

Continuum remover-complex absorbing potential: Efficient removal of the nonphysical stabilization points

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By adding a negative imaginary potential of variable strength η to the Hamiltonian, the resonance state of a system can be found as complex energy stabilized points in the η -trajectories of the eigenvalues. One problem that arises in practical calculations is the appearance of nonphysical complex energy stabilized points. A new method for separating the physical from the nonphysical complex energy stabilized points is proposed. The method is best illustrated with strongly correlated two-electron systems. © 2009 American Institute of Physics. [doi:10.1063/1.3271350]

I. INTRODUCTION

Electronic resonances are frequently encountered in the study of autoionization, photodissociation, and electron-molecule scattering processes.¹⁻³ From the computational point of view, there are several techniques to describe the electronic resonance states of atomic and molecular systems. Instead of extracting resonance energies and widths from the energy dependent scattering cross section calculations, they can be described as discrete eigenvalues of the Schrödinger equation satisfying purely outgoing boundary conditions. These eigenstates, which are called Siegert states, have complex eigenvalues, $E = E_{\text{res}} - i\Gamma/2$, where E_{res} gives the position of resonance and Γ gives the width of resonance. The complex energy E is referred to as Siegert energy.² In contrast to the bound states, because of the outgoing boundary conditions, the Siegert eigenfunction diverges asymptotically, and this makes it difficult to use the bound state *ab initio* methods for calculating the complex electronic energies. Nonetheless, over the past 30 years or so, several techniques have been developed that enable one to calculate the complex electronic energy solutions within the framework of *ab initio* bound state methods. These methods are surveyed, for example, in Refs. 2 and 4–14. Particularly powerful are those approaches that utilize the concept of analytical continuation methods.⁸⁻¹⁰ The Siegert energy is the eigenvalue of an analytically continued (non-Hermitian) Hamiltonian, and the associated eigenfunctions are square integrable. Analytical continuation can be achieved, for example, by complex scaling method.^{15,16} Though conceptually simple, complex scaling is rather cumbersome to implement for molecular electronic resonance states. Alternatively, analytical continuation is possible by using absorbing potential methods.^{17,18} Several authors have addressed the problem of how to construct an optimal absorbing potential for calculating the electronic resonance states.¹⁹⁻²⁴ In general, they can

be divided into two general categories: the absorbing potentials based on the artificial negative imaginary potentials (NIPs)^{17,18,20} and the absorbing potentials derived from the complex scaling based theories.²² Of relevance to the work here is the NIP formalism.

Described so often as complex absorbing potential (CAP) methods, the NIP methods are now considered to be very reliable as well as an efficient method for calculating molecular electronic resonance states.^{12,20} The popularity of the NIPs stems mainly from the ease with which they are implemented in the *ab initio* molecular electronic structure codes: a negative imaginary one-electron potential, $-i\eta\hat{W}$, with the property of being zero in the interaction region is simply added to the Hamiltonian, \hat{H} , and the spectrum of the non-Hermitian operator,

$$\hat{H}(\eta) = \hat{H} - i\eta\hat{W}, \quad (1)$$

is determined as a function of the non-negative parameter η , the so called NIP/CAP-strength. \hat{W} is a local positive semidefinite one-particle potential. A useful choice of \hat{W} for the *ab initio* calculation is described in Refs. 12 and 20. In a complete basis set, analytical continuation is achieved by letting η tend to 0^+ .²⁰ However, for a finite basis set calculation η has to be optimized in order to obtain the best approximation to the Siegert energy of interest. The resonance states are then identified as stabilized complex energy points (slowing down of points) in the η -trajectories, i.e., a graphical search method for the stabilizations points is employed in which the complex eigenvalues are plotted as a function of η (η -trajectories).

Although the NIP method has produced accurate resonance energies and widths for real systems, it can produce, in practice, errors of two basic types: associated respectively with the reflection of the outgoing wave from the absorbing region^{25,26} and the nonphysical artificial stabilization points in the η -trajectories. The first type of error has been studied extensively and requires no further explanation. One method to minimize this error is possible by smoothly turning on the

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potential at the asymptotic region. The second type of error, which is associated with nonphysical stabilization points, has not been widely discussed in the literature and can be more subtle than the first. In a finite basis set calculation this error can be understood as follows: resonance states can be viewed as a bound state coupled to the continuum states. Adding a NIP, $-i\eta\hat{W}$, to the physical Hamiltonian, H , damps the outgoing part of the continuum wave functions contributing to the resonance phenomena, which are thereby converted into a bound eigenstate (resonance state) and continuum states of $\hat{H}(\eta)$, i.e., a resonance state is now associated with a single square-integrable eigenfunction of $\hat{H}(\eta)$. These states can now be identified from a graphical search for the stabilized points in the η -trajectories. However, in a finite square-integrable basis set, nonphysical stabilization points may be introduced in the η -trajectories corresponding to the poorly approximated discretized continuum states of $\hat{H}(\eta)$. This problem will become even more troublesome in complicated molecular systems when accurate resonance energies and widths are not reported in the literature. Identifying the physical resonance stabilization points is therefore a major concern whenever NIPs are employed in the *ab initio* calculation. Toward this end, the purpose of this letter is to present a method, which we found best for this purpose. It is also worth to note here that the nonphysical stabilization points associated with the poorly described Rydberg wave functions²⁷ are not mistaken for the physical resonance states as the Rydberg states are placed energetically below the threshold. On the other hand the physical resonance states and the nonphysical stabilization points corresponding to the discretized continuum states appear above the threshold.

II. CONTINUUM REMOVER-CAP

The basic physical idea underlying our approach is that in the interaction region of the physical Hamiltonian, \hat{H} , the resonance wave function resembles a bound state, although the outer part does not vanish asymptotically. The wave function in the interaction region is kept unaffected by the imaginary potential of the analytically continued Hamiltonian, $\hat{H}(\eta)$, while the asymptotic exponential growing is completely damped, i.e., due to an optimal NIP, $\eta_{\text{opt}}\hat{W}$, the resonance state is completely isolated from the rest of the continuum spectra, and it behaves as a bound state wave function in the interaction region of $\hat{H}(\eta)$. In contrast, states associated with the rest of the continuum spectra of $\hat{H}(\eta)$ possess large amplitudes in the absorbing region, i.e., the amplitude of the nonresonance eigenfunctions are not small where the NIP is large. As a consequence, if one adds an additional artificial real valued potential to the absorbing region of the Hamiltonian $\hat{H}-i\eta_{\text{opt}}\hat{W}$, the new asymptotically damped (“bound”) resonance wave function will be insensitive to such a potential when compared to the rest of the continuum spectra. On the other hand, the nonphysical artificial stabilization points, which appear in the continuum spectra of $\hat{H}(\eta)$, will be significantly affected by the new real valued potential. This should be visible in the graphical

search for the resonances and is the basis of the technique we study. We refer to the real valued artificial potential enhanced NIP as a continuum remover-CAP or CR-CAP.

To make the CR-CAP attractive it must be formulated in a computational feasible way, and the transition from the NIP to the CR-CAP should be smooth and straightforward. In order to achieve these goals we define a CR-CAP Hamiltonian,

$$\hat{H}(\eta, \lambda) = \hat{H} + (\lambda - i\eta)\hat{W}, \quad (2)$$

where λ can be zero, positive, or negative. The real part of this potential, $\lambda\hat{W}$, also shares the property of the NIP, $-i\eta\hat{W}$, that it leaves the interaction region untouched and only “turns on” asymptotically with the NIP. The potential \hat{W} used in the real part can be, in general, different from that used for the NIP. However, the form of CR-CAP selected in Eq. (2) brings computational advantages in the numerical calculations.

A few points need to be made regarding the computational procedure for optimizing the CR-CAP parameters (“turn on” points and η) in a finite basis set calculation for resonance energies and widths. The turn on points and η parameters of the CR-CAP are optimized essentially in the same way as that of NIP.¹¹ One must start the procedure with the η -trajectory spectra generation using the NIP method, whereupon one can identify stabilized eigenvalues, which may safely be omitted using subsequent generation of η -trajectory spectrum from CR-CAP method for a few selected values of λ . It is also important to note that the real part of the CR-CAP is added only to identify the resonance stabilization points, and there is usually no need to optimize the potential strength λ during the procedure.

One should also note that we are not the first to add an artificial real valued potential to a CAP. In Refs. 28 and 29 this has been done, however, with a completely different intention. (1) The role of our real valued CR potential is to remove the nonphysical stabilization points and identify the “correct” resonance stabilization points, whereas Refs. 28 and 29 used an accelerating potential in order to make an efficient absorption of the outgoing particle. (2) Our potential can take negative or positive valued strength parameter (see, for example, Figs. 1 and 2), whereas Refs. 28 and 29 use a negative real part to accelerate the outgoing electron. The negative real part used in Ref. 28 serves to decrease the de Broglie wavelength, and therefore the width of the required absorbing region.

A. Numerical tests

To demonstrate that the proposed CR-CAP works and is efficient, in the following, we present the numerical calculation for the lowest doubly excited 1S resonance states of helium (He) and the lowest doubly excited $^1\Sigma_g^+$ resonance state of molecular hydrogen (H_2). On the theoretical side, the study of these strongly correlated two-electron excited autoionizing states has a long history.^{14,30–32} The increasing computing power together with well adapted basis sets for the two-electron systems permits the use of highest level of

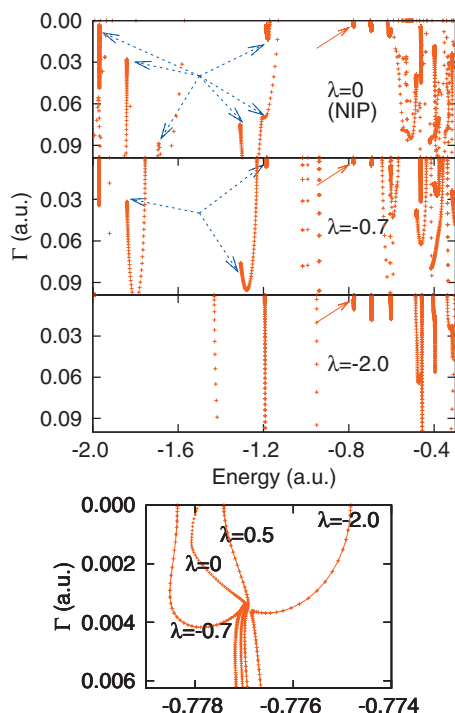


FIG. 1. η -trajectories corresponding to the totally symmetric singlet states of He. The results are obtained by exact diagonalization of the CR-CAP perturbed atomic Hamiltonian [see Eq. (2)]. An optimized box parameter $C=7.5$ a.u. is used in the calculation. The resonance energy of interest is marked by a red arrow. A few examples of nonphysical stabilization points are marked by blue arrows. The nonphysical stabilization points gradually disappear as $-\lambda$ grows. The small box shows a zoomed view of the resonance η -trajectories. Although each resonance trajectory has its own characteristics, all trajectories stabilize visibly at the same complex energy. The results clearly indicate that the resonance stabilization points are little influenced by the real part of the CR-CAP potential $\lambda\hat{W}$.

ab initio theory; exact diagonalization [full configuration interaction (FCI)] method.

We would like to use the CR-CAP procedure in the same way as one commonly uses the NIP procedure in *ab initio* calculation of molecular resonances: we have chosen to use a box-shaped CR-CAP and also a graphical search to identify the resonance trajectories. The potential used in this study is of the very often used box-shaped potential of the form¹¹

$$W(x) = \sum_{i=1}^3 W_i(x_i), \quad (3)$$

$$W_i(x_i) = \begin{cases} (x_i + C_i)^2, & x_i < -C_i \\ 0, & x_i \leq C_i \\ (x_i - C_i)^2, & x_i > C_i, \end{cases} \quad (4)$$

where C is the ‘turn on’ point of the potential. The CR-CAP boxes for He and H_2 are set up by $C_x=C_y=C_z=C$ and $C_x=C_y=(C_z-R/2)=C$, respectively, where H_2 is placed along the z axis and R is the internuclear distance selected (which is 1.4 a.u.) for H_2 . We now briefly outline the procedure for computing the complex eigenvalues of the non-Hermitian Hamiltonian, $\hat{H}(\eta, \lambda)$, for a particular value of η , λ , C , and R values. The complex eigenvalues for He and H_2 are calculated using exact diagonalization of a complex symmetric matrix (FCI method) over a two-electron determinant basis

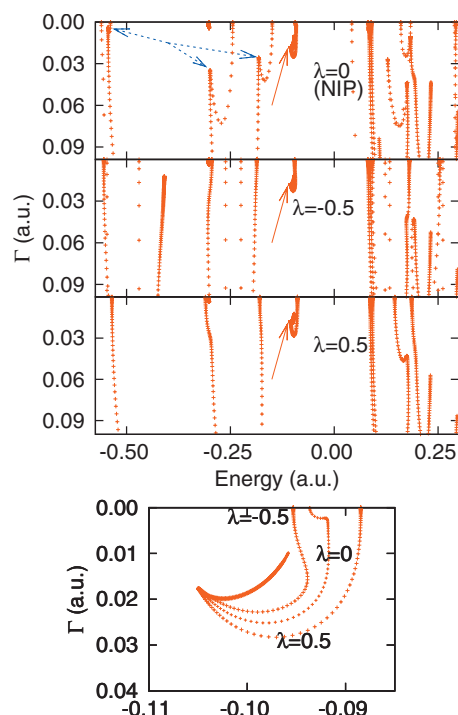


FIG. 2. η -trajectories corresponding to $^1\Sigma_g$ states of (H_2) molecule. The results are obtained by exact diagonalization of the CR-CAP perturbed molecular Hamiltonian for a fixed internuclear separation, which is taken as 1.4 a.u. in our calculation. An optimized box parameter $C=6.0$ a.u. is used in the calculation. The resonance energy of interest is marked by a red arrow. A few examples of nonphysical stabilization points are marked by blue arrows. The nonphysical stabilization points gradually disappear as $|\lambda|$ grows. The small box shows a zoomed view of the resonance η -trajectories. Although each resonance trajectory has its own characteristics, all trajectories stabilize at the same complex energy. The results clearly indicate that the resonance stabilization points are insensitive to the real part of the CR-CAP potential $\lambda\hat{W}$. The resonance η -trajectory of the pure imaginary case (NIP) shows an additional nonphysical stabilization point.

set. The two-electron determinant basis set has been generated using the effective one-electron orbital solutions from Hartree–Fock calculations. An atom centered one-electron aug-cc-PVQZ basis set has been employed for the Hartree–Fock calculation. In the case of He, the aug-cc-PVQZ basis set is further augmented with a set of even-tempered Gaussian basis functions. The exponents of the even-tempered basis functions are calculated using

$$\xi_i^{s/p/d} = (\zeta^{s/p/d})^{(1/N^{s/p/d})} \xi_{i-1}^{s/p/d}, \quad (5)$$

where $\xi_1^{s/p/d}$ is the exponent of the most diffused function in the aug-cc-PVQZ basis, $N^s=16$, $N^p=6$, $N^d=4$ m $\zeta^s=0.001$, $\zeta^p=0.005$, and $\zeta^d=0.01$ are used.

A comparative study of the complex eigenvalue spectrum, which is obtained using the NIP and the CR-CAP, for He and H_2 molecule are shown in Figs. 1 and 2, respectively. The resonance energy parameters for He ($E_{\text{res}}=-0.7772$ a.u. and $\Gamma=0.0034$ a.u.) and H_2 ($E_{\text{res}}=-0.1050$ a.u. and $\Gamma=0.0178$ a.u.) are in good agreement with the previous theoretical works.^{14,31}

Let us now discuss the results obtained from the CR-CAP method. For separating the resonance stabilization points from a set of nonphysical stabilization points, the basic idea behind the CR-CAP is crucial: the resonance stabi-

lization points from the NIP method are less influenced by the addition of a real valued CR potential. For the sake of simplicity, we now focus only on lowest resonance η -trajectory and the continuum η -trajectories below the lowest resonance states. As one can see from Figs. 1 and 2 that there are many nonphysical stabilization points in the NIP calculation for the continuum region below and even more so above the lowest resonance state. A few examples of nonphysical stabilization points are marked in Figs. 1 and 2. As we go from the NIP to the CR-CAP and increase $|\lambda|$, these nonphysical stabilization points start moving away from their original position while keeping the resonance trajectories unaffected. Physical stabilization points that appear in the resonance η trajectories show similar convergence behavior for a wide range of λ , ranging from positive to negative values. The resonance trajectories shown in the small boxes in Figs. 1 and 2 show the characteristic behavior of resonance η -trajectories for various CR potential strengths λ . Comparing the NIP and the CR-CAP results, it is now apparent that the trajectories differ significantly in the region where η is smaller than the optimal η values. As soon as the NIP strength η becomes equal or stronger than the optimal values, the NIP trajectories and the CR-CAP trajectories follow the same behavior. From this result we can infer that by adding a pure imaginary CAP with the optimal CAP strength to the Hamiltonian, one perfectly damps the amplitude of the resonance wave function over the absorbing region, and hence the real part of the CR-CAP does not influence the η -trajectories for the η values, which are larger than the η_{opt} . On the other hand, the wave functions contributing to the nonphysical stabilization points are not completely damped by the NIP potential, and they are very sensitive to the real part of the CR potential. We end this section with the observation that the CR-CAP helps to find the physical stabilization points in the complex energy plane.

III. CONCLUDING REMARKS

The popular L^2 way to determine resonance position and widths requires adding a NIP to the Hamiltonian and computing eigenvalues of the complex symmetric matrix as a function of the NIP strength parameter. This entails doing a graphical search for the complex energy stabilized points. In this method, there is a serious problem of separating the physical stabilization points from the large number of nonphysical stabilization points that also occur. Instead of using a general NIP procedure, we used a CR-CAP procedure that we found useful to deal with such difficulties. The real valued potential added to the NIP for this purpose shares the property of the NIP that it leaves the interaction region untouched and only turns on asymptotically with the NIP. This property also helps us to explore a route where minimal extra

computational effort is being utilized to achieve our goal. Those eigenvalues of $\hat{H} - i\eta\hat{W}$ that correspond to the bound and resonance states of the physical Hamiltonian, \hat{H} , are insensitive to the real valued potential added to the absorbing region of $\hat{H} - i\eta\hat{W}$, whereas those corresponding to the scattering states of $\hat{H} - i\eta\hat{W}$ change significantly. Our results establish that once the η -trajectories has been generated, the CR-CAP procedure is capable of identifying the physical resonances of complex systems.

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