PHYSICAL REVIEW A **91**, 022506 (2015)

Electron-atom resonances: The complex-scaled multiconfigurational spin-tensor electron propagator method for the ^2P Be$^-$ shape resonance problem

Tsogbayar Tsednee, Liyuan Liang, and Danny L. Yeager[*]
Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

(Received 19 December 2014; published 11 February 2015)

We propose and develop the complex-scaled multiconfigurational spin-tensor electron propagator (CMCSTEP) technique for theoretical determination of resonance parameters with electron-atom and electron-molecule systems including open-shell and highly correlated atoms and molecules. The multiconfigurational spin-tensor electron propagator (MCSTEP) method developed and implemented by Yeager and co-workers in real space gives very accurate and reliable ionization potentials and attachment energies. The CMCSTEP method uses a complex-scaled multiconfigurational self-consistent field (CMCSCF) state as an initial state along with a dilated Hamiltonian where all of the electronic coordinates are scaled by a complex factor. The CMCSCF was developed and applied successfully to resonance problems earlier. We apply the CMCSTEP method to get ^2P Be$^-$ shape resonance parameters using $14s11p5d$, $14s14p2d$, and $14s14p5d$ basis sets with a $2s2p3d$ complete active space. The obtained values of the resonance parameters are compared to previous results. Here CMCSTEP has been developed and used for a resonance problem. It appears to be among the most accurate and reliable techniques. Vertical ionization potentials and attachment energies in real space are typically within ±0.2 eV or better of excellent experimental results and full configuration-interaction calculations with a good basis set. We expect the same sort of agreement in complex space.

DOI: 10.1103/PhysRevA.91.022506 PACS number(s): 31.15.A−, 32.10.Hq

I. INTRODUCTION

Resonances in electron-atom or electron-molecule scattering processes have attracted much attention. They play major roles in electron transport and energy exchange between electronic and nuclear motions, in vibrational excitation of molecules or molecular ions by electron impact, in dissociative attachments and recombination [1,2], and as a mechanism for DNA damage by low-energy electrons [3,4].

In order to avoid direct calculation of an outgoing wave in resonance problems, we use a complex coordinate scaling (CS) technique, which was proposed and developed by Aguilar, Balslev, and Combes [5,6] and Simon [7] in the early 1970s. In this approach the electronic coordinates (r) of the Hamiltonian are scaled (or "dilated") by a complex parameter η as $r \rightarrow \eta r$, where $\eta = \alpha e^{i\theta}$ with $\alpha > 0$ and $\theta \in (-\pi,\pi)$. Under this transformation, the bound states are real and are unchanged by complex scaling and the continuum of the complex-scaled Hamiltonian $\bar{H}$ is rotated by an angle 2θ at each threshold such that the continuum states appear as complex eigenvalues of the complex-scaled Hamiltonian $\bar{H}$. The resonance parameters $E = E_r - i\frac{\Gamma_r}{2}$ hidden in the continua are exposed in complex space for some suitable η, where E_r and Γ_r are the resonance position and width of that resonance state, respectively.

Other alternative methods have included the complex absorbing potential (CAP) [8,9] instead of CS. CAP methods have not been shown conclusively to be superior to standard complex scaling.

Previously, we developed the quadratically convergent complex-scaled multiconfigurational self-consistent field [10,11] (CMCSCF) method with step length control to obtain the resonance parameters. In real space, the MCSCF method with a small complete active space (CAS) has been proven to be a very effective method to describe nondynamical and some dynamical correlation correctly and is computationally cheaper than very large or full configuration-interaction (CI) calculations [12] while still incorporating the fundamental physics of what is going on. Based on the CMCSCF initial state, we also developed a method termed the M_1 method [11,13], in which the complex M_1 matrix is constructed from the first block of the M matrix defined in the multiconfigurational spin-tensor electron propagator (MCSTEP) method [14–18]. This block allows for only simple electron removal and addition to orbitals with no more complicated processes allowed to mix in.

The MCSTEP method, however, includes many additional operators which allow for more complicated electron ionization and attachment processes to be included. It is designed to calculate reliably the ionization potentials (IPs) and attachment energies (AEs) for atoms and molecules which cannot generally be handled accurately by perturbation methods. In addition to simple additional electron operators in all orbitals as in the M_1 method, the MCSTEP method includes operators that allow for electron removal and electron addition to all orbitals in excited states within the CAS [14–18]. In complex space, the M_1 and CMCSTEP methods use CMCSCF states as reference or initial states along with $\bar{H}$. Both the CMCSCF and M_1 methods have been previously efficiently used to study the ^2P Be$^-$ shape resonance [10,11,13].

Moreover, we have developed and implemented the complex-scaled multiconfigurational time-dependent Hartree-Fock (CMCTDHF) method [also called the complex-scaled multiconfigurational linear response (CMCLR) method]. The CMCTDHF method uses the CMCSCF state as the initial state. In real space the multiconfigurational time-dependent Hartree-Fock method has been successfully used to study electronic excitation energies and linear response properties [19]. The CMCTDHF method has previously been implemented and successfully employed to study Auger resonances for Li and

---

[*] yeager@mail.chem.tamu.edu

Li-like cations [20], and Be and Be-like cations [21] and Feshbach resonances for both $\mathrm{Be}^+(2p)$ [22] and $\mathrm{He}(2s^2)$ [23] systems, as well.

In this work we implement the CMCSTEP method for the ^2P Be^- shape resonance problem using $14s11p5d$, $14s14p2d$, and $14s14p5d$ basis sets with a $2s2p3d$ CAS and compare our results with previous results. The reasons why we implement this method for resonance problems are as follows: (i) the MCSTEP method in real space works exceptionally well and gives very accurate and reliable values of vertical IPs and AEs for general atomic and molecular systems, which are well consistent with experimental measurements [24–28], so that we expect that the CMCSTEP method is able to give reliable values of resonance parameters; (ii) even though this approach has been implemented here in complex space, this is a direct extension of the CMCSCF [10] and M_1 [11] methods which we previously developed and implemented, so we expect that the obtained results for this resonance problem will be different from those previously obtained and very accurate [10,11].

The paper is organized as follows. In Sec. II we discuss the theoretical part of the CMCSTEP method. In Sec. III we present and discuss our results. Then conclusions follow.

II. THEORY

The complex-scaled electronic Hamiltonian is non-Hermitian. It is complex symmetric. This causes the wave function $|\psi_m\rangle$ to be complex-conjugate biorthogonal (CCBON) where $\langle\psi_i^*|\psi_j\rangle = \delta_{ij}$ ($*$ means the complex conjugate) [29]. Creation operators are introduced as $a^T = a^\dagger = (a^*)^\dagger$ rather than $a^\dagger$ with the usual anticommutation relations for creation and annihilation operators still holding by changing "$\dagger$" to "T" [30,31].

Therefore, the CMCSTEP method may be formulated in the same way as MCSTEP via the single-particle Green's function or electron propagator method [14–18] or superoperator formalism [32] with modified second-quantization operators and $\bar{H}$. We will not discuss the MCSTEP method in detail here, but it can be found in Refs. [14–18].

CMCSTEP IPs and AEs are obtained from the following complex generalized eigenvalue problem:

$$\mathbf{MX}_f = \omega_f \mathbf{NX}_f, \qquad (1)$$

where

$$M_{rp} = \sum_{\Gamma} (-1)^{S_0-\Gamma-S_f-\gamma_r} W(\gamma_r\gamma_p S_0 S_0;\Gamma S_f) \times (2\Gamma+1)^{1/2}\langle N S_0||\{h_r^*(\bar{\gamma}_r),\bar{H},h_p(\gamma_p)\}||N S_0\rangle \qquad (2)$$

and

$$N_{rp} = \sum_{\Gamma} (-1)^{S_0-\Gamma-S_f-\gamma_r} W(\gamma_r\gamma_p S_0 S_0;\Gamma S_f) \times (2\Gamma+1)^{1/2}\langle N S_0||\{h_r^*(\bar{\gamma}_r),h_p(\gamma_p)\}||N S_0\rangle. \qquad (3)$$

ω_f is an IP or AE from the N-electron initial tensor state $|N S_0\rangle$ with spin S_0 to the $(N \pm 1)$-electron final ion tensor state $|N \pm 1 S_f\rangle$ which has spin S_f. W is the usual Racah coefficient, $h_p(\gamma_p)$ and $h_p^*(\bar{\gamma}_r)$ are tensor-operator versions of members of the operator manifold with ranks γ_p and γ_r, respectively, $\{,\}$ is the anticommutator

$$\{A,B\} = AB + BA, \qquad (4)$$

and $\{,,\}$ is the symmetric double anticommutator

$$\{A,B,C\} = \tfrac{1}{2}(\{A,[B,C] + \{[A,B],C\}\}). \qquad (5)$$

The CMCSTEP method uses a CMCSCF initial state with a fairly small CAS and couples tensor ionization and attachment operators to a tensor initial state to a final state that has the correct spin and spatial symmetry even if the initial state is open shell and/or highly correlated.

III. RESULTS AND DISCUSSION

In this study, we investigate the low-lying ^2P Be^- shape resonance problem using the ΔCMCSCF [see Eq. (6)], M_1, and CMCSTEP methods. This resonance problem has been investigated theoretically in the past [33–41,43,44]. Recently, we studied this resonance problem in terms of application of the M_1 method we have developed [11]. The Be atom has a fairly large amount of nondynamical correlation because the $1s^2 2p^2$ configuration has considerable mixing with the principal $1s^2 2s^2$ configuration [15], so that both configurations need to be included nonperturbatively for accurate IP and AE calculations.

It is a common practice to report the resonance energy relative to the total energy of the scattering target. In this work, in ΔCMCSCF calculations we report on the total energy of the continuum Be^- species relative to that of the Be atom as

$$\epsilon_{\Delta\mathrm{CMCSCF}}(\eta) = E_c^{N+1} - E_0^N, \qquad (6)$$

where E_c^{N+1} and E_0^N are the total energies of the $(N+1)$-electron Be^- resonance state under investigation and the N -electron ground state of the neutral Be atom, respectively, and the subscripts c and 0 refer to continuum and bound states, respectively.

In ΔCMCSCF calculations we need to optimize each state separately; however, in M_1 and CMCSTEP calculations we can obtain the energies of all states simultaneously. In order to be consistent with the ΔCMCSCF calculation, we report the resonance parameter $\epsilon_{\mathrm{CMCSTEP}}$ obtained from the CMCSTEP method:

$$\epsilon_{\mathrm{CMCSTEP}}(\eta) = \omega_f^{\mathrm{CMCSTEP}} + E_c^N - E_0^N, \qquad (7)$$

where $\omega_f^{\mathrm{CMCSTEP}} \equiv \omega_f$ is calculated from Eq. (1). In the case of M_1 calculations it is obtained from the M_1 complex eigenvalue problem [11] and we report on results based on complex eigenvalues $\omega_f^{\mathrm{M}_1}$ rather than $\omega_f^{\mathrm{CMCSTEP}}$ in Eq. (7).

For this resonance problem, Venkatnathan *et al.* [33] found the $14s11p$ basis set to be the best one. We subsequently have shown that this $14s11p$ basis set is somewhat inadequate for resonances and that at least $14p$ functions are much more reliable. Hence, we chose this basis set initially and added p and d functions to it using a geometric progression with a view to accounting for the diffuse nature of the resonances. Although for the very accurate IPs and excitation energies of Be, a larger $2s2p3s3p3d$ CAS which enables more correlation is necessary [16], we employ a $2s2p3d$ CAS with basis sets $14s11p5d$, $14s14p2d$, and $14s14p5d$ in this calculation, since we have previously found that a larger CAS is unnecessary for

TABLE I. Ionization potential and attachment energies for $X\,^2S$ of the Be atom and ^2P Be$^-$ ion, respectively.

Method and basis set	IP (eV)	AE (eV)
ΔMCSCF: $14s11p5d$–$2s2p3d$ CAS	8.478	1.027
ΔMCSCF: $14s14p2d$–$2s2p3d$ CAS	8.042	1.124
ΔMCSCF: $14s14p5d$–$2s2p3d$ CAS	8.042	1.121
M_1: $14s11p5d$–$2s2p3d$ CAS	7.571	0.836
M_1: $14s14p2d$–$2s2p3d$ CAS	7.576	0.872
M_1: $14s14p5d$–$2s2p3d$ CAS	7.576	0.871
MCSTEP: $14s11p5d$–$2s2p3d$ CAS	9.508	0.843
MCSTEP: $14s14p2d$–$2s2p3d$ CAS	9.506	0.918
MCSTEP: $14s14p5d$–$2s2p3d$ CAS	9.506	0.906
Ref. [15] $-2s2p$ CAS	9.50	
Ref. [15] $-2s2p3s3p3d$ CAS	9.31	
Expt. [42]	9.32	

accurate shape resonance calculations [13]. However, most of the IP basis sets are designed for IPs where tighter functions are necessary rather than for resonance calculations where what is needed are basis functions to describe the near continuum. First, we performed ΔCMCSCF calculations with all basis sets, and then followed it up with M_1 and CMCSTEP methods. The first two methods have already been implemented for the resonance problem with other basis sets [10,11]; however, here the CMCSTEP method is applied for this resonance problem. Of these, the CMCSTEP should be the most accurate, efficient and reliable method. So far, there appear to be no experimental results for resonance parameters of Be$^-$.

In Table I we present IPs for the $X\,^2S$ state of the Be atom and AEs for ^2P Be$^-$ resonance state obtained from ΔCMCSCF, M_1, and MCSTEP ($\theta = 0$ rad and $\alpha = 1$) calculations, in which $\mathrm{Im}(E) = 0$. A comparison of values of IPs and AEs to previously obtained theoretical values and experimental measurements presented in this table shows that MCSTEP calculations give more reliable values for resonance problems than MCSCF and M_1 approaches.

In Table II we show a summary of the obtained values for the ^2P Be$^-$ shape resonance for three different basis sets. In rows 2–4 of Table II we show results from ΔCMCSCF calculations. These give larger widths than M_1 or CMCSTEP calculations. Resonance parameters obtained from the M_1 and CMCSTEP methods shown in rows 5–10 are fairly consistent with each other, although the CMCSTEP results will be more accurate. The optimal values of α and θ enable one to estimate the resonance parameters, and can be found by the system of equations below:

$$\frac{\partial E}{\partial \alpha} = \frac{\eta}{\alpha}\frac{\partial E}{\partial \eta} = 0, \tag{8}$$

$$\frac{\partial E}{\partial \theta} = -i\eta\frac{\partial E}{\partial \eta} = 0, \tag{9}$$

which form the trajectory method by determining $E(\alpha_{\mathrm{opt}},\theta_{\mathrm{opt}})$ corresponding to the stability (loops, kinks, inflections, or any kind of “slow down”) in the plots of $\mathrm{Im}(E)$ as a function of $\mathrm{Re}(E)$ evaluated as a series of α (α trajectory) and a series of θ (θ trajectory) values [34]. Vertical IPs and AEs in real space are typically within ±0.2 eV or better of excellent experimental results and full configuration-interaction calculations with a good basis set [15]. We expect the same sort of agreement in complex space. Indeed this can be seen by looking at Table II where our results are in general agreement with those of considerably less accurate methods.

In Table III we have listed theoretical results obtained by other workers. Our current results with our best basis set ($14s14p5d$) are quite far from complex CI [39] and density functional theory (DFT) combined with CAP [43] calculations. We note that the CI calculations did not include any effect of quadruple excitations. It is well known that these need to be included for accurate CI energies and properties [44]. The complex DFT calculation contains parameters that are experimentally determined and also the basis set used is small (contracted Gaussian $5s4p1d$ functions) and not adequate for resonance calculations. However, the values obtained from CMCSTEP in this work are fairly comparable with those obtained by ΔSCF [37,38] and electron propagator methods [33,37,38,44], although these other methods will not be as accurate, since they are based on a single configuration and the Be atom is inherently multiconfigurational with the $1s^22p^2$ configuration mixing in strongly (i.e., 10%) with the $1s^22s^2$ configuration for the initial state. From our previous experience with calculations for IPs and AEs for atomic systems [15,24,25], we know that the MCSTEP methods works very well; therefore we can say that the values of resonance parameters obtained from CMCSTEP in this work are reliable.

In Fig. 1 we show the θ trajectories for the ^2P Be$^-$ shape resonance obtained from the CMCSTEP method. The curves shown in panels (a), (b), and (c) correspond to calculations

TABLE II. Summary of theoretical calculations for the ^2P Be$^-$ shape resonance relative to the $1s^22s^2$ ground state.

Method and basis set	α	θ_{opt} (rad)	E_r (eV)	Γ_r (eV)
ΔCMCSCF: $14s11p5d$–$2s2p3d$ CAS	1	0.49	0.714	1.541
ΔCMCSCF: $14s14p2d$–$2s2p3d$ CAS	1	0.55	0.816	1.731
ΔCMCSCF: $14s14p5d$–$2s2p3d$ CAS	1	0.55	0.819	1.736
M_1: $14s11p5d$–$2s2p3d$ CAS	1	0.36	0.764	0.796
M_1: $14s14p2d$–$2s2p3d$ CAS	1.03	0.36	0.790	0.856
M_1: $14s14p5d$–$2s2p3d$ CAS	1.03	0.37	0.789	0.874
CMCSTEP: $14s11p5d$–$2s2p3d$ CAS	1	0.30	0.768	0.740
CMCSTEP: $14s14p2d$–$2s2p3d$ CAS	1.03	0.30	0.795	0.681
CMCSTEP: $14s14p5d$–$2s2p3d$ CAS	1.03	0.36	0.756	0.862

TABLE III. Theoretical calculations for the ^2P Be$^-$ shape resonance.

Method	E_r (eV)	Γ_r (eV)
Static-exchange phase shift [35]	0.77	1.61
Static-exchange phase shift plus polarizability phase shift [35]	0.20	0.28
Static-exchange cross section [36]	1.20	2.60
Static-exchange plus polarizability cross section [36]	0.16	0.14
ΔSCF with complex $14s16p$ Gaussian basis set [37]	0.70	0.51
ΔSCF with complex $5s11p$ (Slater-type) basis set [38]	0.76	1.11
Single, doubles, and triples complex CI [39]	0.32	0.30
S matrix pole (X_α) [40,41]	0.10	0.15
Complex density functional theory [43]	0.580	0.223
Second-order dilated electron propagator based on real SCF [44]	0.57	0.99
Biorthogonal dilated electron propagator (bases set $14s11p$) [33]:		
Zeroth order	0.62	1.00
Quasiparticle second order	0.61	1.00
Second order	0.48	0.82
Quasiparticle third order	0.54	0.82
OVGF third order	0.54	0.78
Third order	0.53	0.85
ΔCMCSCF ($14s11p$–$2s2p3s3p$ CAS) [10]	0.73	1.58
M_1 ($14s11p3d$–$2s2p3s3p3d$ CAS) [11]	0.72	1.12
This work:		
ΔCMCSCF ($14s14p5d$–$2s2p3d$ CAS)	0.819	1.736
M_1 ($14s14p5d$–$2s2p3d$ CAS)	0.789	0.874
CMCSTEP ($14s14p5d$–$2s2p3d$ CAS)	0.756	0.862

with basis sets $14s11p5d$, $14s14p2d$, and $14s14p5d$ with $2s2p3d$ CAS, respectively. Crosses on each trajectory show a stabilized point. All trajectories show resonance points clearly along with an increased density of points. In all trajectories θ starts at $\theta = 0.01$ rad at the top and increases downwards with a step of 0.01 rad.

Although we have here presented results for resonance parameters for an atomic system ^2P Be$^-$, the method can be implemented for investigating shape resonance parameters for molecular systems. We have shown this for the $^2\Pi_g$ N$_2^-$ shape resonance [13] using the M_1 method, and it gives results quite consistent with previous literature results [45–48] and experimental measurements [49,50]. In the molecular case [13], the CS technique for the electron-nuclear Coulomb interaction potential $-Z/|\mathbf{r}-\mathbf{R}|$ has been implemented so that $-(Z\eta^{-1})/|\mathbf{r}-\mathbf{R}\eta^{-1}|$, where Z is the nuclear charge, and $\mathbf{r}$ and $\mathbf{R}$ are the electronic and nuclear positions relative to the origin of a fixed molecular coordinate system [34]. We will report CMCSTEP calculations for several molecules using this procedure elsewhere.

IV. CONCLUSIONS

In this work we have developed the CMCSTEP method and presented theoretical calculations for the ^2P Be$^-$ shape resonance using three different (ΔCMCSCF, M_1, and CMCSTEP) methods. In our group we previously developed the ΔCMCSCF and M_1 methods; however, we here have developed and implemented the CMCSTEP method for resonance problems, using three different bases sets $14s11p5d$, $14s14p2d$, and $14s14p5d$ with a $2s2p3d$ CAS. In the CMCSTEP calculations we use the CMCSCF state as an initial

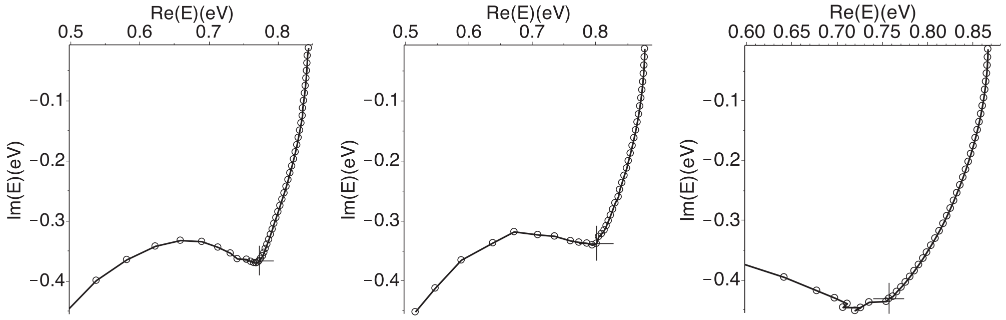

FIG. 1. The θ trajectories for ^2P Be$^-$ shape resonance obtained from the CMCSTEP method. The curves shown in (a), (b), and (c) correspond to basis sets $14s11p5d$, $14s14p2d$, and $14s14p5d$ with $2s2p3d$ CAS, respectively, and the cross shows a stabilized point. Computational parameters are $\alpha = 1$ (a), 1.03 (b),(c), and $\Delta\theta = 0.01$ rad.

state. The obtained values of the ^2P Be$^-$ shape resonance from the CMCSTEP method are compared with previously obtained results in the literature. Based on our previous results from MCSTEP calculations for IPs and AEs for atomic and molecular systems, the results from the CMCSTEP calculations are probably the most reliable and practical for resonance problems.

In next step of our research work we intend to apply the CMCSTEP method to resonance problems for open-shell atomic and molecular systems, as well as studies for Feshbach and Auger resonances.

ACKNOWLEDGMENTS

We thank the Robert A. Welch Foundation for financial support via Grant No. A-770. Fruitful discussions with Dr. Songbin Zhang and Dr. K. Samanta on implementing the complex version of the codes are gratefully acknowledged.

[1] J. N. Bradsley and M. A. Biondi, Adv. At. Mol. Phys. **6**, 1 (1970).
[2] H. Massey, *Negative Ions*, 3rd ed. (Cambridge University Press, Cambridge, 1970).
[3] R. Barrios, P. Skurski, and J. Simons, J. Phys. Chem. B **106**, 7991 (2002).
[4] J. Simons, Acc. Chem. Res. **39**, 772 (2006).
[5] J. Aguilar and J. M. Combes, Commun. Math. Phys. **22**, 269 (1971).
[6] E. Balslev and J. M. Combes, Commun. Math. Phys. **22**, 280 (1971).
[7] B. Simon, Commun. Math. Phys. **27**, 1 (1972).
[8] U. V. Riss and H.-D. Meyer, J. Phys. B **26**, 4503 (1993).
[9] R. Santra and L. Cederbaum, Phys. Rep. **368**, 1 (2002).
[10] S. Samanta and D. L. Yeager, J. Phys. Chem. B **112**, 16214 (2008).
[11] S. Samanta and D. L. Yeager, Int. J. Quantum Chem. **110**, 798 (2010).
[12] R. Graham, D. L. Yeager, J. Olsen, P. Jorgenson, R. Harrison, S. Zarrabian, and R. Bartlett, J. Chem. Phys. **85**, 6544 (1986).
[13] S. Samanta and D. L. Yeager, Adv. Chem. Phys. **150**, 103 (2012).
[14] J. A. Nicols, D. L. Yeager, and P. Jorgenson, J. Chem. Phys. **80**, 293 (1984).
[15] J. T. Golab and D. L. Yeager, J. Chem. Phys. **87**, 2925 (1987).
[16] R. Saha, Dongxia Ma, and Danny L. Yeager, Int. J. Quantum Chem. **107**, 694 (2007).
[17] Dongxia Ma and Danny L. Yeager, Int. J. Quantum Chem. **108**, 100 (2008).
[18] Dongxia Ma and Danny L. Yeager, Int. J. Quantum Chem. **108**, 1130 (2008).
[19] D. L. Yeager and P. Jorgenson, Chem. Phys. Lett. **65**, 77 (1979).
[20] S. B. Zhang and D. L. Yeager, J. Mol. Struct. **1023**, 96 (2012).
[21] S. B. Zhang and D. L. Yeager, Phys. Rev. A **85**, 032515 (2012).
[22] S. B. Zhang and D. L. Yeager, Mol. Phys. **110**, 663 (2012).
[23] L. Liang and D. L. Yeager, J. Chem. Phys. **140**, 094305 (2014).
[24] R. L. Graham, D. L. Yeager, and A. Rizzo, J. Chem. Phys. **91**, 5451 (1989).
[25] D. L. Yeager, J. A. Nichols, and J. T. Golab, J. Chem. Phys. **97**, 8441 (1992).
[26] V. G. Zakrzewski, J. V. Ortiz, J. A. Nichols, D. Heryadi, D. L. Yeager, and J. T. Golab, Int. J. Quantum Chem. **60**, 29 (1996).
[27] S. Mahalakshmi and D. L. Yeager, Mol. Phys. **101**, 165 (2003).
[28] S. Mahalakshmi and D. L. Yeager, in *Fundamental World of Quantum Chemistry: A Tribute to Per-Olov Löwdin*, edited by E. J. Brändas and E. S. Kryachko (Kluwer Academic Publishers, Dordrecht, 2004), p. 547.
[29] P.-O. Löwdin, Adv. Quantum Chem. **19**, 87 (1988).
[30] S. Yabushita and C. W. McCurdy, J. Chem. Phys. **83**, 3547 (1985).
[31] D. L. Yeager and M. K. Mishra, Int. J. Quantum Chem. **104**, 871 (2005).
[32] D. J. Rowe and C. Ngo-Trong, Rev. Mod. Phys. **47**, 471 (1975).
[33] A. Venkatnathan, M. Mishra, and H. J. Jensen, Theor. Chim. Acta **104**, 445 (2000).
[34] R. A. Donnelly and J. Simons, J. Chem. Phys. **73**, 2858 (1980).
[35] H. A. Kurtz and Y. Öhrn, Phys. Rev. A **19**, 43 (1979).
[36] H. A. Kurtz and K. D. Jordan, J. Phys. B **14**, 4361 (1981).
[37] C. W. McCurdy, T. N. Rescigno, E. R. Davidson, and J. G. Lauderdale, J. Chem. Phys. **73**, 3268 (1980).
[38] T. N. Rescigno, C. W. McCurdy, and A. E. Orel, Phys. Rev. A **17**, 1931 (1978).
[39] J. F. McNutt and C. W. McCurdy, Phys. Rev. A **27**, 132 (1983).
[40] P. Krylstedt, M. Rittby, N. Elander, and E. Brändas, J. Phys. B **20**, 1295 (1987).
[41] P. Krylstedt, M. Rittby, N. Elander, and E. Brändas, J. Phys. B **21**, 3969 (1988).
[42] S. Bashkin and J. A. Stoner, Jr., *Atomic Energy Levels and Grotrian Diagrams* (North-Holland, New York, 1975), Vol. 1.
[43] Y. Zhou and M. Ernzerhof, J. Phys. Chem. Lett. **3**, 1916 (2012).
[44] S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).
[45] T. Rescigno, A. Orel, and C. McCurdy, J. Chem. Phys. **73**, 6347 (1980).
[46] H. Meyer, Phys. Rev. A **40**, 5605 (1989).
[47] S. Mahalakshmi, A. Venkatnathan, and M. K. Mishra, J. Chem. Phys. **115**, 4549 (2001).
[48] Y. Sajeev, R. Santra, and S. Pal, J. Chem. Phys. **122**, 234320 (2005).
[49] G. J. Schultz, Rev. Mod. Phys. **45**, 423 (1971).
[50] T. Sommerfeld, U. Riss, H. Meyer, L. Cederbaum, B. Engels, and H. Suter, J. Phys. B **31**, 4107 (1998).