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Second order Møller-Plesset and coupled cluster singles and doubles methods with complex basis functions for resonances in electron-molecule scattering

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The method of complex basis functions is applied to molecular resonances at correlated levels of theory. Møller-Plesset perturbation theory at second order and equation-of-motion electron attachment coupled-cluster singles and doubles (EOM-EA-CCSD) methods based on a non-Hermitian self-consistent-field reference are used to compute accurate Seigert energies for shape resonances in small molecules including N_2^-, CO^-, CO_2^-, and CH_2O^-. Analytic continuation of complex θ-trajectories is used to compute Seigert energies, and the θ-trajectories of energy differences are found to yield more consistent results than those of total energies. The ability of such methods to accurately compute complex potential energy surfaces is investigated, and the possibility of using EOM-EA-CCSD for Feshbach resonances is explored in the context of e-helium scattering.

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I. INTRODUCTION

Metastable electronic states, or resonances, have long been recognized as important intermediate states in a variety of chemical applications.[1] Such states can decay and are therefore characterized by a finite lifetime, $\tau = \hbar/\Gamma$, where the "width" of the resonance, Γ, has units of energy. The width and the energetic position of the resonance above the ground state, E_r, can be specified by a complex energy,

$$E = E_r - i\Gamma/2, \tag{1}$$

called a Seigert energy, which is the location of the S-matrix pole associated with the resonance.[2] Despite their importance, simple, black-box, methods for the computation of electronic resonances have been elusive. The difficulty is a result of the complexity of the quantum many-body problem with the additional difficulty of scattering boundary conditions.

One solution to the difficulty of scattering boundary conditions is offered by complex scaling and related methods,[3–5] which are originally based on the theorems of Aguilar, Balslev, Combes, and Simon.[6–8] These mathematically rigorous theorems offer an attractive solution to the scattering problem: the resonance parameters are found as a complex eigenvalue of the non-Hermitian Hamiltonian obtained by scaling the coordinates by a complex number, $e^{i\theta}$. The eigenvalue is discrete and the corresponding eigenfunction is square-integrable. The problem can then be solved by variational, finite basis methods.

For the molecular Born-Oppenheimer problem, complex scaling is not appropriate, and the method of exterior complex scaling[9] is the most rigorously justifiable means of obtaining an appropriate non-Hermitian Hamiltonian. In this method, the coordinates of electrons are scaled along a contour that remains real at the positions of the nuclei. Unfortunately the method is difficult to apply, though applications to resonances in diatomic molecules have been reported.[10,11] In practice one is forced to use a more approximate method for polyatomic molecules. One such method is the method of complex basis functions (CBFs) in which the transformation is applied to the basis set itself.[12] The result is that standard electronic structure methods can be used but in a basis set including Gaussians with complex exponents. The method is related to the analytic continuation of matrix elements[13] and is a complex-variational[14,15] approximation to the exterior-scaled wavefunction.[16] The method of complex basis functions has been most extensively applied to molecular shape-resonances at the Hatree-Fock level of theory. There have been various applications to diatomic molecules,[17–20] and a recent application to some polyatomic molecules.[21]

A closely related method involves the addition of a complex absorbing, usually negative-imaginary, potential (CAP or sometimes NEP).[22–24] These methods can be shown to be related to a variant of exterior scaling,[25] and share many features of other complex-coordinate methods. These methods have been successful for calculations on shape resonances, but application to Feshbach resonances has proven difficult.[26,27]

In addition to complex coordinate methods, several other methods are commonly used for the computation of resonance parameters in molecular systems. Scattering methods compute scattering observables directly.[28–31] Stabilization methods use the behavior of discretized continuum eigenvalues to compute resonance parameters.[32–34] Stieltjes imaging uses the discretized continuum to compute cross-sections and widths.[35] Bound state extrapolation and analytic continuation methods rely on the extrapolation of bound-state

energies to compute resonance parameters.[36–39]

Since molecular resonances are ultimately a many-body problem, accurate computation necessitates taking account of electron correlation effects. Feshbach resonances in particular have lifetimes that are entirely determined by electron correlation. While correlated calculations on atomic resonances are fairly routine,[40–43] correlated calculations on molecular resonances are not as commonplace. Electron correlation effects on resonance parameters in electron-molecule scattering have been incorporated into a variety of methods. Configuration interaction (CI)[13] and electron-propagator methods[44–47] have been used in conjunction with complex scaling to capture electron correlation. In past complex basis function calculations, correlation has been taken into account by means of various types of CI,[20,48–50] but these studies have been limited to atoms and diatomic molecules. The CAP method is by far the most popular choice for use with correlated electronic structure, and applications using CI,[24,51,52] electron propagator,[53] and coupled-cluster/SAC-CI[54–58] methods have been reported. The stabilization method has also been recently applied to medium-sized molecules at various correlated levels of theory.[59,60] Stieltjes imaging has been used in conjunction with correlated electronic structure methods to compute widths of autoionizing states of benzene.[61] Bound state analytic continuation methods have recently been utilized for molecular resonances with the express goal of using correlated quantum chemical methods.[62–66] Our pursuit of correlated complex basis function methods is motivated by the generality of the method in applications to shape and Feshbach resonances.

In the present study, we discuss the application of correlated electronic structure methods to molecular resonances using the method of complex basis functions. Møller-Plesset perturbation theory at second order[67] (MP2) and coupled-cluster singles and doubles[68] (CCSD) are both size-consistent, correlated methods with computational scaling with the system size of N^5 and N^6 respectively. Specifically, we evaluate the ΔMP2 and equation of motion, electron attachment CCSD[69] (EOM-EA-CCSD) methods for accurate computation of resonance parameters. Furthermore, we explore the possibility of using EOM-EA-CCSD to obtain accurate complex potential energy surfaces, and to compute positions and widths of Feshbach resonances.

II. THEORY

A. Complex basis functions

To compute the complex Seigert energy associated with a narrow resonance, we employ the method of complex basis functions for all calculations. This method is described in detail in the literature.[12,16,21] Diffuse Gaus-

sian basis functions of the form

$$\phi_\theta(\mathbf{r}) = N(\theta)(x - A_x)^l (y - A_y)^m (z - A_z)^n \\ \times \exp\left[-\alpha e^{-2i\theta}(\mathbf{r} - \mathbf{A})^2\right] \quad (2)$$

are included in the basis set. For atoms, the θ appearing in this equation is identical to that of complex-scaling, while for molecules, it is related to a particular exterior scaling contour. These basis functions provide a reasonable basis for representing the exterior-scaled resonance wavefunction in a c-normalized space. The c-product, in which the bra-side is not complex conjugated, will be denoted using curved brackets $(\ldots|\ldots)$. The application of the complex variational principle[14,15] allows for derivations of electronic structure methods in this space of c-normalized states.

B. The non-Hermtian SCF reference

As in traditional electronic structure theory, the starting point for the correlated calculations is a self-consistent field (SCF) reference. The theories considered here are based upon a single, c-normalized, determinant. The methods described in Ref. 21 can be used to obtain the single determinant reference from a non-Hermitian SCF (NH-SCF) calculation. For the NH-MP2 methods considered here, the reference is a single determinant from a non-Hermitian unrestricted Hartree-Fock or non-Hermitian restricted open-shell Hatree-Fock calculation on the anion. For EOM-EA-CCSD, the reference can come from a NH-SCF calculation on the neutral molecule.

C. Non-Hermitian MP2

The application of many-body perturbation theory through second order to the problem of electron correlation is well established in quantum chemistry. The derivation of the analogous non-Hermitian method (NH-MP2) exactly parallels that of the Hermitian case. The MP2 correction to the energy in terms of canonical spin-orbitals is given by

$$E^{(2)} = -\frac{1}{4}\sum_{ijab} t_{ij}^{ab}(ij||ab) \quad (3)$$

where

$$t_{ij}^{ab} \equiv \frac{(ab||ij)}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}. \quad (4)$$

Here and elsewhere we use $(ab||ij)$ to indicate the antisymmetrized electron repulsion integral in 12-12 (or "physicist's") notation. The curved bracket is used to indicate the use of the c-product. This equation assumes that the spin-orbital Fock matrix is diagonal where the occupied and virtual eigenvalues are given by ϵ_i and ϵ_a

respectively. For an RHF or a UHF reference, the spin-orbital Fock matrix is diagonal and Equation 3 is used to compute the MP2 correction to the energy.

In the case of an ROHF reference, the spin orbital Fock matrix is not diagonal. We therefore apply the restricted Moller-Plesset perturbation theory of Knowles *et al.*[70] This non-Hermitian restricted MP2 (NH-RMP2) yields an energy expression in the pseudo-canonical basis that takes explicit account of non-zero off-diagonal matrix elements of the Fock matrix (f):

$$E^{(2)} = -\sum_{ia} \frac{(f_i^a)^2}{\epsilon_a - \epsilon_i} - \frac{1}{4} \sum_{ijab} t_{ij}^{ab} (ij||ab). \qquad (5)$$

In the Δ-MP2 method, the excitation/attachment energy is found as the difference between the MP2 energies of the excited/electron-attached state and the ground state.

D. Complex coupled cluster methods

The theory behind the coupled cluster method has been described in detail (See recent reviews of CC[71] and EOM-CC[72] theory). Here we review only those points relevant to our complex implementation. From the reference NH-SCF wavefunction, the coupled-cluster equations are solved to determine the T-amplitudes:

$$(\Phi_\mu | e^{-T} H e^T | \Phi_0) = (\Phi_\mu | \bar{H} | \Phi_0) = 0. \qquad (6)$$

Again we have used curved brackets to indicate the c-product. $|\Phi_0)$ is the reference wavefunction, and $|\Phi_\mu)$ is an excited determinant relative to the reference. For CCSD, μ runs over all single and double excitations, and the equations are used to determine T truncated to include only the singles and doubles part.[68]

The equation of motion (EOM) formalism can then be used to compute electron affinities (EA) or excitation energies (EE).[69,73] In this method, one ultimately diagonalizes $\bar{H}$ in the basis of excited determinants:

$$(\bar{H} - E_{\text{CCSD}}) R | \Phi_0) = \omega R | \Phi_0). \qquad (7)$$

R is an excitation operator,

$$R^{\text{EA}} = \sum_a r^a a^\dagger + \frac{1}{2} \sum_{ia,b} r_i^{ab} a^\dagger i b^\dagger \qquad (8)$$

$$R^{\text{EE}} = \sum_{ia} r_i^a a^\dagger i + \frac{1}{4} \sum_{ia,jb} r_{ij}^{ab} a^\dagger i b^\dagger j, \qquad (9)$$

where the r-amplitudes are determined from the eigenvalue problem. Note that in a c-normalizable space, the creation and annihilation operators are related by the transpose and not the adjoint.[74] However, we still use $\dagger$-notation to indicate creation operators to avoid confusion. The complex CCSD and EOM-CCSD methods have already been described in conjunction with complex scaling[75] and complex absorbing potentials.[55,56,75–77]

The biorthogonal version of Davidson's iterative diagonalization method[78] is used to solve the large eigenvalue problem. For temporary anion shape-resonances, the orbital of the neutral molecule associated with the resonance is easily identified from its behavior as we vary θ. This orbital is used to construct a simple Koopman's type guess that is input to the Davidson procedure.

E. θ-trajectories and the computation of the Siegert energy

Despite the θ-independent properties of the exact theory, it has long been recognized that in a finite basis set, the results will depend heavily on the value of θ. We therefore search for solutions that satisfy

$$\frac{dE}{d\theta} = 0. \qquad (10)$$

This is equivalent to treating θ as a variational parameter. The stationary point is found by computing the energy for many values of θ. This "θ-trajectory" is then used as input into the analytic continuation procedure described in Ref. 16. This is a reproducible method to compute Seigert energies from θ-trajectories. However, within this method, there are still three different ways that the stationary point may be computed in practice.

For the moment, we ignore the complication that there are in general multiple points where the energy is stationary with respect to variations in θ and define a functional $\mathcal{S}[f(\theta)]$ that returns the value of the function at the point that it is stationary:

$$S[f(\theta)] = f(\theta_0) \quad \text{s.t.} \quad \left. \frac{df}{d\theta} \right|_{\theta=\theta_0} = 0. \qquad (11)$$

Using this notation, we can describe three methods, all equivalent in the complete basis set limit, for finding the Siegert energy of temporary anions as a complex attachment energy:

1. $E_{\text{res}} = S\left[E^{\text{anion}}(\theta)\right] - E^{\text{neutral}}(0)$

2. $E_{\text{res}} = S\left[E^{\text{anion}}(\theta)\right] - S\left[E^{\text{neutral}}(\theta)\right]$

3. $E_{\text{res}} = S\left[E^{\text{anion}}(\theta) - E^{\text{neutral}}(\theta)\right]$.

In general, these methods will yield different results in a finite basis. In Ref. 21, method 1 was used to determine the stationary point for NH-SCF calculations. While these three methods yield very similar results in the case of NH-SCF, we will see that this is not the case in correlated calculations. Because the stationary point in a calculation on a neutral molecule is usually very nearly on the real axis, method 2 will in practice yield very similar results to method 1 and we will be primarily concerned with the differences between methods 1 or 2 and method 3. In Sections III A and III B we will find that method 3 is the most reliable.

III. RESULTS

All methods are implemented in a development version of the QChem 4.4 package.[79] Libtensor[80] is used for all tensor manipulations, and the complex EOM-CC code presented in Refs. 56, 75, and 76 is reused. The basis sets are the same as those presented in Ref. 16. They are constructed from Dunning's augmented correlation-consistent basis sets (aug-cc-pVXZ),[81,82] but with added diffuse functions on the center of mass. The basis sets including core-valence polarization functions are constructed in precisely the same manner, but from the corresponding cc-pCVXZ basis.[83]

A. Benchmark calculations on N_2^-

The $^2\Pi_g$ shape resonance in e^--N_2 scattering is nearly unique in that there is a experimentally derived estimate of the position and width of the *pure electronic* resonance.[84] We will refer to this position of 2.32 eV and width of 0.41 eV as the accepted values. The resonance parameters computed in different basis sets at different levels of theory are shown in Table I. Here the stationary point is computed using method 1 of Section II E.

Note that while the NH-SCF results are unchanged by the inclusion of core-valence polarization functions, the results of the correlated calculations change significantly when core-valence polarization functions are included. Furthermore, while there is evidence of convergence with respect to basis set size, it is clear that even in the caug-cc-pCVQZ(cm+) basis set, the results are not entirely converged with respect to basis set size. This is in contrast to the NH-SCF results which are largely converged in the smallest caug-cc-pVDZ(cm+) basis set.

In Table II we show results from the same set of calculations, but compute the stationary point using method 3 of Section II E. While the method used for finding the stationary point makes little difference in the case of NH-SCF calculations, there are significant differences in the correlated calculations. In particular, the widths tend to be larger when computed using method 3. Only in the largest basis (caug-cc-pCVQZ(cm+)) do the two methods provide similar results. In all other cases, method 3 is clearly superior: the results are much less sensitive to the inclusion of core-valence polarization functions and the basis set effects are less pronounced. For this reason, we advocate the use of this method for all complex-basis function calculations.

While we cannot be entirely certain as to the origin of the differences between the use of method 1 and method 3, these differences are very likely due to basis set incompleteness. The less pronounced differences in larger basis sets as well as the negligible differences at the Hartree-Fock level of theory support this claim. Furthermore, it is notable that the accuracy of propagator methods (see the discussions given in Refs. 44 and 85) and EOM methods (see the discussions of EOM-CC in Refs. 71 and 72)

can be largely attributed to the cancellation of errors inherent to the direct computation of excitation energies. It makes sense that method 3 would maximize the benefit from this same cancellation of error, because this cancellation of error will be able to occur separately at each θ-point.

This is, to our knowledge, the first explicit application of a complex-coordinate based MP2 theory to molecular resonances, and we note that while the MP2 methods are unable to fully reproduce the EOM-EA-CCSD results, they represent a significant improvement relative to the NH-SCF results. In general, the effect of correlation is to lower the position but increase the width relative to NH-SCF methods. This is consistent with previous observations of similar behavior in CAP calculations.[86] We cannot entirely account for the sometimes significant differences between NH-UMP2 and NH-RMP2 energies. They are based upon entirely different Hartree-Fock references, and the explicit appearance of the non-Brillouin singles amplitudes in RMP2 may lead to a larger correlation energy.

Some selected literature results are shown in Table III. We note that at the highest level of theory (EOM-EA-CCSD), our results do not reproduce the accepted value, even in the largest basis set (caug-cc-pCVQZ(cm+)). We still overestimate both the position and width by approximately 0.15-0.2 eV. This is not surprising considering that the results are not entirely converged with respect to basis set size or level of correlation. Based on the effect of changing the basis set size, we estimate the effect of basis set incompleteness to be less than 0.05eV in the caug-cc-pCVQZ(cm+) basis. The correlation energy due to full inclusion of triple and higher excitations is more difficult to quantify. Our method can be viewed as an analytic continuation of the Gaussian-exponent stabilization method of Ref. 59. For this reason, we would expect agreement at a given level of theory and basis set. The agreement with other theoretical results is reasonable considering the basis/method-dependence of most of these methods. Also, the width is highly dependent on the bond length as will be shown in Figure 1. This means that even small geometrical discrepancies can lead to significant differences in the computed width.

B. Shape resonances in small molecules

Seigert energies for several well-known low-energy shape resonances in the caug-cc-pVTZ(cm+) and caug-cc-pCVTZ(cm+) basis sets are shown in Table IV.

These values are computed using method 3 of Section II E. Method 1, which we do not recommend, yields results that are considerably less consistent and more dependent on the basis set. These results are given in the Appendix (Table VII), and we do not refer to them further.

Again we note that the results obtained with method 3 show little sensitivity to the inclusion of core-valence

	caug-cc-pVDZ(cm+)		caug-cc-pVTZ(cm+)		caug-cc-pVQZ(cm+)	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.9517	-0.1566	2.9704	-0.1692	2.9525	-0.1547
NH-UHF	2.8366	-0.1087	2.8330	-0.1167	2.8271	-0.1078
NH-RMP2	2.6899	-0.2009	2.5203	-0.0500	2.4245	-0.1828
NH-UMP2	2.8226	-0.1661	2.5733	-0.2475	2.5532	-0.1916
EOM-EA-CCSD	2.7616	-0.1961	2.5418	-0.0223	2.5178	-0.1332

	caug-cc-pCVDZ(cm+)		caug-cc-pCVTZ(cm+)		caug-cc-pCVQZ(cm+)	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.9472	-0.1565	2.9709	-0.1657	2.9523	-0.1544
NH-UHF	2.8328	-0.1087	2.8380	-0.1152	2.8159	-0.1239
NH-RMP2	2.6922	-0.1995	2.5082	-0.1856	2.4493	-0.3030
NH-UMP2	2.8273	-0.1622	2.6701	-0.2633	2.6193	-0.2805
EOM-EA-CCSD	2.7571	-0.1931	2.5300	-0.1873	2.4591[a]	-0.2069[a]

[a] The EOM results in the largest basis are based on only 5 θ-points and are therefore more uncertain.

TABLE I. Computed Seigert energies for the lowest $^2\Pi_g$ shape resonance of N_2^-. The energies are computed as a stationary point using method 1 of Section II E. We attribute the significant differences between the energies in valence polarized and core-valence polarized basis sets to use of method 1. Method 3 (see Table II) provides more consistent results.

	caug-cc-pVDZ(cm+)		caug-cc-pVTZ(cm+)		caug-cc-pVQZ(cm+)	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF[a]	2.9531	-0.1593	2.9513	-0.1551	2.9529	-0.1511
NH-UHF[a]	2.8346	-0.1178	2.8261	-0.1067	2.8267	-0.1040
NH-RMP2	2.6726	-0.3624	2.5054	-0.2841	2.4719	-0.3121
NH-UMP2	2.8042	-0.3198	2.6612	-0.2885	2.6066	-0.2888
EOM-EA-CCSD	2.6974	-0.3137	2.5653	-0.2770	2.5205	-0.2759

	caug-cc-pCVDZ(cm+)		caug-cc-pCVTZ(cm+)		caug-cc-pCVQZ(cm+)	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.9493	-0.1602	2.9711	-0.1432	2.9530	-0.1517
NH-UHF	2.8289	-0.1164	2.8338	-0.1167	2.8145	-0.1221
NH-RMP2	2.6687	-0.3647	2.5017	-0.2860	2.4957	-0.3269
NH-UMP2	2.7950	-0.3217	2.6452	-0.3091	2.6175	-0.3150
EOM-EA-CCSD	2.6844	-0.3166	2.5342	-0.2584	2.5360[b]	-0.2604[b]

[a] These results were also reported in Ref. 21
[b] The EOM results in largest basis are based on only 5 θ-points and are therefore more uncertain.

TABLE II. Computed Seigert energies for the lowest $^2\Pi_g$ shape resonance of N_2^-. The energies are computed as a stationary point using method 3 of Section II E.

method	position	width
Stieltjes imaging[87]	2.23	0.40
Schwinger variational + ADC(3) optical potential[88]	2.53	0.54
3rd order decouplings of dilated electron propagator[89]	2.11	0.18
Multi-partitioning perturbation theory stabilization[90]	2.36	0.43
Analytic continuation in the coupling constant CCSD[39]	2.56	0.55
CAP EOM-EA-CCSD (11s,8p,3d)[54]	2.44	0.39
EOM-EA-CCSD stabilization (aug-cc-pV5Z)[59]	2.49	0.50
CAP EOM-EA-CCSD (1st order, aug-cc-pVQZ + 3s3p3d)[56]	2.48	0.29
Analytic continuation in the coupling constant CCSD(T)[66a]	2.46	0.49
Experimental estimate (accepted value)[84]	2.32	0.41
This work (EOM-EA-CCSD)	2.54	0.52

[a] The results using the attenuated Coulomb potential with $\omega = 0.01$ in the t-aug-cc-pVQZ basis set are given here.

TABLE III. Selected literature values (in eV) for the $^2\Pi_g$ shape resonance in electron-N_2 scattering from experiment and various *correlated* levels of theory. The EOM-EA-CCSD results from the caug-cc-pCVQZ(cm+) are given as the results of "This work."

caug-cc-pVTZ(cm+)	CO⁻		CO₂⁻		CH₂O⁻	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.5367	-0.3576	4.4648	-0.0780	1.7769	-0.2003
NH-UHF	2.4194	-0.2964	4.3063	-0.0619	1.6399	-0.1411
NH-RMP2	2.1193	-0.5200	4.1018	-0.1832	1.0120	-0.3011
NH-UMP2	2.1968	-0.4826	4.1829	-0.1555	1.0986	-0.2859
EOM-EA-CCSD	2.0395	-0.4974	4.0193	-0.1422	1.1810	-0.2788
caug-cc-pCVTZ(cm+)	CO⁻		CO₂⁻		CH₂O⁻	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.5405	-0.3542	4.4654	-0.0801	1.7696	-0.2113
NH-UHF	2.4241	-0.3004	4.3114	-0.0634	1.6313	-0.1478
NH-RMP2	2.1149	-0.5026	4.0919	-0.1871	1.0066	-0.2997
NH-UMP2	2.1892	-0.4784	4.1734	-0.1576	1.0934	-0.2836
EOM-EA-CCSD	2.0434	-0.5164	3.9951	-0.1432	1.1632	-0.2837

TABLE IV. Computed Seigert energies for low energy shape resonances in some molecules in caug-cc-pVTZ(cm+) and caug-cc-pCVTZ(cm+). The energies are computed as a the stationary point using method 3 of Section II E.

polarization functions. We make no attempt to fully explore the basis-set convergence, but these numbers are very unlikely to be fully converged in the triple-zeta basis sets. The true values of the pure electronic Seigert energies are not known in these cases. From the basis set convergence of N_2^- and the level of correlation, we are likely overestimating positions by 0.1-0.3 eV and width by 0.05-0.2eV. As in the case of N_2^-, the NH-MP2 results are improved significantly over the NH-SCF results.

We show some selected literature values which include electron correlation effects in Table V. Note that the experimental results listed in Table V cannot be directly compared with theory because they have not been corrected to extract the location of the pure electronic resonance. As with N_2, our results for the position of these resonances agree fairly well with other theory. Our estimates for the widths are a bit high compared with other theoretical results, but not unreasonably so. Comparing complex basis functions to CAPs at the EOM-EA-CCSD level of theory, we find that the positions agree quite well, but widths computed with complex basis functions are consistently larger than those computed with CAPs.

C. Complex potential energy curves

An important challenge for electronic resonance methods is the computation of smooth, consistent potential energy surfaces. By "consistent," we mean that the imaginary part of the resonance goes to zero at the same point that the state crosses the ground state of the target. A potential energy curve for N_2^- at the EOM-EA-CCSD level of theory is shown in Figure 1. We used a spin-restricted, NH-RHF determinant as the reference wavefunction. This choice of reference prevents us from obtaining a qualitatively correct potential energy surface at significantly stretched geometries, but we can still observe the behavior of the resonance as it crosses the ground state of the neutral. The two curves are not com-
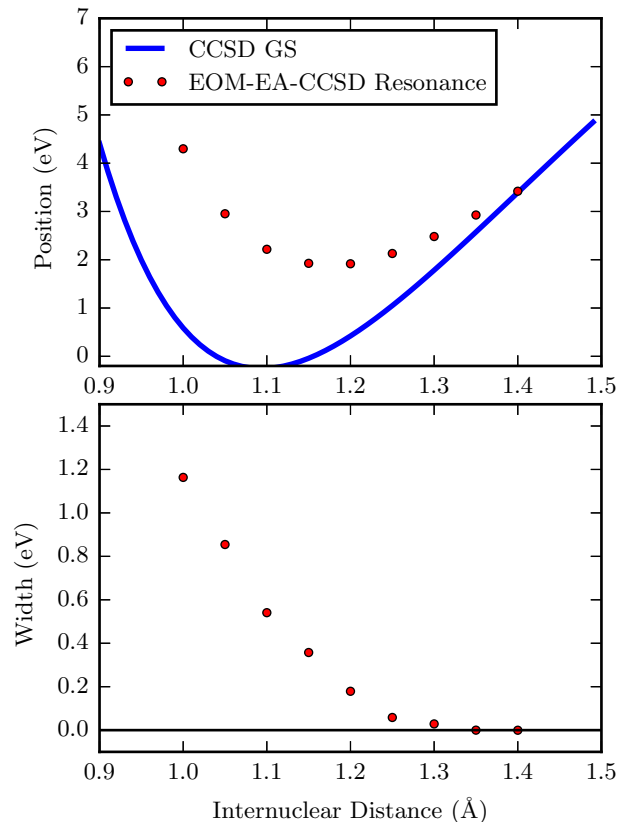

FIG. 1. Potential energy curve of N_2 neutral and anion. The neutral is computed at the complex RCCSD level of theory, and the complex excitation energy of the anion is computed at the complex restricted EOM-EA-CCSD level of theory. The basis set is caug-cc-pCVTZ(cm+).

pletely consistent: the width of the temporary anion goes to zero a bit before the two curves cross. However, this discrepancy (~ 0.05Å) is fairly small considering that the width depends only weakly on internuclear distance near

molecule	method	position	width
	2nd order electron propagator[91]	1.71	0.08
	3rd order decouplings of the electron propagator[89]	1.65	0.14
	Multi-partitioning perturbation theory stabilization[90]	2.02	0.35
CO	CAP EOM-EA-CCSD (largest basis)[54]	2.07	0.42
	CAP EOM-EA-CCSD (1st order, aug-cc-pV5Z + 3s3p3d)[56]	1.76	0.60
	Experiment[92]	1.50	0.40
	This work (EOM-EA-CCSD)	2.04	1.03
	CAP EOM-EA-CCSD(aug-cc-pVTZ-f+ 1s3p)[55]	4.20	0.22
	CAP EOM-EA-CCSD (1st order, aug-cc-pVTZ + 3s3p3d)[56]	4.00	0.20
CO_2	Analytic continuation in the coupling constant SAC-CI[64]	4.18	0.24
	CAP SAC-CI (cc-pVDZ + (2s5p2d))[64]	4.21	0.20
	Experiment[93]	3.14	0.20
	This work (EOM-EA-CCSD)	4.00	0.29
	2nd order decouplings of the dilated electron propagator (largest basis)[47]	0.89	0.076
	CAP SAC-CI (cc-pVQZ + diffuse)[94]	1.09	0.42
CH_2O	CAP EOM-EA-CCSD (1st order, aug-cc-pVTZ + 3s3p3d)[56]	1.31	0.28
	Experiment[95]	~0.67	-
	This work (EOM-EA-CCSD)	1.16	0.57

TABLE V. Selected literature values (in eV) for the resonances studied here from experiment and various levels of theory. The experimental values are uncorrected and therefore do *not* represent the properties of the pure electronic resonance. The results from EOM-EA-CCSD in the caug-cc-pCVTZ(cm+) basis are also given labelled as "This work."

the crossing region. This means that a very small absolute error in the width can lead to much larger errors in apparent point where it goes to zero. Similar curves are provided in Ref. 76 at the CAP-EOM-EA-CCSD level of theory in a very similar basis set. The positions agree very well (see the upper panel of Figure 2 of Ref. 76) with our results. The widths (see the lower panel of Figure 2 of Ref. 76) agree qualitatively, but disagree in the point where they go to zero. There is agreement that the position goes to zero at 1.40Å, but we find the width goes to zero closer to 1.35Å whereas it goes to zero around 1.45Å in Ref. 76.

Nitrogen is a difficult case for potential energy curves because it is a triple bonded system and because its dissociation products are bound by very little. For simpler, single-bonded cases, a qualitatively correct potential energy curve can be obtained from EOM-EA on top of a triplet reference. We demonstrate this process for H_2 in Figure 2. H_2 has two temporary anions of Σ symmetry that are anti-symmetric (u) and symmetric (g) with respect to inversion. The $^2\Sigma_u$ state is the lowest energy resonance and has been studied extensively.[13,18,96,97] This resonance is quite broad near equilibrium and we were unable to easily distinguish it from the continuum in this region. However, as the bond is stretched, it becomes bound near 1.60Å. There is also a $^2\Sigma_g$ state[97–99] which is not easily discernible in our calculations until around 2.6Å where it is briefly a Feshbach resonance: its position is above the singlet ground state but below the triplet parent state. Near 2.7Å this state becomes bound. The results for the crossing points agree to within 0.1Å with the calculations of Bardsley and Cohen.[98] Both these states can be obtained by adding an electron to the triplet configuration. Even though both singlet and
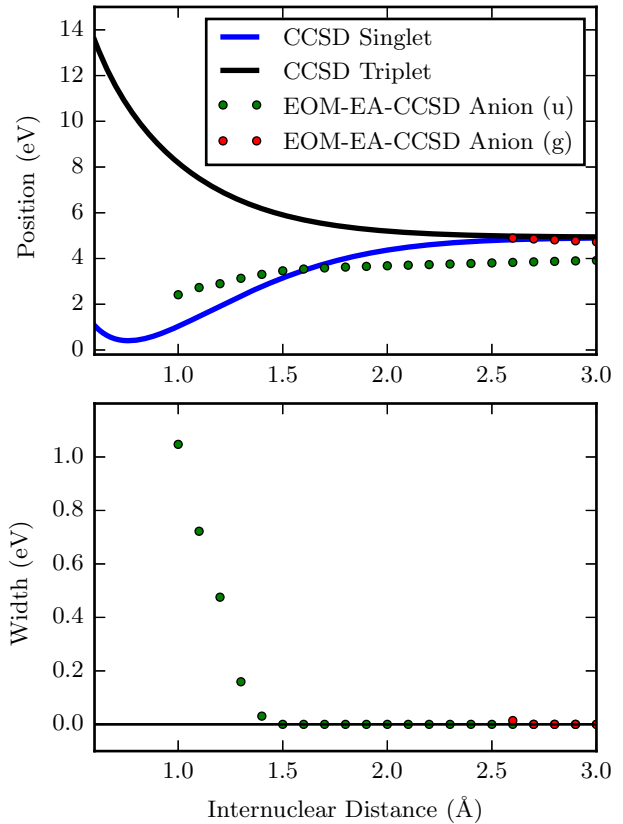

FIG. 2. Potential energy curve of H_2 neutral and anion. The neutral curves are computed at the CCSD level of theory, and the complex excitation energy of the anion is computed at the complex EOM-EA-CCSD level of theory relative to the triplet reference. The basis set is caug-cc-pVDZ(cm+). For H_2, CCSD reproduces full-CI.

Experiment		
Reference	position (eV)	width (meV)
Brunt *et al*[103]	19.366(5)	9.(1)
Kennerly *et al*[104]	19.36(2)	11.0(5)
Buckman *et al*[105]	19.367(5)	-
Dube *et al*[106]	-	10.3(3)
Gopalan *et al*[102]	19.365(1)	11.2(5)
Theory		
Reference	position (eV)	width (meV)
Junker[40]	19.387	11.72
Bylicki[107]	19.367	8.6
Gil *et al*[108]	19.357	14
Gopalan *et al*[102]	19.366	10.7
Results of the present study		
Basis	position (eV)	width (meV)
basis 1	19.28200	7.02475
basis 2	19.33005	6.88694

TABLE VI. Results from the literature and from this study for the $1s2s^2$ Feshbach resonance in e-helium scattering. Note the high precision to which the resonance parameters are known both theoretically and experimentally. The basis sets used for these computations are described in the text of Section III D

triplet states are treated exactly at the CCSD level of theory, the triplet reference is preferable because it can be reached from either anion state by a single excitation. In this way, we are able to treat both states consistently throughout the full potential energy surface in the spirit of spin-flip methods.[100] The point where the lowest energy resonance crosses the ground state of the neutral to become bound differs from the point where the width goes to zero. This is not necessarily surprising considering that the basis is relatively small and that the singlet CCSD neutral and EOM-EA anion (from the triplet reference) are *not* eigenfunctions of the same effective Hamiltonian.

D. The $1s2s^2$ Feshbach resonance in e-helium scattering

One of the simplest and most well-studied Feshbach resonances is the $1s2s^2$ Feshbach resonance in e-helium scattering. See Ref. 101 for a recent review and Ref. 102 for a fairly complete table of experimental and theoretical results. Selected theoretical and experimental results (largely reproduced from Ref. 102) are given in Table VI along with the results of this study.

EOM-EA-CCSD was used to compute the the complex energy relative to a triplet He reference. The energy relative to the singlet ground state is reported in Table VI, for two different basis sets. The basis sets were chosen to be small enough that full diagonalization of $\bar{H}$ is feasible while still including functions necessary to describe the principal contribution to the correlation energy. The first basis set is caug-cc-pVTZ(cm+) but with no d-functions. The second basis set is the caug-cc-pVTZ(cm+) basis set including valence and augmenting d-functions but with-

out the additional diffuse d-functions. The agreement with precise theoretical and experimental results is good: the width is underestimated by a large relative amount that is nonetheless very small in absolute terms. We cannot expect to be able to reproduce the accuracy of atomic calculations employing numerical basis sets, but the modest agreement in fairly small Gaussian basis sets is encouraging.

Despite this encouraging result, it can be difficult to converge iterative diagonalization algorithms to the high lying roots that are associated with Feshbach resonances. More development is necessary to make this approach applicable in general to molecular Feshbach resonances. However, this study shows that the EOM-CCSD method is, as we might expect, capable of qualitative, and maybe even quantitative, calculations on Feshbach resonances.

IV. CONCLUSIONS

We have presented an efficient implementation of correlated electronic structure methods utilizing complex basis functions for the computation of positions and widths of molecular resonances. Benchmark calculations on temporary anions of small molecules indicate that analytic continuation of the complex excitation energy (method 3 of Section II E) is the preferred method for extracting resonance parameters from θ-trajectories. Our results for the positions of these resonances agree well with the literature values, while our results for the widths are larger than those of most other correlated methods. However, because of the very large number of diffuse basis functions included in our basis sets, we believe our results to be among the most accurate available. The consistent accuracy of the NH-MP2 results should be viewed as one of the primary successes of this project. While EOM-EA-CCSD is more accurate, its computational cost makes NH-MP2 a more attractive candidate for larger systems.

We have also explored the ability of EOM-EA-CCSD to accurately describe complex potential energy surfaces and the essential physics of Feshbach resonances. The results are very encouraging overall, but currently, the computational cost and extreme basis-set requirements of the EOM-EA-CCSD method make it impractical for all but the smallest polyatomic molecules. Feshbach resonances bring additional difficulty in the convergence of the iterative diagonalization method. Further work is needed to improve the efficiency and general convergence properties of the iterative diagonalization step.

Δ-NH-MP2 is cheaper and has the advantage that it does not require solution of a large NH eigenvalue problem. However, it does require the convergence of NH-SCF calculations which can be difficult and it will break down when bonds are stretched. Further work is needed in the form of:

1. Better NH-SCF optimization algorithms for more consistent convergence

2. EOM-EA-MP2 for Feshbach resonances

3. Orbital optimized MP2 methods for an improved description of open-shell resonances

ACKNOWLEDGMENTS

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caug-cc-pVTZ(cm+)	CO^-		CO_2^-		CH_2O^-	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.5242	-0.3485	4.4625	-0.0677	1.7861	-0.2012
NH-UHF	2.4020	-0.2914	4.3096	-0.0516	1.6472	-0.1541
NH-RMP2	1.9277	-0.5528	4.2200	0.1516	1.1039	-0.1326
NH-UMP2	1.9968	-0.4565	4.2916	0.1967	1.1965	-0.1204
EOM-EA-CCSD	2.1717	0.0569	4.1477	0.1960	1.3333	-0.2025

caug-cc-pCVTZ(cm+)	CO^-		CO_2^-		CH_2O^-	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
NH-ROHF	2.5192	-0.3450	4.4599	-0.0795	1.7970	-0.1712
NH-UHF	2.4045	-0.2934	4.3140	-0.0569	1.6735	-0.1589
NH-RMP2	2.0872	-0.4445	4.0971	-0.0727	1.0269	-0.1852
NH-UMP2	2.1716	-0.4042	4.1792	-0.0481	1.0968	-0.2151
EOM-EA-CCSD	1.9148	-0.2368	3.9970	-0.0426	1.1876	-0.1808

TABLE VII. Computed Seigert energies for low energy shape resonances in some molecules in caug-cc-pVTZ(cm+) and caug-cc-pCVTZ(cm+). The energies are computed as a the stationary point using method 1 of Section II E.

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