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Journal

The Journal of Chemical Physics, 142(5)

ISSN

0021-9606

Authors

White, Alec F
Head-Gordon, Martin
McCurdy, C William

Publication Date

2015-02-07

DOI

10.1063/1.4906940

Peer reviewed

Complex basis functions revisited: implementation with applications to carbon tetrafluoride and aromatic N-containing heterocycles within the static-exchange approximation

Alec F. White,¹ Martin Head-Gordon,¹ and C. William McCurdy^{2,3}

¹*Department of Chemistry, University of California, Berkeley and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

²*Chemical Sciences and Ultrafast X-ray Science Laboratory, Lawrence Berkeley National Laboratory, Berkeley CA 94720*

³*Department of Chemistry, University of California, Davis, CA 95616 USA*

(Dated: 12 January 2015)

The method of complex basis functions for computing positions and widths of molecular resonances is revisited. An open-ended and efficient implementation is described. The basis set requirements of the complex basis are investigated within the computationally inexpensive static-exchange approximation, and the results of this investigation lead to a hierarchy of basis sets for complex basis function calculations on small molecules. These basis sets are then applied in static-exchange calculations on some larger molecules with multiple low energy shape resonances: carbon tetrafluoride, benzene, pyridine, pyrimidine, pyrazine, and s-triazine. The results indicate that more sophisticated methods using complex basis functions are worth pursuing in the search for accurate and computationally feasible methods for computing resonance energies in molecular systems.

PACS numbers: 34.80.Bm, 34.20.-b, 32.80.Zb 33.80.Eh

I. INTRODUCTION

Over the past 40 years, complex coordinate methods have proven to be useful for the computation of Siegert energies of atomic and molecular resonances.¹⁻⁴ Originally motivated by the theorems of Aguilar, Balslev and Combes,^{5,6} and Simon,⁷ these methods involve some analytic continuation of the Hamiltonian to generate a non-Hermitian effective Hamiltonian that includes in its spectrum discrete, complex, Siegert energies corresponding to square-integrable eigenfunctions.

Unfortunately, the extension of the mathematically rigorous techniques to the molecular problem in the Born-Oppenheimer (fixed-nuclei) approximation, is not straightforward. Of the many suggested solutions to this problem, the most popular method has been to add to the molecular Hamiltonian a complex-absorbing-potential (CAP).⁸⁻¹¹ This method is related to complex scaling^{12,13} and simple to apply, but suffers from a significant dependence of the complex-energies on the form of the CAP and a perturbation of the bound state energies.¹⁴ These issues have been largely overcome in recent work using a density matrix approach,¹⁵ however calculations with CAPs have indicated that the application of this method to Feshbach resonances is not straightforward.^{16,17}

The complex basis function technique of McCurdy and Resigno¹⁸ does not suffer from the same problems, but is difficult to implement in an efficient manner. Even so, many older calculations¹⁹⁻²⁵ as well as some more recent calculations by Honigmann et al.²⁶⁻²⁹ have demonstrated the practicality of the method. Specifically, the method of complex basis functions has been shown to provide a description of molecular resonances including polarization effects in the context of complex restricted open-shell Hartree-Fock (ROHF).^{21,22,24,27} Calculations using a multi-configurational self-consistent field (MCSCF)²⁵ or multi-reference configuration interaction (MRCI)²⁶⁻²⁹ wavefunction are capable of describing correlation and are therefore applicable to Feshbach resonances. However, these previous applications have been limited to atoms and diatomic molecules and there has been no systematic investigation of the basis set requirements of this method. In fact, despite the numerous complex-coordinate and CAP methods, there are only a few investigations of the basis set requirements. Specifically, there has been recent work on the basis set requirements of CAP methods,³⁰ construction of Gaussian basis sets for Rydberg and resonance states of helium,³¹ and on construction of complex STO-NG basis sets for photoionization calculations of atoms

and diatomic molecules.³²

In the present study, an efficient implementation of the method of complex basis functions within the static-exchange approximation is used to explore the basis set requirements of the method, and some applications to shape resonances in larger molecules are presented.

In the static-exchange (SE) approximation, the orbitals of the target are assumed to be frozen, but exchange effects are taken into account. It is the simplest approximation that could be expected to yield qualitatively correct results for low-energy shape resonances. SE calculations have been used to generate guesses for ROHF calculations employing complex basis functions,²² but the static-exchange energies are not reported. The SE approximation is not particularly useful for quantitative estimates of Siegert energies, but its simplicity makes it ideal for investigations of basis set convergence. Also, as the fastest method, it will always be the only practical method for the largest systems.

II. THE METHOD OF COMPLEX BASIS FUNCTIONS

The method of complex basis functions, originally introduced by McCurdy and Recigno,¹⁸ uses the unscaled molecular Hamiltonian in a basis set including Gaussian functions with complex exponents. The justification originally given is that a matrix element of the complex scaled Hamiltonian over basis functions of a real valued coordinate can be equivalently written as a matrix element of unscaled Hamiltonian over basis functions with a complex coordinate. In a Gaussian basis this is asymptotically equivalent to using basis functions with complex exponents. This method is equivalent to analytic continuation of the matrix elements of the Hamiltonian which was shown by Moiseyev and Corcoran³³ to effectively avoid the non-analyticities introduced by complex scaling in the Born-Oppenheimer approximation.

Another justification can be made by applying the complex variational principle³⁴⁻³⁶ to the exterior scaled molecular electronic Hamiltonian \tilde{H} . The spectrum of the exterior scaled, non-dilatation-analytic, molecular electronic Hamiltonian has been rigorously shown to mimic the behavior of the spectra of complex scaled dilatation-analytic Hamiltonians.³⁷ Applying the complex variational principle to the exterior scaled Hamiltonian we get that:

$$\frac{(\psi|\tilde{H}|\psi)}{(\psi|\psi)} = E_{\text{trial}}. \tag{1}$$

This provides a stationary approximation to the true Siegert energy, where the rounded brackets indicate that the c-product,³⁵ where the bra is not complex conjugated, is used, and $|\psi\rangle$ is some c-normalizable trial function. A change of variables followed by a contour distortion reveals one may just as well search for stationary points of the functional

$$\frac{(\tilde{\psi}|H|\tilde{\psi})}{(\tilde{\psi}|\tilde{\psi})} = E_{\text{trial}} \quad (2)$$

where $|\tilde{\psi}\rangle$ is also just a c-normalizable function. Note that the transformation is also applied to the denominator so as to absorb the Jacobian of the transformation into the new trial function $|\tilde{\psi}\rangle$. In this sense, the method of complex basis functions can be viewed as a finite basis approximation to exterior complex scaling, a point that was argued by Morgan and Simon.³⁸

In theory, any c-normalizable basis can be used, but in practice Gaussian basis sets are a practical choice because the Gaussian product theorem greatly simplifies the computation of multicenter integrals. In order to reproduce as closely as possible the correct asymptotic form of the matrix elements of the exterior scaled Hamiltonian, a mixed one-electron basis set of tight real Gaussians and diffuse Gaussians with complex exponents will be used. The complex Gaussians have the form

$$\begin{aligned} \phi_{\theta}(r) &= N(\theta)(x - A_x)^l(y - A_y)^m(z - A_z)^n \\ &\times \exp[-\alpha e^{-2i\theta}(\mathbf{r} - \mathbf{A})^2] \end{aligned} \quad (3)$$

where θ mimics the rotation angle in traditional complex scaling, and $N(\theta)$ is a normalization factor. Although the problem has been reduced to a finite basis set expansion, the requirements of this complex basis have the potential to be complicated and problem dependent. It then becomes necessary, as in traditional complex scaling calculations, to do a variational search in an auxiliary parameter. This one-electron basis is convenient because it has much in common with the basis sets of electronic structure theory including manageable analytic schemes for computing two-electron integrals.

In the simplest approximation, molecular anions can be described by the static-exchange Hamiltonian

$$H = h_{\text{core}} + 2J - K \quad (4)$$

where orbitals of the N electron target are fixed, and the density is used to generate J and K . The core orbitals are assumed to be doubly occupied and can be generated with a

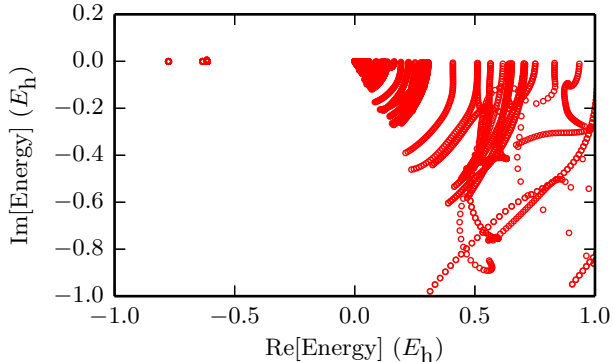


FIG. 1. Theta trajectories for N_2 in the caug-cc-pVTZ(cm+) basis.

restricted Hartree-Fock (RHF) calculation in a basis of purely real functions. The matrix representation of H in the basis of particle configurations including complex basis functions is diagonalized to get approximations to the Siegert energies of the $N + 1$ electron state. This simple method reduces to building a Fock matrix using a real N -electron density in a basis including complex basis functions, then diagonalizing the virtual block to get new, complex, virtual orbital energies which correspond to complex energies of the $N + 1$ electron state. If the full Fock matrix is diagonalized, the first N orbital energies should correspond to the ionization energies needed to access various $N - 1$ electron states. These energies should closely approximate the real occupied orbital energies obtained in the initial N electron calculation since they are not self-consistent. The static-exchange approximation is generally a quite poor approximation, but the low cost of the method allows for a detailed study of basis set requirements and application to shape resonances in some larger molecules.

An example of this method applied to N_2^- is shown in Figure 1. In this case the full Fock matrix was diagonalized in a basis including complex Gaussians to get energies of $N - 1$ and $N + 1$ electron states. The process was repeated for θ going from 0.5° to 30° in intervals of 0.5° . Detailed plots of the behavior of continuum, bound, and resonance roots are shown in Figure 2. The low energy continuum roots are rotated into the lower half plane at an angle of approximately θ as in complex scaling. The energies of the $N - 1$ electron states which are all bound remain mostly real with the small imaginary part attributable to basis-set incompleteness. The well-characterized ${}^2\Pi_g$ resonance stands out clearly from the continuum, and the stationary point is easily identified with the Siegert energy.

Though the stationary points are almost always recognizable from visual inspection, a

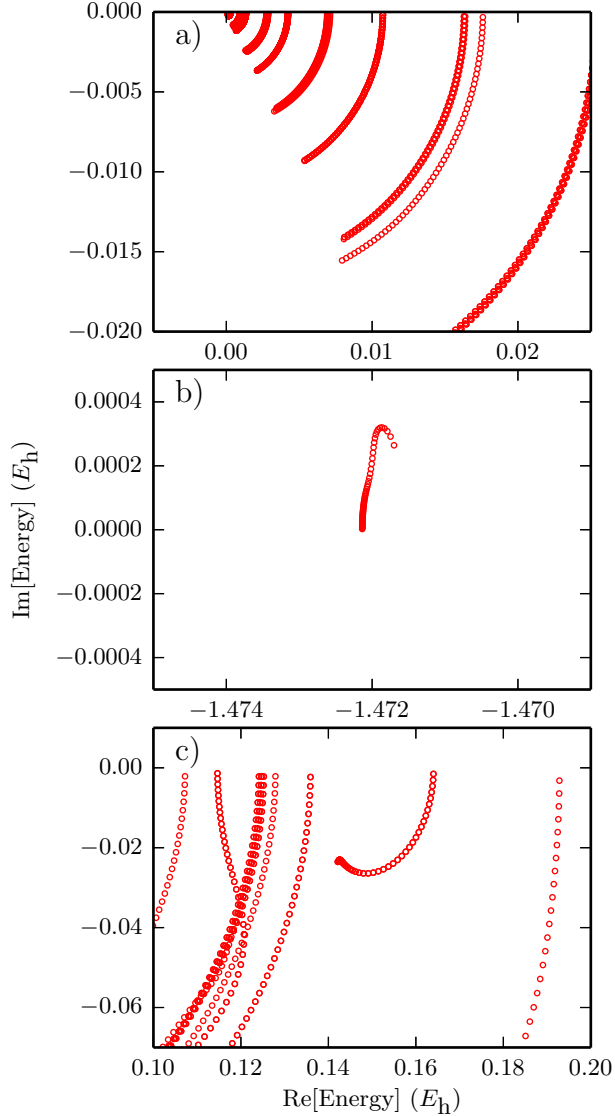


FIG. 2. Detailed plots of continuum (a), bound (b), and resonance (c) eigenvalues from Fig 1.

method to identify them consistently and precisely is desirable. This is accomplished via analytic continuation of the energy of the resonance as a function of θ .²² The “point method” of Schlessinger³⁹ is used to construct a rational interpolant that goes through all the available points. This interpolant is constructed from a continued fraction representation that is equivalent to an $[N/M]$ Pade Approximant given $N + M + 1$ energy points. The continued fraction has the form

$$C(\theta) = \frac{E(\theta_1)}{1+} \frac{a_1(\theta - \theta_1)}{1+} \dots \frac{a_n(\theta - \theta_n)}{1} \quad (5)$$

where the coefficients a_i are determined from the conditions that the function passes through

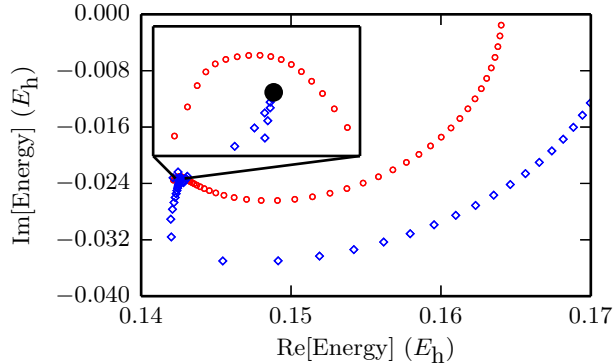


FIG. 3. Plot of resonance theta trajectory (\circ), stationary point (\bullet), and theta trajectory with optimized exponents (\diamond). The optimized exponents correspond to an optimal value of $\theta = 0.408 + i0.040$.

the specified points. The derivative of the continued fraction can be found analytically, and the zeros of this function can be computed using Newton's method. In this way, the variational stationary point with respect to the scaling parameter can be found by fitting the complex energies from any variational calculation performed at a series of θ values to a Pade approximant and numerically finding the solution of

$$\left. \frac{dE_{\text{trial}}(\theta)}{d\theta} \right|_{\theta_s} = 0. \quad (6)$$

The value of θ_s found in this way can be complex-valued, corresponding to an overall real scaling of the complex exponents. Allowing θ to obtain a complex value has been shown to be important in finding the truly stationary point,⁴⁰ but in practice the imaginary parts of the optimal θ are found to be generally less than 0.05. An example of the application of this method to N_2^- is shown in Figure 3. The stationary point was computed from the θ -trajectory in the caug-cc-pVTZ(cm+) basis (\circ) which will be described in Section IV. Given the approximation to the stationary θ_s found in this way, the complex exponents in the basis were scaled so that the resulting curve (\diamond) should pass through the stationary point. This result shows the validity of this analytic continuation method. In practice, this method is assumed to give an accurate value for the stationary energy if the computed stationary energy and θ -value lie close to the actual trajectory.

The wavefunction corresponding to the complex SE energy is of course square integrable and is not unlike the orbitals obtained from bound state calculations. However, because of the complex normalization, the magnitude of the wavefunction does not integrate to one,

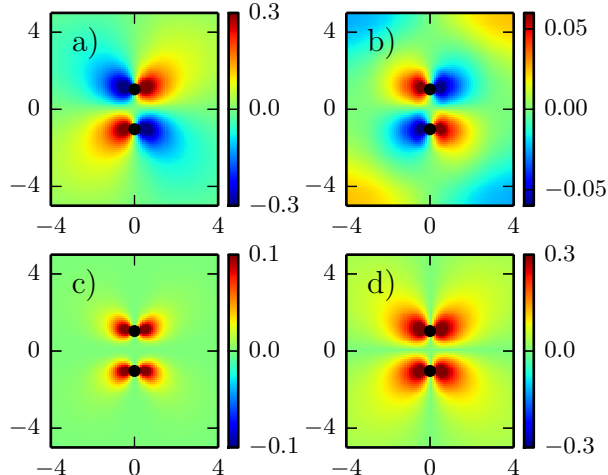


FIG. 4. Contour plots in the xz -plane of the real part (a), imaginary part (b), and magnitude (d) of the resonance orbital as well as the real part of the resonance density (c). The atomic centers are denoted by (\bullet), and the z -axis is the molecular axis. Both axes are in atomic units (a_0)

and it is instead the real part of the complex density

$$\rho(\mathbf{x}) = (\phi|\mathbf{x})(\mathbf{x}|\phi) = \phi(\mathbf{x})^2 \quad (7)$$

that will integrate to 1. The normalization also guarantees that the imaginary part of the density is traceless. These quantities are visualized for a typical case (one component of the π_g resonance orbital, N_2 , c-aug-cc-pVTZ(cm+) basis) at the stationary value of θ in Figure 4. In the valence region, the wavefunction resembles a π_g antibonding orbital. At larger distances the oscillations characteristic of complex-scaled wavefunctions become apparent. These oscillations are shown in more detail in Figure 5. Despite the prominent oscillations in real and imaginary parts of the wavefunctions, the real part of the density has only very small oscillations and largely resembles the density of a real bound state orbital.

III. IMPLEMENTATION

The static-exchange method using complex basis functions has been implemented in the Q-Chem electronic structure package.⁴¹ The Armadillo C++ linear algebra library was used for all matrix operations.⁴²

The basis set representation of the Hamiltonian in a c-orthonormal complex basis requires one- and two-electron integrals common to standard electronic structure methods. The one-

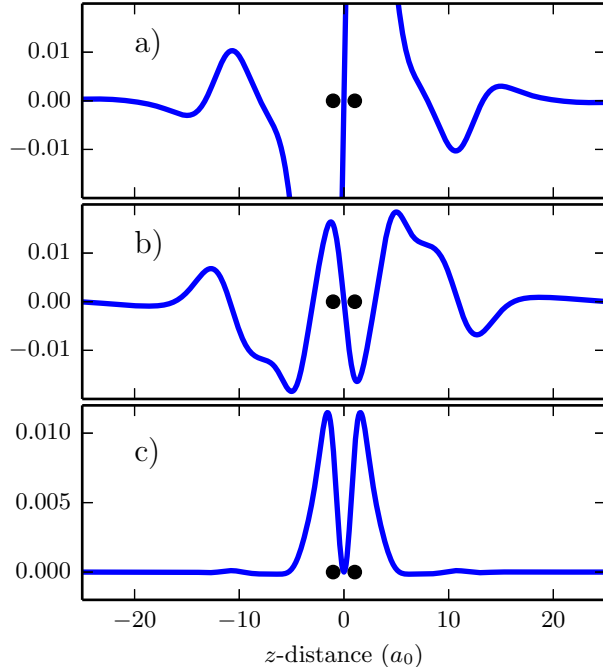


FIG. 5. Plots along the line $x = 2, y = 0$ a_0 of the real part (a) and imaginary part (b) of the xz -component of the resonance orbital, and the real part of the complex density (c). The positions of the atomic centers along the z -axis are denoted by (•)

electron integrals are computed using general explicit formulas originally given by Taketa et al.⁴³ These formulas are also valid for Gaussian basis functions with complex exponents, α , provided that $\text{Re}[\alpha] > 0$.

The computation of the two-electron integrals, also called electron repulsion integrals (ERIs), can be computed in the same manner as in standard electronic structure codes. Unlike in previous implementations of complex basis functions, the integrals are computed directly and never explicitly stored as is common in modern electronic structure programs. The recursion relations common in ERI evaluation are in general the same for basis functions with complex exponents. The Head-Gordon Pople (HGP)⁴⁴ method and one path (operator, contraction, momentum, and density or OCLD) of the COLD-PRISM⁴⁵ method, both implemented in Q-Chem, were appropriately modified for complex arithmetic. These evaluation schemes are both based on the recurrence relations of Obara and Saika⁴⁶ and additionally on those of McMurchie and Davidson⁴⁷ in the case of the COLD-PRISM. These recurrences have the same analytic form when exponents are complex as long as $\text{Re}[\alpha] > 0$.

As in the real case, the first step in ERI evaluation is the computation of the Boys

function,

$$F_m(T) = \int_0^1 t^{2m} e^{-Tt^2} dt \quad (8)$$

where the index m runs from 0 to $l_a + l_b + l_c + l_d$ and T depends on the exponents and centers of the 4 basis functions. For basis functions with complex exponents, T is complex. In the case of real basis functions, this step is often accelerated using Chebyshev interpolation;⁴⁸ however, an interpolation scheme for complex F as a function of complex T is necessarily two-dimensional and is significantly more difficult. Instead, the Boys function is computed on the fly when it is evaluated for complex T . For small values of T ($|T| < 10$), F is computed for the maximum required m according to

$$F_m(T) = \frac{1}{2} e^{-T} \Gamma\left(m + \frac{1}{2}\right) \sum_{n=0}^{\infty} \frac{T^n}{\Gamma(m + n + 3/2)} \quad (9)$$

where the sum is truncated when the terms become negligible. The Boys function for the remaining values of m is computed by recursion:

$$F_{m-1}(T) = \frac{1}{2m-1} [2TF_m(T) + e^{-T}]. \quad (10)$$

For large T ($|T| \geq 10$), the downward recursion becomes unstable, so $F_0(T)$ is computed by the explicit formula,

$$F_0(T) = \frac{1}{2} \sqrt{\frac{\pi}{T}} \operatorname{erf}(\sqrt{T}) \quad (11)$$

and recursion is used to compute F for the remaining values of m :

$$F_{m+1}(T) = \frac{(2m+1)F_m(T) - e^{-T}}{2T}. \quad (12)$$

After the Boys function has been computed for a given shell-quartet of integrals, the application of the recursion relations proceeds as in the real case. This implementation is sufficiently general so as to also allow for Hermitian calculations using complex basis functions. The algorithm described here provides at least 11 significant figures in the relevant regions of the complex plane, and an algorithm capable of providing machine accuracy has been described elsewhere.⁴⁹

In the Hermitian case it is common to ignore certain shell-quartets that can be shown to be negligible due to the so-called Schwarz bound,⁵⁰ but for a non-Hermitian calculation this bound does not apply because the ERIs are not positive definite.

The implementation of the required matrix manipulations is straightforward, though some care must be taken with notions of orthogonality and unitarity. In the complex, bi-orthogonal

space relevant to the problem, complex-orthogonal (c -product preserving) matrices replace unitary matrices. In all relevant cases, the eigenvectors of a complex-symmetric matrix can be made c -orthonormal so that the matrix of eigenvectors is complex-orthogonal. However, if two eigenvalues lie close together, there is no guarantee that the eigenvectors found by a general non-symmetric eigensolver will have this property. Therefore, a modified Gram-Schmidt method that utilizes the c -product must be used to ensure that the matrix of eigenvectors obtained from a complex-symmetric matrix are complex-orthogonal.

IV. BASIS SETS

The reduction of the scattering problem to a variational search within a basis set is undoubtedly a simplification of the problem, but the requirements and convergence properties of the c -normalizable basis set are not known. It is therefore of great practical importance to explore the basis set requirements of a typical molecular shape resonance and construct a hierarchy of basis sets for general applications.

A. Requirements for a complex basis

In previous applications of complex basis functions, knowledge of the symmetry of the resonance was generally used to pick the basis set on a case by case basis.^{22,23} While this method can be successful, it is difficult to apply in cases where the symmetry of the resonance is not known or the molecule has low symmetry. This method also precludes using the same basis set to describe multiple resonances. In addition to being sufficiently general to describe resonances of different symmetry, an ideal hierarchy of basis sets would be computationally practical, converge to the basis set limit, and have a well-defined relationship with the real basis sets of quantum chemistry that have already been optimized for bound states.

As in many types of basis set calculations, linear dependence in the basis can be a problem. This is a particular difficulty for complex basis function calculations, because the matrix playing the role of the metric is not a Hermitian matrix. Also, any analytic continuation scheme will suffer if basis functions are discarded in a discontinuous manner. Ideally, linear dependence should be avoided.

A further problem is that there is no guarantee that the complex energy will have only

one stationary point as a function of θ . This is not necessarily surprising, because θ is a highly non-linear parameter. However, the basis set should be large enough that artificial stationary points associated with basis set incompleteness are avoided.

In practice these requirements will be impossible to satisfy for all systems. In the following sections, the ${}^2\Pi_g$ resonance in N_2^- at an inter-nuclear distance of 1.094\AA is used as a typical example of a molecular shape resonance. The basis set requirements of this system are explored in detail and simple generalizations are made about basis sets for general molecular resonances. In all cases, the static-exchange energies were computed for $\theta = 0^\circ$ to $\theta = 30^\circ$ at intervals of 0.5° . The analytic continuation scheme described earlier is used to precisely find the stationary point in the complex plane.

B. The role of diffuse complex functions

In order to explore the role of diffuse complex basis functions in the description of the resonance, shells of d-functions on the center of the molecule or shells of p-functions on each nitrogen were added one by one. In both cases, an even-tempered set of functions with a spacing of 2.3 and starting at 1.75×10^2 is used. The most diffuse exponent in this series is $\alpha = 1.24 \times 10^{-4}$. Table I shows the resonance energy with added complex functions using 6-31G* as the real basis. As expected, tight functions alone do not allow for any description of the resonance, and it is only with functions with exponents on the order of 1 that the resonance can be found at all. In both cases, the resonance energy converges, and functions beyond a certain diffuseness are not necessary. However the energies with p-functions and with d-functions converge to slightly different values. This can be attributed to the tight p-functions which may be necessary to describe the resonance near the nuclei.

The same calculations were performed in the cc-pVQZ real basis set and the results are also shown in Table I. For this particular resonance, there is relatively little change in the limiting results as the real basis is changed from 6-31G* to cc-pVQZ. Similar conclusions can be drawn about the relevant range of exponents necessary for describing the resonance, but in the larger basis, the calculations involving p-functions and those involving d-functions converge to almost the same energy. This is likely because the real basis is much closer to completeness, and adding tight p-functions is redundant.

This importance of the tight complex functions is examined by systematically removing

# of shells	6-31G*				cc-pVQZ			
	d-functions		p-functions		d-functions		p-functions	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
7	4.6810	-0.0196			4.2293	-0.0001		
8	4.6837	-0.0157	4.5570	-0.0043	4.2259	-0.0147	4.1875	-0.0339
9	4.6790	-0.0149	4.5550	-0.0099	4.2265	-0.0204	4.1831	-0.0147
10	3.9172	-0.5155	3.7876	-0.5816	3.8171	-0.6080	3.7750	-0.5298
11	3.8808	-0.5662	3.8503	-0.6390	3.8120	-0.7023	3.8721	-0.6071
12	3.8489	-0.5778	3.8449	-0.5999	3.8228	-0.6372	3.8329	-0.6072
13	3.8799	-0.6000	3.8499	-0.6023	3.8299	-0.6306	3.8440	-0.6126
14	3.8859	-0.6099	3.8507	-0.6033	3.8534	-0.6197	3.8461	-0.6151
15	3.8874	-0.6134	3.8509	-0.6037	3.8545	-0.6200	3.8466	-0.6160
16	3.8878	-0.6147	3.8509	-0.6038	3.8534	-0.6208	3.8468	-0.6164
17	3.8879	-0.6151	3.8510	-0.6039	3.8534	-0.6209	3.8468	-0.6165
18	3.8880	-0.6153	3.8510	-0.6039	3.8534	-0.6210	3.8468	-0.6165

TABLE I. Energy of the ${}^2\Pi_g$ resonance in N_2 as more shells of functions are added to the center (d-functions) or to the two Nitrogen atoms (p-functions). The real basis is 6-31G* or cc-pVQZ.

the shells of tight functions. The results for 6-31G* and for cc-pVQZ are shown in Table II. As expected, the tight d-functions are not necessary for describing the resonance, and the tight p-functions are only necessary in the case of an incomplete real basis. In other words, only the diffuse functions need be complex. This makes physical sense because the functions with complex exponents are necessary to implicitly apply correctly decaying outgoing wave boundary conditions in the asymptotic region where only diffuse functions are significantly non-zero.

C. The role of the even-tempered spacing

The role of the even-tempered spacing is explored in the 6-31G* and cc-pVQZ basis sets (Table III). The even-tempered spacing of the added complex functions was systematically

# of shells	6-31G*				cc-pVQZ			
	d-functions		p-functions		d-functions		p-functions	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
18	3.8880	-0.6153	3.8510	-0.6039	3.8534	-0.6210	3.8468	-0.6165
17	3.8880	-0.6151	3.8511	-0.6029	3.8534	-0.6210	3.8467	-0.6156
16	3.8880	-0.6144	3.8482	-0.6008	3.8534	-0.6210	3.8456	-0.6120
15	3.8880	-0.6123	3.8625	-0.5488	3.8534	-0.6210	3.8507	-0.5888
14	3.8878	-0.6065	3.9110	-0.4755	3.8534	-0.6209	3.8270	-0.5922
13	3.8866	-0.5912	3.8925	-0.5100	3.8533	-0.6209	3.8311	-0.5949
12	3.8757	-0.5560	3.8806	-0.5322	3.8528	-0.6202	3.8289	-0.6123
11	3.8619	-0.5687	3.8680	-0.5504	3.8523	-0.6193	3.8592	-0.6260
10	3.8354	-0.5988	3.8376	-0.5967	3.8513	-0.6173	3.8532	-0.6168
9	3.9209	-0.5921	3.9195	-0.5928	3.8399	-0.6120	3.8410	-0.6114
8	3.8225	-0.5561	3.8238	-0.5555	3.8039	-0.6361	3.8042	-0.6354

TABLE II. Energy of the ${}^2\Pi_g$ resonance in N_2 as tight functions are removed. The real basis is 6-31G* and cc-pVQZ.

changed, and the number of shells was changed as well so that the exponents span roughly the same range. The largest exponent was 1.75×10^2 in all cases, and the smallest exponent is shown in Table III.

The two most striking effects are that the energies in the smaller basis are more sensitive to the even-tempered spacing than the energies in the larger basis, and that the energies computed with complex d-functions are much more sensitive than those computed with complex p-functions. The first of these effects is easily attributable to the incompleteness of the real basis. The second is likely due to the fact that for the d-functions centered in the middle of the molecule, the even-tempered spacing affects the behavior near the two nitrogen centers. This accounts for the oscillatory behavior of the energy as the even-tempered spacing is changed. The basis set is clearly starting to break down around an even-tempered spacing of 2.8, and the spacing of 2.3 that was used in the previous calculations is relatively conservative.

spacing	# of shells	min. exponent	6-31G*				cc-pVQZ			
			d-functions		p-functions		d-functions		p-functions	
			Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
2.0	21	1.67E-04	3.9652	-0.6177	3.8443	-0.6020	3.8503	-0.6219	3.8448	-0.6245
2.1	20	1.32E-04	3.8540	-0.6858	3.8454	-0.6095	3.8512	-0.6302	3.8441	-0.6264
2.2	19	1.20E-04	3.9177	-0.6781	3.8330	-0.6041	3.8379	-0.6232	3.8414	-0.6280
2.3	18	1.24E-04	3.8880	-0.6153	3.8493	-0.5989	3.8534	-0.6210	3.8468	-0.6165
2.4	17	1.44E-04	3.9819	-0.6141	3.8382	-0.6214	3.8210	-0.6191	3.8405	-0.6411
2.5	16	1.88E-04	3.8161	-0.5814	3.8316	-0.5866	3.8472	-0.6156	3.8316	-0.6023
2.6	16	1.04E-04	3.7830	-0.6030	3.8576	-0.5855	3.8360	-0.6617	3.8398	-0.6110
2.7	15	1.60E-04	3.9430	-0.5933	3.8647	-0.5850	3.8404	-0.6131	3.8719	-0.6188
2.8	14	2.68E-04	3.7497	-0.6779	3.8621	-0.5629	3.8365	-0.6123	3.8122	-0.6521
2.9	14	1.71E-04	3.7493	-0.7132	3.8205	-0.6684	3.8770	-0.6776	3.8129	-0.6706
3.0	14	1.10E-04	3.7589	-0.7482	3.8601	-0.6863	3.8911	-0.6752	3.8275	-0.6953
3.2	13	1.52E-04	3.8589	-0.5229	3.7144	-0.5637	3.8161	-0.6162	3.8097	-0.5811
3.4	12	2.49E-04	3.8812	-0.8710	3.6648	-0.6613	3.9321	-0.6563	3.9324	-0.6885
3.6	12	1.33E-04	3.8138	-0.5460	3.9349	-0.4971	3.9490	-0.6439	3.9524	-0.6583

TABLE III. Energy of the ${}^2\Pi_g$ resonance in N_2 as the even tempered spacing of the added complex functions is changed. The real basis sets are 6-31G* and cc-pVQZ. The even tempered series was extended so that the exponents are of more than sufficient diffuseness based upon the results of section IV B.

D. General scheme: caug-cc-pVXZ(cm+) basis sets

In general, the angular momentum requirements of the basis set will be highly problem-dependent. A flexible one-electron basis set should therefore contain complex functions on multiple centers so that functions of very high angular momentum can be avoided. Something akin to Dunning's scheme of adding diffuse functions to each center⁵¹ is necessary so that the complex part of the basis is flexible enough to describe molecular resonances of different character. However, this protocol will often be accompanied by problems with

linear dependence that can be avoided by a single center expansion. For this reason, it seems advisable to combine atom-centered and center of mass complex basis functions to define a viable basis set.

In this section, a general scheme for complex basis sets for small molecules is presented. This scheme, which will be referred to as the *caug-cc-pVXZ(cm+)* ($X = D, T, Z, \dots$), consists of the real correlation consistent basis sets,⁵² each angular momentum augmented by a shell of complex functions with diffuse of on each center. Additionally, diffuse complex functions with maximum angular momentum equal to the maximum angular momentum of the real basis are added on the center of mass. The atomic centered diffuse functions have the same exponents as the corresponding *aug-cc-pVXZ*⁵¹ basis set but scaled by the complex number $e^{-2i\theta}$. The diffuse functions on the center of mass are even-tempered, and start at one even-tempered spacing more diffuse than the most diffuse atom-centered function.

In the following calculations, an even-tempered spacing of 2.3 was used for all center of mass functions. The DZ basis was augmented with 7 shells of s-functions, 7-shells of p-functions, and 6-shells of d-functions. The TZ basis also includes 5 shells of f-functions, and the QZ basis additionally includes 4 shells of g-functions. These are very large basis sets and are probably larger than necessary in terms of both the even-tempered spacing and the diffuseness of the center of mass functions. However, despite the large number of basis functions including some very diffuse functions, linear dependence is not a problem when these basis sets are used for small molecules.

Table IV shows resonance energies of N_2^- (Π_g), CO_2 (Π_u), and formaldehyde (B_1). Since the symmetry of these resonances are known, the *caug-cc-pVXZ(cm+)* basis sets are not the most efficient choice, since they are based on the presumption that the symmetry of the resonance is not known *a priori*. Furthermore, the simple nature of these resonances means that even the smallest of these basis sets offers a good descriptions of the resonance with the possible exception of CO_2 . Indeed the reasonable energy of the Π_u resonance of CO_2 in the *caug-cc-pVDZ(cm+)* basis is a bit surprising since the atomic centered p-functions would be expected to provide only a limited description of a diffuse π_u orbital. The important point is that these basis sets offer a systematic way to examine the convergence of a Siegert energy with respect to basis set size in the context of the method of complex basis functions. The QZ basis used here is by far the largest basis set hitherto employed in this kind of calculation.

Basis	N ₂		CO ₂			CH ₂ O	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	
caug-cc-pVDZ(cm+)	3.9752	-0.6363	5.5268	-0.2972	2.6848	-0.8078	
caug-cc-pVTZ(cm+)	3.8818	-0.6301	5.5035	-0.3435	2.6459	-0.7887	
caug-cc-pVQZ(cm+)	3.8413	-0.6215	5.4733	-0.3500	2.5775	-0.8170	
geometry	N≡N(1.094Å)		C=O(1.16Å)		CH(1.11Å), C=O(1.205Å), H-C-H(116.2°)		

TABLE IV. SE energies of resonances in N₂, CO₂ and formaldehyde as the basis size is increased

For larger molecules, the center of mass is less important, and this basis set scheme is likely not ideal. Something akin to a double or triple augmentation on each center would likely be most effective, but linear dependence is a serious problem for such a scheme, and an effective method for dealing with linear dependence will likely be necessary to perform reliable calculations on large, asymmetric molecules.

V. APPLICATIONS

In this section, Siegert energies are calculated using the method described above for more complicated molecules with multiple resonances. These energies are compared with literature and experiment and some features of the method are explored.

A. Overlapping resonances in carbon tetrafluoride

Carbon tetrafluoride has been observed to have two low energy shape resonances of A₁ and T₂ symmetry. A summary of older experimental results can be found in Ref. 53. More recently, CF₄ has been the subject of some studies of orientation effects in dissociative electron attachment processes that may proceed through these resonances.^{54,55}

The resonance energies of the two lowest shape resonances of CF₄ (C-F = 1.33Å) are reported in Table V along with other calculations from the literature. The complex basis function results show the T₂ resonance position to be lower in energy than that of the A₁ resonance which is in agreement with most of the previous theoretical and experimental results. The best theoretical treatment to date is the Schwinger multichannel calculations

reference	T ₂ resonance		A ₁ resonance		method/basis
	Position	Width	Position	Width	
Huo ⁵⁷	6.6	4.1	11.7	22.8	Schwinger Variational(SE)
Modelli et al ⁵⁸	8.95	-	8.70	-	Multiple Scattering-X α
Modelli et al ⁵⁸	8.58	-	8.98	-	Continuum Multiple Scattering-X α
Winstead et al ⁵⁹	11.5	-	13.0	-	Schwinger Multichannel (SE)
Varella et al ⁵⁶	9.9	-	11.0	-	Schwinger Multichannel (SEP)
this work	10.6301	2.0553	12.7184	2.0902	caug-cc-pVDZ(cm+)
this work	11.0816	1.9737	12.0561	1.9617	caug-cc-pVTZ(cm+)
this work	11.0410	1.9090	12.1620	1.9621	caug-cc-pVQZ(cm+)

TABLE V. Calculated positions and widths (eV) of low energy shape resonances in CF₄. Static-exchange plus polarization is abbreviated SEP.

of Ref 56 in the static-exchange plus polarization (SEP) approximation. The method goes beyond the static-exchange approximation, but the Schwinger method requires a basis set representation of the potential that can introduce an unknown amount of error. The complex basis function calculations reported here are the only calculations to date that provide any idea of convergence to the basis set limit. Based on the energies in the different caug-cc-pVXZ basis sets, it is likely that these energies are within 0.05 eV of the basis set limit. This provides a valuable benchmark for evaluating different basis sets and methods.

B. Low energy resonances of some nitrogen-containing heterocycles

In this section, we compare energies of some low energy shape resonances in benzene and a series of nitrogen-containing heterocycles (pyridine, pyrimidine, pyrazine, s-triazine). This series of molecules was first studied in detail by Pisanias et al.,⁶⁰ and later by Nenner and Schulz,⁶¹ who suggested that pyrazine, s-triazine, and possibly pyrimidine have bound anions while benzene and pyridine have only low energy resonances. These results are shown in Table VI; note that the energies of bound anions are from polarography experiments and not directly from scattering experiments. Shortly afterward, Mathur and Hasted^{62,63}

Benzene	Pyridine	pyrimidine	pyrazine	s-triazine
1.14	0.62	0.0	-0.4	-0.45
	1.20	0.77	0.87	
4.85	4.58	4.24	4.10	4.0

TABLE VI. Positions (eV) of the lowest three resonances/anions of benzene, pyridine, pyrimidine, pyrazine, and s-triazine from Ref. 61

Benzene	Pyridine	pyrimidine	pyrazine
1.086	0.79	0.33	0.08
	1.15	0.82	0.92

TABLE VII. Positions (eV) of the lowest two resonances of benzene, pyridine, pyrimidine, and pyrazine as reported in Ref. 62 and 63

reported observing low energy temporary anions in benzene, pyrimidine, and pyrazine (see Table VII) in apparent contradiction to the results of Nenner and Schulz. There has since been conflicting reports on the sign of the electron affinity of pyrazine as noted by Song et al.,⁶⁴ who also noted that clusters of various sizes and components will have bound anions even if the gas phase monomer does not.

CCSD(T) calculations in the aug-cc-pVTZ basis were performed on the neutral and anionic forms of these molecules at geometries optimized at the DFT- ω B97X-V level of theory. The results of these calculations are shown in Table VIII. These results strongly suggest that these anions are unbound, but have limited quantitative value since these EAs will converge to 0 as the basis set size is increased. This justifies the use of scattering/complex-coordinate methods for these states.

The results in the static-exchange approximation are shown in Table IX. In two cases, multiple stationary points were found from the same θ -trajectory. The reported value is the stationary point that occurs at a complex θ that is closest to values of the θ actually used in the computation. In practice however, these multiple stationary points lie quite close together. An example of this behavior is shown in Figure 6. The two stationary points are

	Benzene	Pyridine	Pyrimidine	Pyrazine	s-Triazine
vertical		1.0390	0.6766	0.3987	0.4685
adiabatic	0.7878	0.8246	0.4183	0.1417	0.2015

TABLE VIII. Vertical and adiabatic electron affinities (eV) calculated with CCSD(T) in the aug-cc-pVTZ basis. The “vertical” EA’s were determined from calculations both done at the geometry of the neutral while for the “adiabatic” EA, the anion geometry was optimized separately.

benzene(e_{2u}, b_{2g})		pyridine(b_1, a_2, b_1)		pyrimidine(a_2, b_1, b_1)		pyrazine(b_{3u}, a_u, b_{2g})		s-triazine(e'', a_2')	
Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
3.1301	-0.2647	2.6493 ^a	-0.1861	2.3639	-0.1430	2.1014	-0.1877	2.2702 ^a	-0.0814
		3.0235	-0.2260	2.7557	-0.1681	2.8270	-0.1661		
9.4337	-1.2197	9.2772	-1.1519	8.9607	-0.9640	8.8174	-0.8005	8.1209	-0.6744

TABLE IX. Complex energies (eV) of the lowest three resonances of benzene, pyridine, pyrimidine, pyrazine, and s-triazine in the static-exchange approximation. The basis set is caug-cc-pVDZ(cm+).

^a multiple stationary points

viable from the θ -trajectory, but differ by an amount that is significantly less than either the error from the static-exchange approximation or from basis set incompleteness. It is likely that these molecules represent close to the upper limit of the usefulness of basis sets including center of mass functions. A double or triple augmentation on each atomic center would likely provide a more complete and more efficient representation of the resonances.

Despite the crudeness of the static-exchange approximation, these energies reproduce the qualitative trends of the experimental data. This is demonstrated in Table X by showing the experimental and calculated resonances relative to the energies of the pyridine resonances. Note that all the qualitative trends from the experimental data are reproduced in the SE calculations.

Because of the relevance of these molecules to biomolecular processes, they have been the subject of a number of recent scattering calculations.^{65–72} The results presented here agree

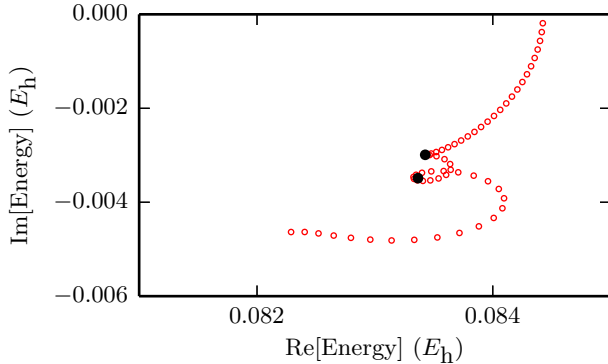


FIG. 6. Example of multiple stationary points (\bullet) for the lowest energy resonance of s-triazine.

present work					experiments of Nenner and Schulz ⁶¹				
benzene	pyridine	pyrimidine	pyrazine	s-triazine	benzene	pyridine	pyrimidine	pyrazine	s-triazine
0.4808	0.0000	-0.2854	-0.5479	-0.3791	0.52	0.00	-0.62	-1.02	-1.07
	0.0000	-0.2678	-0.1966			0.00	-0.43	-0.33	
0.1565	0.0000	-0.3165	-0.4598	-1.1563	0.27	0.00	-0.34	-0.48	-0.58

TABLE X. Complex energies (eV) of the lowest three resonances of benzene, pyridine, pyrimidine, pyrazine, and s-triazine in the static-exchange approximation (caug-cc-pVDZ(cm+)) compared with the experimental results of Nenner and Schulz.⁶¹ All values are relative to the three pyridine resonances.

qualitatively with most of these calculations. In particular, the SE results for pyrazine and pyrimidine are compared the R-matrix results of Mašín and Gorfinkiel⁶⁸ in Table XI. Because of the polarization effects included in the R-matrix expansion, the computed resonance positions are lower and the widths are significantly smaller than in the SE approximation. However, despite the predictable differences stemming from the use of different approximations, the trends agree qualitatively.

These molecules are by far the largest to have been investigated with complex basis functions, and even in the simplest approximation, the method can be used to obtain qualitatively correct results.

present work				Mašín and Gorfinkiel ⁶⁸			
pyrimidine		pyrazine		pyrimidine		pyrazine	
pos.	width	pos.	width	pos.	width	pos.	width
2.3639	0.2860	2.1014	0.3754	0.554	0.016	0.14	0.015
2.7557	0.3362	2.8270	0.3322	1.068	0.015	1.12	0.03
8.9607	1.9280	8.8174	1.6011	5.328	0.574	5.19	0.527

TABLE XI. Comparison of positions and widths (eV) to the SEP results of Mašín and Gorfinkiel.⁶⁸

system	basis size	time (s)	time (relative)
N ₂	105	4.2	1.0
CO ₂	127	15.6	3.6
Benzene	251	233.6	55.6

TABLE XII. Timings in seconds and relative to N₂ for a single calculation in the the caug-cc-pVDZ(cm+) basis set.

C. Computational requirements and timings

The method presented here differs from previous implementations in that the integrals are calculated in a direct manner and never explicitly stored which leads to a memory requirement of order N^2 and avoids storing integrals on disk. The actual computation is dominated by the Hamiltonian build which formally scales as N^4 if all ERIs are explicitly computed. In principle, integral screening techniques can be used to significantly reduce this scaling. However, the lack of an obvious Schwarz inequality for the complex ERIs limits available screening techniques to those based on overlaps of charge distributions and those based on the magnitude of density matrix elements. These methods are likely only significant in the limit of a very large molecule.

Timings in the caug-cc-pVDZ(cm+) basis are shown in Table XII. These timings represent the effort required to do the calculation at a single value of θ . Unlike in conventional complex scaling, all matrix elements must be recomputed for every value of θ . As expected, the scaling is roughly quartic. Symmetry is not used in the computation of the integrals,

but the integral algorithms utilized in this implementation are more efficient for integrals involving fewer centers. Because the ERIs must be recomputed many times for these calculations and many more times in complex self-consistent field (SCF) calculations, it is worth further effort to reduce this scaling so that computations on truly large molecular systems are feasible.

VI. CONCLUSIONS

In this study, an efficient and open-ended implementation of complex basis functions has been described, and the static-exchange approximation has been used to investigate the basis set requirements of the method. Some applications to larger molecules with multiple low energy shape resonances has been presented, and some general purpose complex basis sets for small molecules were introduced and used throughout.

Despite the limited utility of the static-exchange approximation, the results presented here set the stage for a general and efficient implementation of more sophisticated methods using complex basis functions. In particular, the complex SCF method is of considerable interest because the cost is just a multiple of the SE method and polarization effects are included.

ACKNOWLEDGMENTS

Support for this work was provided through the Scientific Discovery through Advanced Computing (SciDAC) program funded by the U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research, and Basic Energy Sciences. The authors thank Satoshi Yabushita for providing valuable computational benchmarks using an independent complex Gaussian implementation based on the COLUMBUS quantum chemistry codes. The authors thank Zhengting Gan for advice on the implementation of the complex ERIs.

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