instead of angle brackets. The difference from the regular scalar product is that the bra state is not complex conjugated. Equation 5 does not induce a valid metric norm and the eigenfunctions of \( H^\theta \) do not necessarily form a complete set. Hence, the formulation of completeness and closure relations requires special consideration (3). Fortunately, these peculiarities do not prevent combining complex-valued approaches with quantum-chemical methods developed for bound states. The justification for doing so is the complex variational principle (85–87), which can be formulated as

\[
\bar{E} = \langle \tilde{\Psi}|H^\theta|\tilde{\Psi}\rangle/(\tilde{\Psi}|\tilde{\Psi}\rangle,
\]

for a c-normalizable trial wave function \( \tilde{\Psi} \). In contrast to the regular variational principle, this is a stationarity principle for the complex energy and the wave function and not an upper or lower bound of the real or imaginary energy. In EOM-CC, Equation 6 is modified to account for different left and right eigenvectors of \( \bar{H} \), giving rise to the complex bivariational principle.

The expectation value of operator \( A \) with respect to Equation 5 is defined as \( \langle A \rangle \equiv (\Psi|A|\Psi)/(\Psi|\Psi) \), where the denominator ensures invariance with respect to multiplication of \( \Psi \) by a phase factor. Thus, the formulas defining a quantum-chemical method need not be modified in a complex-valued approach. However, the change of metric entails that the adjoint operators as used in Section 2 need to be replaced by the transposed operators, because creation and annihilation operators are the transpose of each other and modified anticommutation relations hold.

Complex orthogonality and complex normalization are defined with respect to Equation 5, in analogy with the usual metric, but several important differences arise relative to Hermitian theory: The c-norm is, in general, complex and may become zero for nonzero functions (self-orthogonality) (3, 85). Also, the c-norm of a wave function is not invariant to rotation by \( e^{i\alpha} \), and the real and imaginary parts of a c-normalized wave function are orthogonal to each other:

\[
1 = (\Psi|\Psi) = \int dr \left[ \text{Re}(\Psi)\text{Re}(\Psi) - \text{Im}(\Psi)\text{Im}(\Psi) \right] + 2i \int dr \text{Re}(\Psi)\text{Im}(\Psi).
\]

In an electronic-structure calculation, similar relations hold for the orbitals from which the many-body wave function is constructed (26). Moreover, the complex density does not integrate to the number of electrons; instead, its real part does, whereas the imaginary part integrates to zero. Consequently, the trace of the real part of the density matrix equals the number of electrons, whereas the imaginary part of the density matrix is traceless.

### 3.3. Complex Scaling in a Finite Basis Set

Because upon CS the resonances appear as discrete eigenstates in a generalized Hilbert space, their positions and widths can be computed with bound-state methods through projection of the operator \( H^\theta \) onto a finite one-electron basis set and diagonalization of the resulting matrix. Unfortunately, such numeric applications of the CS technique suffer from several undesirable features: The bound-state energies and resonance energies become \( \theta \)-dependent, with the former acquiring unphysical finite resonance widths, and the density of states in the rotated continua is no longer uniform.

Thus, one needs to compute \( \theta \)-trajectories, \( E(\theta) \), and evaluate the resonance position and width at the optimal value \( \theta_{\text{opt}} \), determined through \( \min |dE/d\theta| \). At \( \theta_{\text{opt}} \), the trajectory is slowest, the
Balslev–Combes theorem holds approximately, and the complex virial theorem is satisfied to the best possible degree (85, 86). Apart from the obvious consequences in terms of computational cost, \( \theta \)-dependence implies that different resonance states have different \( \theta_{\text{opt}} \), which complicates the analysis of interstate properties.

As an example of a complex-scaling calculation, Figure 5b shows a \( \theta \)-trajectory for the \((2s)^2\) resonance in He computed with complex-scaled full configuration interaction. Using an even-tempered set of 125 Gaussian basis functions, the resonance position and width were obtained as \( E_R = -0.77776 \) a.u., \( \Gamma = 0.00446 \) a.u. at \( \theta_{\text{opt}} = 0.325 \) rad (15), in excellent agreement with the reference values obtained with a Hylleraas basis \((E_R = -0.77787 \) a.u., \( \Gamma = 0.00454 \) a.u.) (88). This calculation also demonstrates the arduous basis-set requirements of CS methods and shows that resonance widths are particularly sensitive. In practice, even-tempered basis sets are most commonly employed (50, 89, 90) or standard bases are augmented with even-tempered diffuse functions (15).

Interestingly, it is not only the diffuseness of the basis that is important; the inclusion of higher angular momentum and an accurate description of the valence part are critical as well (15). Why are complex-scaled calculations so sensitive to the quality of the basis set? First, describing the interaction of the resonance with the continuum demands a relatively diffuse basis set. Second, whereas the eigenvalues of \( H^\theta \) are independent of \( \theta \), its eigenfunctions are not. CS introduces oscillations into resonance and bound-state wave functions. The correct description of this behavior requires additional tight functions in the valence part of the basis. This is especially important for core electrons and heavier atoms (91). Third, the importance of higher angular momentum can be explained in terms of angular electron correlation. Including higher angular momentum leads to a wave function that is radially more compact, because the electrons can avoid each other in the angular dimensions. In the example of the \((2s)^2\) resonances in He (Figure 5b), up to three additional sets of \( d \)-functions need to be included on top of the aug-cc-pVTZ basis set to obtain results that are converged with respect to angular correlation.

### 3.4. Complex Scaling for Molecular Systems

Formally, CS can be applied in the same manner to both atomic and molecular systems. However, electronic-structure calculations on molecules are usually carried out within the Born–Oppenheimer approximation, where nuclear and electronic degrees of freedom are separated. This separation is essential for the application of quantum chemistry to systems of practical interest, but, unfortunately, it is not straightforward to combine the Born–Oppenheimer approximation with CS (1, 3, 92, 93). If only electronic coordinates are scaled, i.e., if the nuclei are clamped to the real axis, the electron–nuclear attraction operator and, hence, the electronic Hamiltonian are not dilation analytic (1, 92). An alternative, preserving dilation analyticity, is to scale both electronic and nuclear coordinates (1). This results in an electronic Hamiltonian with nuclear positions shifted to the upper half of the complex plane and complex internuclear distances. The potential energy surfaces (PESs) computed using such a formulation of the Born–Oppenheimer approximation are unphysical (93) because there is no meaningful connection between complex nuclear coordinates and molecular structures. To overcome the problems of CS for molecular systems, several approaches have been proposed, e.g., back-rotation transformation (93), exterior scaling (94), smooth exterior scaling (38, 95), and using complex basis functions (92, 96).

### 3.5. Complex Hamiltonians versus Complex Basis Functions

Scaling the coordinates in the Hamiltonian as \( r \rightarrow re^{i\theta} \) is mathematically equivalent to scaling the basis functions as \( r \rightarrow re^{-i\theta} \). As long as \( H \) is dilation analytic and represented in a complete
Static-exchange (SE) approximation: the Fock operator of the (N + 1)-electron state is constructed using the electron density of the N-electron state basis, both procedures yield the same expectation value (3, 92, 96):

$$E = \frac{\langle \Psi(r)|H^*(re^{-i\eta})|\Psi(r)\rangle}{\langle \Psi(r)|\Psi(r)\rangle} = \frac{\langle \Psi(re^{-i\eta})|H(r)|\Psi(re^{-i\eta})\rangle}{\langle \Psi(re^{-i\eta})|\Psi(re^{-i\eta})\rangle}.$$  \hspace{1cm} (8)

For atoms, both approaches are identical when an atom-centered basis is used and all basis-set exponents are scaled. Thus, there are two strategies for the implementation of a complex-valued ab initio method.

In the first case, the so-called direct approach, one works in a real one-electron basis and scales the matrix elements of the Hamiltonian as $T_{pq} \rightarrow e^{-2i\eta}T_{pq}$ and $V_{pq} \rightarrow e^{-i\eta}V_{pq}$. This approach allows one to employ standard quantum chemistry codes for computing one- and two-electron integrals over unmodified Gaussian basis functions. Our implementation (15) of the cs-EOM-EE-CCSD method is based on the direct approach; details are discussed in Section 5.

In the second case, one keeps the unscaled Hamiltonian but works in a basis of functions with a complex coordinate. Actual implementations of the approach (40, 57, 82) rely on using Gaussian basis functions with complex exponents, which is asymptotically equivalent to using standard Gaussians with complex coordinates (92). The advantage of this approach is additional flexibility, as it is possible to scale only the exponents of the most diffuse basis functions.

One can describe mixed bases as an approximation to exterior CS (39, 97), which is equivalent to scaling only the coordinates of the electrons in the most diffuse orbitals. Hence, the method of complex basis functions can be applied to molecular resonances (40, 48, 49, 57, 98); however, integration with existing electronic-structure codes requires evaluation of one- and two-electron integrals over nonstandard basis functions. Only very recently has an efficient implementation of the respective integrals enabled the first applications of the complex basis function method to polyatomic molecules at the static-exchange (SE) and HF levels of theory (52, 53).

4. COMPLEX ABSORBING POTENTIAL METHODS

4.1. General Aspects of Complex Absorbing Potentials

In CAP methods, the physical Hamiltonian $H$ is augmented by an artificial local potential $i\eta W(r)$, $H_\eta = H - i\eta W(r)$, devised to absorb the diverging tail of the resonance wave function (35, 46, 47) (see Figure 6). CAPs were first used in time-dependent calculations to prevent artificial reflections of wave packets at the edges of numerical grids. The application of CAPs to electronic resonances was guided by intuition at the beginning (34) and put on a solid mathematical foundation by Riss & Meyer (35), who showed that $H_\eta$ has a purely discrete spectrum for finite values of $\eta$.

In the limit $\eta \rightarrow 0$, the spectrum becomes continuous, and for each resonance there exists an eigenvalue of $H_\eta$ that converges to the exact resonance position and width provided that $W$ goes to infinity for $r \rightarrow \infty$, is piecewise continuous, and satisfies a few more general requirements (35). That is, an infinitesimally weak CAP ($\eta \rightarrow 0$) is sufficient to stabilize the resonance without perturbing it.

Most common in practice are quadratic potentials of cuboid shape (54, 58–60, 99–101):

$$W = W_x + W_y + W_z, \quad W_\alpha = \begin{cases} 0 & \text{if } |r_\alpha| < r_0, \\ (|r_\alpha| - r_0^\alpha)^2 & \text{if } |r_\alpha| > r_0^\alpha, \end{cases}$$

with $r_\alpha$ denoting the three Cartesian coordinates ($\alpha = x, y, z$). Such CAP is defined by four parameters: three parameters for the onset in each direction ($r_0^x, r_0^y, r_0^z$) and the strength $\eta$. A variety of other CAPs have also been used: isomorphic spherical CAPs (59, 60), Voronoi CAPs (102), and quartic instead of quadratic potentials. The numerical differences between these approaches
are usually small. CAPs of a more involved form include the transformative CAP (36, 37, 103), where the kinetic energy operator is modified, and reflection-free CAPs (38, 104), which feature first and second derivatives in addition to the multiplicative term in the CAP operator. The latter approaches are based on the relation between CAPs and exterior CS, which can be rationalized in different ways (37, 38, 105, 106). Generally speaking, one can pursue two strategies: (a) start from existing CAPs and construct a CAP that does not perturb the system even at finite strength (36), or (b) start from the exterior complex-scaled Hamiltonian, which has perfect absorbing properties, and aim at recasting the theory in a CAP-like form (38). Importantly, CAPs are not subject to the limitations of CS discussed in Section 3.4 and can be readily applied to molecules.

4.2. Complex Absorbing Potentials in Finite Basis Set Calculations

In electronic-structure calculations, the CAP is commonly projected onto a finite basis set, usually a set of atom-centered Gaussians. Unfortunately, the representation of the CAP in such bases is quite different from the idealized shape shown in Figure 6. The value of the CAP represented in an orthonormal basis set, \( \phi_p(r) \), at point \( r \), is

\[
W(r) = \sum_{pq} (\phi_p | \hat{W} | \phi_q)(\phi_p(r)\phi_q(r)) = W_{pq}\phi_p(r)\phi_q(r).
\]

How different is \( W(r) \) represented in an atomic-orbital basis from \(|r - r_0|^2\)? First, instead of going to infinity at large \( r \), the CAP eventually drops to zero, following the decay of the most diffuse basis function. Consequently, one needs to use sufficiently large \( \eta \) to create a barrier 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). Second, because atomic-centered functions have the largest values at the positions of the nuclei, the values of \( W(r) \) are always finite in the interaction region, not zero, as suggested by the CAP expression.

Consequently, taking the limit \( \eta \to 0 \) is not meaningful in this case. Instead, an optimal finite value \( \eta_{opt} \) that is large enough to stabilize the resonance has to be found. Figure 7 visualizes this.
stabilization by means of the spatial extent ($\langle R^2 \rangle$) and the Dyson orbital of the resonance wave function of N$_2^-$. Once $\eta$ is large enough, $\langle R^2 \rangle$ is stable and the Dyson orbital resembles that of bound N$_2^-$. (Figure 3), whereas it approximates a plane wave at too-low $\eta$. Using finite $\eta$ leads to a perturbation of the bound and resonance states in the interaction region due to reflections from the CAP. In Figure 7, this perturbation is apparent from the linear dependence of the energy on $\eta$ at large $\eta$. In addition, false resonances can occur, i.e., stabilization of pseudocontinuum wave functions without correspondence to physical resonances (17, 36, 37).

The commonly used strategy for finding an optimal value of $\eta$ is to compute trajectories, $E(\eta)$, and then determine $\eta_{opt}$ through (35, 46) $\min \eta |dE/d\eta|$. The rationale for this criterion is that it minimizes the first-order term in a Taylor expansion of the energy in $\eta$ (35), but unfortunately, the resonance position and width computed using this criterion are very sensitive to the CAP onset (46, 60, 100).

Can we use physical considerations for choosing the CAP onset? When considering temporary anions, we would like to minimize the perturbation of the stable neutral state by the CAP. A reasonable choice of the CAP onset in this case is the spatial extent of the wave function of the corresponding neutral species (or a little larger) (59). Can we further reduce the perturbation and obtain converged results by pushing the CAP onset further away from the molecule? As illustrated in Figure 8a, increasing the CAP onset leads to seemingly convergent behavior. However, the results converge to CAP-free values (100) because, when the onset is distant enough, the CAP’s basis-set representation (Equation 9) becomes zero.

Several strategies have been proposed to mitigate the sensitivity of resonance positions and widths to the CAP parameters (35, 46, 60, 107). A conceptually simple idea is to explicitly remove the perturbation due to the CAP in first order (35, 59, 60, 108). The first-order deperturbed energy $U$ is computed according to

$$U(\eta) = E(\eta) + i \eta \text{Tr}[\gamma(\eta) W'] = E(\eta) - \eta dE/d\eta,$$

with $\gamma(\eta)$ as the one-particle density matrix. Physically, this approach is grounded in the behavior of the resonance wave function and not that of the resonance energy. As Figure 7 shows, when the CAP is sufficiently strong, both the real and imaginary parts of the wave function become nearly

---

**Figure 7**
Stabilization of the resonance wave function with increasing complex absorption potential (CAP) strength illustrated for a EOM-EA-CCSD calculation of the $^2\Pi_1$ resonance of N$_2^-$ using a shifted quadratic CAP. Shown are the (a) real and (b) imaginary parts of the resonance energy, the expectation value of $R^2$, and the Dyson orbital. Figure adapted from Reference 26 with permission. Copyright 2016 AIP.
stationary, and the perturbation can be eliminated from the energy according to Equation 10. A more elaborate way of removing the perturbation by the CAP involves using Padé approximants of $E(\eta)$, which allows the limit $\eta \to 0$ to be taken explicitly (107). If $E(\eta)$ is strictly linear in $\eta$, the approach is equivalent to Equation 10.

Figure 8b demonstrates that the corrected energy $U$ is nearly constant for large $\eta$ once stabilization has been reached; i.e., the wave function does not change anymore. Furthermore, the corrected trajectories computed using different CAP onsets become much more similar in the asymptotic region compared to the uncorrected trajectories. $\eta_{opt}$ is determined through minimizing the second-order term in the Taylor expansion:

$$\min \left| \eta \frac{d^2 E}{d\eta^2} \right| = \min \left| \eta \frac{dU}{d\eta} \right|.$$  \hspace{1cm} 11.

Benchmarks illustrated (59, 60) that an approach based on Equations 10 and 11 results in a computationally robust scheme in which the dependence on the CAP onset is significantly reduced.

Another way to reduce the unphysical perturbation of the interaction region by the CAP is to project the CAP on the virtual orbital space, i.e., to retain only the virtual–virtual block of the CAP matrix (109):

$$W_{pq} = \begin{cases} 
(\phi_p | W | \phi_q) & \text{if } p \text{ and } q \notin \Phi_0, \\
0 & \text{if } p \text{ or } q \in \Phi_0.
\end{cases}$$  \hspace{1cm} 12.

As discussed below, the magnitude of the first-order correction is significantly reduced when such a projected CAP is employed to describe temporary anions. It is, however, unclear how to generalize Equation 12 to other resonances besides temporary anions.
5. IMPLEMENTATION OF COMPLEX-VALUED METHODS

Complex-valued (CV) EOM-CC can be formulated using three different approaches that can be arranged in the following hierarchical order: (a) CV-EOM-CC/CC/HF, in which CS or the CAP is introduced only in the EOM calculation; (b) CV-EOM-CC/CC/CV/HF, where both the EOM and the CC step are performed employing a CV Hamiltonian; and (c) a fully complex-valued approach, CV-EOM-CC/CV-CC/CV-HF. Because the similarity-transformed Hamiltonian $\hat{H}$ has the same spectrum as the original Hamiltonian in the limit of a complete many-electron basis, all three approaches yield identical results. However, for approximate wave functions, the results may vary. Scheme c, in which the usual hierarchy of methods is applied systematically to the complex-valued Hamiltonian, is the most consistent one. Here, the form of the CC and EOM-CC equations is the same as in the real-valued formalism, and the size extensivity of the theory is rigorously preserved. However, one can argue that in cases with bound reference states, such as EOM-EA calculations of metastable anions or EOM-EE calculations of highly excited states, CS or the CAP should be applied only at the EOM level, as the bound part of the spectrum should be the same as in unscaled (or CAP-free) calculations. The EOM-CC equations then need to be modified, as the CC equations are not satisfied at $\theta/\eta \neq 0$. The attractive feature of these approaches is that only one set of HF and CC equations needs to be solved for each trajectory, as only the EOM-CC equations employ a $\theta/\eta$-dependent Hamiltonian. However, the size intensivity of the theory is lost.

For complex-scaled EOM-EE-CCSD, all three models have been implemented and analyzed (15), and it was demonstrated that the scaling should be performed either at the HF level or, at least, the CCSD level. The situation is different for CAP-EOM-CCSD methods, as the effect of the CAP on the bound-state wave functions is rather small. Several CAP-EOM-CCSD implementations have been reported. In References 59 and 60, the CAP was introduced at the HF level of theory. Pal and co-workers (58) advocated the strategy in which the CAP is included only at the EOM level. Another degree of flexibility is the representation of the CAP operator in the molecular orbital basis: one can employ full CAP matrices or project them onto the virtual orbital subspace (see Equation 12). The latter procedure (58) may alleviate the perturbation of bound states and inner parts of the resonance states by the CAP. Figure 9 demonstrates that for EOM-EA-CCSD calculations of shape resonances, the inclusion of the CAP only at the EOM level yields results that are practically indistinguishable from full CAP calculations if the projected form of the CAP is used. The deviations are slightly larger in calculations involving the full CAP matrix: 0.01 eV for the resonance position and 0.07 eV for the resonance width.

6. COMPLEX-VALUED EQUATION-OF-MOTION COUPLED-CLUSTER AT WORK

Having presented the theory of complex-valued approaches and its application to the EOM-CC ansatz, we now adopt the user’s perspective and discuss how to employ these methods in actual electronic-structure computations.

6.1. Polarization and Electron Correlation

To introduce the issue, consider temporary anions in which the target states are derived by electron attachment to neutral species. Adding an extra electron polarizes the core and increases the correlation energy. As we know from studies of bound anions (110, 111), both effects need to be carefully taken into account for reliable computations of EAs. In contrast to ionized states
Figure 9

η-Trajectories for the $^2\Pi_g$ $N_2^-$ shape resonance computed with various CAP-EOM-EA-CCSD models (aug-cc-pVTZ with extra 3s3p3d set of diffuse functions on the ghost atom at the center of mass). CAP$\gamma$ and CAP denote the projected and full CAP representations. The effect on the CCSD reference state is negligible in the case of projected CAP (compare the purple and blue curves) but is more pronounced when the full CAP is used.

(110, 111), polarization and correlation effects tend to add up rather than cancel, which is why Koopmans’ theorem generally yields worse estimates for EAs than for IPs. For temporary anions, additional challenges arise, as polarization and correlation effects are difficult to disentangle from limitations due to the different complex-variable techniques and from consequences of truncating the one-electron basis. Hence, comparing different studies may lead to contradictory trends and dubious conclusions.

Table 1 compares results for the $^2\Pi_g$ shape resonance in $N_2^-$ obtained using the same one-electron basis set and complex-variable technique. This is a well-suited example, as a reliable reference value for the fixed-nuclei limit of the complex resonance energy has been extracted from experimental data (112). The upper part of Table 1 illustrates the impact of polarization. The SE approximation severely overestimates the resonance position and width because $N_2^-$ is described using orbitals of neutral $N_2$, i.e., the molecule is unable to adjust to the extra electron and the bound character of the resonance wave function is underestimated. This effect is independent of the underlying complex-variable technique (35, 52, 53, 103). Yet the SE approximation is of some value, as it properly accounts for exchange effects and hence provides a computationally cheap and qualitatively correct representation of electronic shape resonances. Explicit treatment of target polarization is achieved in ΔHF approaches where the HF equations are solved for both the bound and the resonance states. As Table 1 shows, this lowers the values for the position and width significantly. Unrestricted HF (UHF) yields a slightly lower value compared to restricted open-shell HF (ROHF) due to additional flexibility in the wave function (53). The lower part of Table 1 illustrates that electron correlation leads to a further lowering in $E_R$, whereas $\Gamma$ increases. ΔCCSD and EOM-EA-CCSD yield roughly comparable results. The trend in the position can be explained by the correlation energy being an extensive quantity, which implies that correlation lowers the energy of the anion more than that of the neutral species. The increase in the width is due to the excited determinants present in a correlated wave function, affording a better
Table 1  Position and width of the $^2\Pi_g$ shape resonance in $N_2^-$

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_R$ (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>cbf-SE/caug-cc-pVTZ(cm+)</td>
<td>3.88</td>
<td>1.26</td>
<td>Reference 53</td>
</tr>
<tr>
<td>cbf-ROHF/caug-cc-pVTZ(cm+)</td>
<td>2.96</td>
<td>0.32</td>
<td>Reference 53</td>
</tr>
<tr>
<td>cbf-UHF/caug-cc-pVTZ(cm+)</td>
<td>2.83</td>
<td>0.23</td>
<td>Reference 53</td>
</tr>
<tr>
<td>CAP-UHF/aug-cc-pVTZ+3spd(C)</td>
<td>2.79</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>CAP-UCCSD/aug-cc-pVTZ+3spd(C)</td>
<td>2.43</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>CAP-EOM-EA-CCSD/aug-cc-pVTZ+3spd(C)</td>
<td>2.47</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Reference value</td>
<td>2.32</td>
<td>0.41</td>
<td>Reference 112</td>
</tr>
</tbody>
</table>

Abbreviation: cbf, complex basis functions.

description of the unbound aspect of the resonance wave function compared to an HF treatment (103). This analysis applies to shape resonances; Feshbach resonances behave differently, as they decay via a two-electron process.

6.2. Molecular Properties of Resonance States

Expectation values for resonance wave functions ($\langle \Psi_{\text{res}} | A | \Psi_{\text{res}} \rangle$) as well as higher-order molecular properties are generally complex. The real and imaginary parts of ($\langle \Psi_{\text{res}} | A | \Psi_{\text{res}} \rangle$) can be related to the resonance position and width through the extended Hellmann–Feynman theorem (3, 85),

$$ \frac{dE_R}{d\lambda} = \text{Re} \left( \langle \Psi_{\text{res}} | \frac{dH}{d\lambda} | \Psi_{\text{res}} \rangle \right) = \text{Re} \langle \Psi_{\text{res}} | A | \Psi_{\text{res}} \rangle, \tag{13} $$

$$ \frac{d\Gamma}{d\lambda} = -2 \cdot \text{Im} \left( \langle \Psi_{\text{res}} | \frac{dH}{d\lambda} | \Psi_{\text{res}} \rangle \right) = -2 \cdot \text{Im} \langle \Psi_{\text{res}} | A | \Psi_{\text{res}} \rangle, \tag{14} $$

and are, in principle, both observable. For approximate wave functions, Equations 13 and 14 are not necessarily fulfilled and the evaluation of a property as expectation value or energy derivative usually yields different results, as discussed in Section 2.

Transition properties ($\langle \Psi_{\text{I}} | A | \Psi_{\text{F}} \rangle$) between a resonance and a bound state or between two resonances are also complex, but here an interpretation of the real and imaginary parts along the lines of Equations 13 and 14 is not easily obtained. Of practical interest are transition dipole moments between resonance and bound states and the derived oscillator strengths, because these quantities are accessible by spectroscopic techniques (26).

6.3. Potential Energy Surfaces of Resonance States

The concept of PESs is central to the quantum chemistry of bound electronic states. By virtue of the Born–Oppenheimer approximation, one solves the electronic Schrödinger equation at fixed nuclear positions and obtains the electronic energy as a function of the nuclear coordinates. These PESs are then used to describe the nuclear dynamics, either adiabatic, when nuclei are constrained to a single PES, or nonadiabatic, when transitions between different electronic states are allowed.

Taking into account nuclear motion is equally important for a complete picture of molecular autodetachment and autoionization. In many cases, nuclear motion happens on the same timescale as autodetachment, so that vibrational effects leave distinct fingerprints in scattering or photodetachment cross sections. Also, some anions, such as $F_2^-$, are adiabatically bound, and the
autodetachment proceeds through coupling of nuclear and electronic degrees of freedom. Other anions, such as \( \text{CO}_2^- \), are adiabatically unbound but capable of trapping a vibrational state (113). In both cases, autodetachment would not happen in a fixed-nuclei picture. Modeling processes such as dissociative electron attachment also requires consideration of the nuclear motion.

In the Siegert formalism, resonances are described as adiabatic states so that the concept of a PES can be readily applied. The real part of the complex PES can be interpreted in analogy to bound states, whereas the imaginary part yields the resonance width as a function of the molecular structure. In contrast, the Feshbach formalism describes the resonance as a diabatic state embedded in the continuum, and the width is nonlocal and energy-dependent. The connection between the local width and the nonlocal width has been discussed in detail by Sommerfeld & Meyer (45).

Complete mapping of the PES of a polyatomic molecule is a computationally expensive task. Fortunately, it is often sufficient to locate special points, such as minima or transition states, a routine task in the case of bound states, provided that analytic energy gradients are available for a method. For resonances, however, analytic gradients were not available for any method until very recently (114), which is why only the PESs of diatomic or triatomic resonances, such as the anions of \( \text{N}_2 \) or \( \text{CO}_2 \), are well investigated, whereas little is known about the PESs of polyatomic resonances.

To discuss further aspects of constructing PESs for resonances, we focus again on the \( ^2\Pi_1 \) shape resonance of \( \text{N}_2^- \). Figure 10 shows PESs computed with CAP-UHF, CAP-UCCSD (unrestricted CCSD), and CAP-EOM-EA-CCSD together with the curves for the parent \( \text{N}_2 \) molecule. \( \text{N}_2^- \) becomes a bound anion at longer bond distances. One would expect the resonance width to become zero (i.e., the lifetime to become infinite) at the same bond length where the PESs of \( \text{N}_2^- \) and \( \text{N}_2 \) cross. This holds if the electronic Schrödinger equation is solved exactly, but it is not necessarily the case for approximate methods. The ΔHF approach yields an inconsistent description, where, at bond lengths between 1.2 and 1.33 Å, it is unclear whether or not \( \text{N}_2^- \) is subject to autodetachment. Similar inconsistencies have been observed in ΔHF calculations using complex basis functions (49, 53, 98). For ΔCCSD, the problematic region of the PES is considerably smaller, but the inconsistency is not resolved completely. These shortcomings of ΔHF and ΔCCSD are due to the anionic and neutral species being computed using different

![Figure 10](https://www.annualreviews.org/doi/abs/10.1146/annurev-physchem-033116-053408)

**Figure 10**

Potential energy curves and resonance widths for the \( ^2\Pi_1 \) resonance of \( \text{N}_2^- \) computed using (a) CAP-augmented UHF and (b) UCCSD and EOM-EA-CCSD, with aug-cc-pVTZ+3spd(C). Potential energy curves for the \( \text{N}_2 \) ground state are shown as well. CAP-UHF and, to a lesser extent, CAP-UCCSD are inconsistent in describing the conversion of the resonance into a bound state: The resonance width becomes zero despite that the \( \text{N}_2^- \) curve is still above the \( \text{N}_2 \) curve.
model Hamiltonians. In contrast, EOM-EA-CCSD yields the wave functions of an anion/neutral pair as eigenfunctions of the same model Hamiltonian, so that the conversion of a resonance into a bound state is described consistently (61). This is an important advantage of EOM-CC methods and should equally apply to other approaches where resonances and their parent stable states are obtained from the same model Hamiltonian.

In CAP methods, constructing PESs is further complicated by the optimal CAP strength being different at different structures. Especially when using basis sets with relatively few diffuse functions, the optimal CAP strength sometimes changes abruptly. This can lead to discontinuities in PESs (61). The deperturbative correction from Equation 10 mitigates this problem. Also, these artifacts usually disappear when including more diffuse functions in the basis. Overall, CAP-EOM-CCSD augmented by the deperturbative correction yields smooth and consistent PESs.

6.4. Characterization and Interpretation of Resonance Wave Functions

The visualization and analysis of orbitals and wave functions helps to rationalize and predict molecular properties and reactivity patterns. For example, in the case of bound anions, the character of the orbital hosting the extra electron determines which bonds contract, stretch, or break upon electron attachment and whether new reaction channels open up that were inaccessible in the corresponding neutral species. The wave functions determine molecular properties, which can be observed experimentally. Thus, information about wave functions and orbitals can be inferred from experimental measurements. For example, orbital shapes and symmetries can be reconstructed from cross sections and angular distributions of photoelectrons (115). Because of their similarity to bound states, it is desirable to characterize temporary anions and other resonances by means of orbitals as well, so that one can classify them by chemical terms such as $\sigma^*$ or $\pi^*$. This goal is readily achieved with complex-variable approaches. By means of Dyson orbitals (Equation 3), the molecular-orbital concept can be applied to many-electron wave functions, taking into account correlation and orbital relaxation. Dyson orbitals are particularly well suited for characterizing shape resonances where the attachment is of one-electron character (26).

Examples of Dyson orbitals of temporary anions are shown in Figure 11 and as insets in Figure 12. The real parts of these orbitals meet the chemist’s intuition for the MOs of hypothetical bound anions. The imaginary parts of all orbitals are governed by the requirement that the real and imaginary parts be orthogonal (see Equation 7), which is often realized by means of a different nodal structure. The orbitals for the polyatomic $\pi^*$ resonances in Figure 11 can be rationalized by the Hückel model, whereas the diatomics in Figure 12 can be described as symmetric $\sigma^*$ ($F_2^-$), symmetric $\pi^*$ ($N_2^-$), and highly distorted $\pi^*$ (CuF$^-$) orbitals.

$N$-methylformamide features, in addition to the valence-like $\pi^*$ resonance, a dipole-bound anionic state in which the attached electron resides in an orbital outside the molecular core, on the positive side of the molecular dipole. Due to this orbital shape, the structures and many molecular properties of dipole-bound anions are very similar to those of the parent neutral molecules (16, 110, 111). There also exist metastable analogs of dipole-bound states (116). An example is the distorted $\pi^*$ resonance of CuF$^-$ ($\mu$(CuF) = 5.3 D) in Figure 12. Similar dipole-stabilized $\sigma^*$ and $\pi^*$ resonances have been described in AgF$^-$ (116) and nitrogen-containing carbon chains (117).

Figure 12 illustrates that different types of resonances feature different PESs. Valence shape resonances, such as $F_2^-$ and $N_2^-$, are stabilized by stretching bonds. The energy of the attached state drops below that of the neutral and its width becomes zero; $F_2^-$ is even bound adiabatically. In contrast, the energy and lifetime of a dipole-stabilized resonance such as CuF$^-$ change much less, and the potential energy curves of CuF$^-$ and CuF$^-$ are almost parallel. This implies that vibrational motion should have stronger impact on lifetimes of resonances of the first type than on those of...
C6H6–/2E

\[ E_R = 1.64 \text{ eV} \]
\[ \Gamma = 0.04 \text{ eV} \]

C6H6–/2B

\[ E_R = 6.75 \text{ eV} \]
\[ \Gamma = 0.35 \text{ eV} \]

CH3NHCHO–

\[ E_R = 2.88 \text{ eV} \]
\[ \Gamma = 0.012 \text{ eV} \]

\[ C_6H_4O_2–/2A^u \]

\[ E_R = -0.015 \text{ eV} \]
\[ \Gamma = 0.27 \text{ eV} \]

\[ C_6H_6–/2A^u \]

\[ E_R = 2.91 \text{ eV} \]
\[ \Gamma = 0.35 \text{ eV} \]

\[ C_6H_6–/2E_{2u} \]

\[ E_R = 1.64 \text{ eV} \]
\[ \Gamma = 0.04 \text{ eV} \]

\[ C_6H_6–/2B_{2g} \]

\[ E_R = 6.75 \text{ eV} \]
\[ \Gamma = 0.35 \text{ eV} \]

\[ 2A' \]

\[ E = -0.015 \text{ eV} \]
\[ \Gamma = 0.27 \text{ eV} \]

\[ 2A'' \]

\[ E_R = 2.91 \text{ eV} \]
\[ \Gamma = 0.35 \text{ eV} \]

**Figure 11**

Dyson orbitals for various temporary anions computed with CAP-EOM-EA-CCSD. The upper and lower plots show the real and imaginary parts, respectively. For N-methylformamide (b), the Dyson orbital for attachment to the dipole-bound \( 2A' \) state is shown as well. Figure adapted from Reference 26 with permission. Copyright 2016 AIP.

the second. **Figure 12** also demonstrates that the width of a \( \sigma^* \) resonance (F2−) increases faster at shorter bond lengths than that of a \( \pi^* \) resonance (N2−), owing to the lower angular momentum barrier for \( p \)-wave detachment compared to \( d \)-wave detachment. The same argument explains the different lifetimes of the isoelectronic species N2− and CO−. The outgoing electron has pure \( d \)-wave character for N2−, but mixed \( p \)- and \( d \)-wave character for CO−.

Complex-valued methods also allow for characterizing resonances in terms of the electron density and state density matrices, providing complementary analysis. In particular, an analysis based on the complex difference density has been introduced for HF resonance wave functions in Reference 53. Splitting the difference density of an anion/neutral pair into attachment and detachment components allowed for the quantification of polarization effects.

### 6.5. Connecting Theory and Experiment: Resonances in Photodetachment

Photodetachment spectroscopy (115) is a powerful experimental technique for identifying and characterizing stable and temporary anions. By illuminating anions \( X^- \),

\[
X^- + hv \rightarrow X^- + e^- (eKE),
\]

and measuring the detached electrons’ kinetic energy (eKE), the electronic and often the vibrational energy differences can be determined as electron binding energies (eBE) through \( hv = eBE + eKE \). From Franck–Condon progressions, structural changes between the anionic and neutral systems can be deduced. Information about the wave functions of an anion/neutral pair can be obtained from photoelectron angular distributions (PADs) \( I(\theta) \) (118). These are experimentally characterized by the anisotropy parameter \( \beta \), which assumes values between −1 and +2, corresponding to polarization of the photoelectrons perpendicular or parallel to the laser electric vector, respectively.
Resonances manifest themselves in different ways in photodetachment spectra. In general, the presence of a resonance opens a second channel,

$$X^- + h\nu \rightarrow [X^-]^* \rightarrow X + e^-(\text{eKE}),$$  

in addition to Equation 15. This gives rise to enhanced cross sections, resulting in sharp peaks in photoelectron spectra superimposed on a broad background signal corresponding to direct detachment; similar features are also common in photoionization experiments (119).

Often, resonances are revealed through their signatures in PADs, which result from the different selection rules for Equations 15 and 16 and lead to sudden changes in PADs at photon energies near a resonance. An example of resonances in photodetachment, we consider the case of CuF$^-$ (116). The energies and Dyson orbitals of the relevant electronic states are compiled in Figure 13a. There are two bound anionic states, the valence ground state ($X^2\Sigma^+$) and a dipole-bound state ($1^2\Sigma^+$), as well as two low-lying dipole-stabilized resonances ($2^2\Sigma^+$, $1^2\Pi$). These states can be described in a balanced way by a CAP-EOM-EA-CCSD calculation using the ground state of neutral CuF as reference.

Photons with energies of 1.6–2.1 eV produce the ground electronic state of CuF in various vibrational levels. The selection rules for the different channels, Equations 15 and 16, are illustrated
in Figure 13b. Direct detachment primarily yields $p$-wave photoelectrons polarized along the electric vector of the incident radiation, as the Dyson orbital of the anion ground state is largely of $s$ character. Autodetachment via the $2\Sigma^+$ and $1\Pi$ resonances is a two-step process. At first, molecules oriented perpendicular or parallel to the laser polarization axis are selected according to the transition dipole moments, $(X \Sigma^+ | \mu | 1\Pi)$ and $(X \Sigma^+ | \mu | 2\Sigma^+)$, respectively. The Dyson orbital of the resonance (see Figure 13a) then represents the initial wave function of the detached electron. Importantly, in each case of autodetachment, the outgoing electrons are less polarized along the laser electric vector than in direct detachment.

The experimental anisotropy parameter $\beta$ is shown in Figure 13c. Consistent with the preceding considerations, $\beta$ is highly positive at most photon energies, which corresponds to direct
detachment. However, at photon energies of 1.7 and 1.9 eV, $\beta$ shows rapid undulations in all vibrational channels. These features are signatures of the two autodetachment channels (Equation 16), both of which yield less polarized PADs, as explained above. Theoretical (1.64 eV and 1.92 eV) and experimental (1.7 eV and 1.9 eV) values are in excellent agreement, which demonstrates the capability of CAP-EOM-EA-CCSD.

### SUMMARY POINTS

1. We have discussed recent progress in complex-valued approaches, which enable the application of bound-state quantum chemistry to electronic resonances. Techniques such as CS, complex basis functions, and CAP lead to a non-Hermitian formulation of quantum mechanics and allow one to describe resonances as discrete $L^2$-integrable states, in contrast to Hermitian quantum mechanics, in which resonances manifest themselves by increased density of states in the continuum.

2. We emphasize the importance of predictive models, which do not involve system-dependent parameterization and can be applied in a black-box fashion, similar to theoretical model chemistries developed for bound states (62).

3. Multistate methods (such as EOM-CC), which compute several target states in one step, treat states of various nature on an equal footing; these methods also describe the states’ interactions and facilitate calculations of inter-state properties.

4. Different variants of EOM-CC enable access to different types of resonances: EOM-EE allows one to compute highly excited states (e.g., core-excited), EOM-EA describes temporary anions, and EOM-IP is suitable for core-ionized states.

5. Complex-valued extensions of EOM-CC show good numeric performance and are capable of describing PES and molecular properties of resonances as well as modeling experimental observables.

### FUTURE ISSUES

1. Computational efficiency needs to be improved to enable studies of large systems, such as those of relevance to molecular electronics and plasmonic catalysis.

2. Techniques such as Cholesky decomposition and density fitting can be employed to mitigate the consequences of large basis sets needed for resonance calculations.

3. Getting rid of $\theta/\eta$ dependence would be highly desirable.

4. For higher accuracy and for modeling Feshbach resonances, inclusion of higher-order excitations in the EOM-CC ansatz is necessary.

5. Improving eigensolvers for robust access to high-lying resonances is also important.

6. Apart from these algorithmic improvements, there is a need to extend the theory to describe physical processes associated with resonances.

7. Critically important are implementation of analytic gradients, nonadiabatic and spin-orbit couplings, tools for cross section calculations, and integration of electronic structure with coupled electron-nuclear dynamics.
DISCLOSURE STATEMENT

A.I.K. is a member of the Board of Directors and partial owner of Q-Chem, Inc.

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84. Mathematical analysis of the spectral changes associated with the complex scaling transformation.

RELATED RESOURCES

*Q-Chem*, a comprehensive quantum chemistry package. [http://www.q-chem.com](http://www.q-chem.com)

Gozem S, Krylov AI. *ezDyson*, a program for computing photoionization and photodetachment cross-sections. [http://iopenshell.usc.edu/downloads/ezdyson](http://iopenshell.usc.edu/downloads/ezdyson)

Mozhayskiy VA, Krylov AI. *ezSpectrum*, a program for calculating Franck–Condon factors. [http://iopenshell.usc.edu/downloads/ezspectrum](http://iopenshell.usc.edu/downloads/ezspectrum)
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