Computation of resonances by two methods involving the use of complex coordinates

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We have studied two different systems producing resonances, a highly excited multielectron Coulombic negative ion (the He$^-$ $2s2p^2\,^4P$ state) and a hydrogen atom in a magnetic field, via the complex-coordinate rotation (CCR) and the state-specific complex-eigenvalue Schrödinger equation (CESE) approaches. For the He$^-$ $2s2p^2\,^4P$ resonance, a series of large CCR calculations, up to 353 basis functions with explicit r_{ij} dependence, were carried out to serve as benchmarks. For the magnetic-field problem, the CCR results were taken from the literature. Comparison shows that the state-specific CESE theory allows the physics of the problem to be incorporated systematically while keeping the overall size of the computation tractable regardless of the number of electrons.

I. FOUNDATIONS AND CHARACTERISTICS OF TWO METHODS FOR THE *AB INITIO* COMPUTATION OF RESONANCES

In this paper we present results from the application of two computational strategies to the determination of energies and widths of resonances. The first is the complex-coordinate rotation (CCR) method, whose validity and practice are justified as follows: if the transformation $\rho = re^{i\theta}$ is applied to the coordinates of a number of real or model Hamiltonians, $H(r)$, the non-Hermitian property of the new, rotated Hamiltonian, $H(\rho)$, leads, upon its diagonalization in a complete space of $\mathcal{L}^2$ functions, to complex eigenvalues which are independent of θ beyond a critical value and correspond to resonances (e.g., [1–7]). The identification of these complex eigenvalues with physical resonance states was initially based on various mathematical arguments from the spectral theory of classes of Hamiltonian operators ([3,7], and references therein). In the CCR method [1–6], $H(\rho)$ is diagonalized repeatedly in a given $\mathcal{L}^2$ space of real functions as a function of θ, until a region of relative stability of the looked-for complex eigenvalue is reached.

The CCR method is conceptually simple, but not general enough to allow certain physically observable quantities such as partial widths, to be computed. Furthermore, it is limited because it is very demanding in terms of the size of the $\mathcal{L}^2$ function space required for reliable convergence to occur. This was concluded already in the 1970s [1–5], and will be discussed again here. It was recognized [8,9] that its slow convergence was due, to a large extent, to the use of only a single set of basis functions which is not necessarily appropriate for describing simultaneously the interactions leading to the position as well as those leading to the width of the resonance. This realization has been incorporated in a general theory of multielectron, multichannel, multiphoton resonances [9–15], which is the second approach used here, whose aim is the state-specific solution of the complex eigenvalue Schrödinger equation (CESE).

The state-specific CESE theory has its origin in the recognition of the following: (1) The problem can be understood in terms of the concept of perturbation of the asymptotic boundary conditions [9,13,16,17]. (2) Given the localized part of the resonance, Ψ_0, which is the square-integrable projection of the resonance function, Ψ, on the real axis [9,18], the rotated $\Psi(\rho)$ has the form [9,13]

$$\Psi(\rho) = a(\theta)\Psi_0(\rho) + b(\theta)\chi_{as}(\rho), \quad |a|^2 + |b|^2 = 1 \qquad (1)$$

where χ_{as} represents the contributions of the continuum component on resonance. (3) Using $\Psi(\rho)$ of Eq. (1) and the rotated $H(\rho)$, in practice matrix elements involving Ψ_0 or final-state bound orbitals remain θ independent, while only configurations containing the square-integrable Gamow orbital give rise to complex integrals. In this way, the Hamiltonian need not be rotated (see also Ref. [4]), and the question of the spectrum of $H(\rho)$ is replaced by the question of the appropriate coordinate transformation which will regularize its nonsquare-integrable eigenfunction [9,16,17], as was done for the short-range potential by Dykhne and Chaplik [19].

The above observations were then incorporated into the state-specific electronic structure theory of resonances and autoionizing states ([12–18] and references therein) with the result that properties such as partial and total energy shifts and widths of simple as well as complex polyelectronic systems can be analyzed and calculated systematically and without unreasonable computational requirements.

The comparative results presented here have been obtained from the application of the aforementioned two methods, the state-specific CESE and the CCR, to two problems. The first is the computation of the position and width of the He$^-$ $2s2p^2\,^4P$ resonance by the CCR method. For this state results obtained from very small computations in the context of the state specific CESE theory, have already been published [20]. The second is the computation of resonances of the hydrogen atom in a magnetic field by the CESE method. This case has already been treated by the CCR method [21–23].

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For both problems, the efficiency and physical transparency of the CESE approach is superior.

II. MANY-ELECTRON AUTOIONIZING RESONANCES: THE $2s2P^2\,{}^4P$ STATE OF He$^-$

The CCR method has allowed the accurate computation of resonances of two-electron atoms [2–5]. However, an early attempt by Bain et al. [1] to use this method for computation of the three-electron $1s2s^2\,{}^2S$ resonance in He$^-$ failed to produce a converged complex energy. This state was recomputed recently by the CCR method using a larger space [24]. A basis of 184 configurational functions containing explicitly interelectronic distances resulted in a position of 19.367 eV above the ground level of He, and a width of 8.6 meV. To further test convergence, we repeated this calculation using the same method and a basis of 579 functions with r_{ij} factors. We obtained essentially the same results: $E = 19.370$ eV and $\Gamma = 8.8$ meV.

In order to test the application of the CCR method to a three-electron resonance with intrashell correlation, now we have computed the He$^-$ $2s2p^2\,{}^4P$ state which decays into the $1s2p\,{}^3P^\circ$ open channel. We used basis sets of two types. One of them contained only configurations constructed from one-electron orbitals. In the other basis we also included functions containing interelectronic distances r_{ij}. These computations were carried out as in the previous CCR work [24] using the techniques developed by Woznicki [25] for real Hamiltonians.

In Table I we show the rate of convergence of our CCR calculations. Results of three series of calculations are presented from which conclusions can be drawn as to the particulars of radial and angular correlation and as to the importance of the r_{ij} factors. Each of these series was carried out in such a way that the basis used in one calculation was included in a larger basis of subsequent calculations. In the first series of computations we used only orbital sets. We observed that when enlarging the basis set the energy of the resonance converges monotonically to the value 57.454 eV above the He ground level. On the other hand, the width of the resonance does not converge so smoothly. The addition of a few configurations of a new angular type changes the width significantly, e.g., the addition of only 9 sdd configurations to the spp-type basis set changes the value of width from 9.8 to 17.7 meV (almost twice the original value). However, adding more radial terms of the same angular type brings the width close to the value of 11 meV. This suggests that the sudden jump of the width is not a physical effect of a particular angular term, but rather a disturbance caused by lack of radial correlation. The radial correlation also affected the stabilization property of θ trajectories. We observed that adding more and more radial terms of a given angular type stabilized the complex energy of the resonance, whereas the addition of a few terms of a new angular type destabilized it. Finally, our largest orbital configuration interaction (CI) (208 configurations) gave $\Gamma = 10.9$ meV.

In the next series of computations we used r_{ij}-correlated basis sets which account for the angular correlation better. However, we used a relatively small number of radial terms. The position of the resonance converged, again monotonically, but faster than in the orbital CI computation, to the value 57.420 eV. The width was found in the range 10–11 meV, but without convergence because of the lack of radial correlation. In the

TABLE I. CCR calculation of the $2s2p^2\,{}^4P$ resonance of He$^-$. The energy E is given in eV, above the He ground level, and the width Γ in meV (1 a.u. = 27.211 65 eV).

Type of functions	Number of functions	E (eV)	Γ (meV)
	Orbital basis sets		
spp	69	57.690	11.0
	115	57.689	10.3
	146	57.668	9.8
$+sdd$	155	57.581	17.7
	164	57.574	11.9
	173	57.574	11.0
$+pp(P)d$	180	57.474	12.9
	187	57.474	10.8
	194	57.474	11.0
$+pp(D)d$	201	57.455	9.7
	208	57.454	10.9
	r_{ij}-correlated basis sets[a]		
$spp*(r_{12}+r_{23})$	136	57.430	10.8
$+sdd*r_{12}$	153	57.424	11.2
$+ppd*r_{12}$	173	57.420	9.8
	Enlarged r_{ij}-correlated basis sets[a]		
$spp*r_{12}$	225	57.552	10.0
$+spp*r_{23}$	258	57.430	10.3
$+sdd*r_{12}$	303	57.423	10.3
$+ppd*r_{12}$	353	57.420	10.4

[a]Only terms that are linear with respect to r_{ij} were used.

third series of computations we included more radial terms and obtained converged results: $E = 57.420$ eV (in agreement with previous real energy calculations [20,26,27]) and $\Gamma = 10.4$ meV. The total number of basis functions was 353.

We now turn to the calculation from the state-specific CESE theory. It has been argued repeatedly (e.g., [13,14,20]) that the correlated wave functions of multiply excited states (MES), such as the He^- $2s2p^2$ ^4P state, are computable very efficiently and accurately within the multiconfigurational Hartree-Fock (MCHF) approximation with suitably selected few configurations. Thus, a three-term MCHF calculation $(2s2p^2, 2p^23d, 2s2d^2)$ with the $2s$ orbital kept orthogonal to the He^+ $1s$, yields $E_{MCHF} = 57.648$ eV above the He ground state, which is only about 0.25 eV above the previously mentioned accurate values. Using this approximate Ψ_0 and ten "asymptotic" configurations $(1s2p$ $^3P^0)$ "ε"p, with ten complex Slater-type orbitals (STO's) "ε"p, results in only an 11×11 complex Hamiltonian matrix whose diagonalization gave $\Gamma = 0.015$ eV and the energy shift $\Delta = 0.027$ eV [20]. Given the very small size of this computation, the predicted width is in very satisfactory agreement with the present CCR results.

A better total energy can be obtained trivially by augmenting slightly the Fermi sea to include the $3s$ and $3p$ orbitals. Thus, just a five-term self-consistent solution gives

$$\Phi_{MCHF}(^4P) = 0.982(2s2p^2) + 0.100(2p^23d)$$
$$-0.097(2s3p^2) - 0.087(2s3d^2)$$
$$+0.088(2p3s3p) ,$$

with $E_{MCHF} = -0.79209$ a.u. $= 57.461$ eV above He ^1S. Finally, a 14-configuration MCHF solution gives $E_0 = 57.408$ eV. If we add $\Delta = 0.027$ eV obtained earlier [20], then $E = 57.435$ eV, in very good agreement with the results of the large CCR calculations.

III. AUTOIONIZING STATES OF A HYDROGEN ATOM IN A MAGNETIC FIELD

The system of a hydrogen atom in a strong uniform magnetic field can be described by the nonrelativistic single-particle Hamiltonian (in a.u.)

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{\gamma}{2}m + \frac{\gamma^2}{8}(x^2+y^2) , \qquad (2)$$

where γ is the magnetic-field strength in a.u. ($\gamma = B/B_0$, $B_0 = 2.35 \times 10^5$ T) and m is the z component of angular momentum parallel to the magnetic field. The symmetry is cylindrical so the states of the system can be classified according to a given m and z parity π (parity with respect to the $z = 0$ plain).

The wave function of the system, $\psi^{m,\pi}$, can be expanded in Landau states

$$\psi^{m,\pi} = \sum_N \Phi_N^m(\rho,\varphi)f_N^\pi(z) , \qquad (3)$$

where (ρ,φ,z) are cylindrical coordinates and $\Phi_N^m(\rho,\varphi)$

are Landau orbitals, which are the transversal eigenstates of the Hamiltonian (2) without the $1/r$ term, i.e., in the absence of the nucleus. For strong fields ($\gamma \geq 1$, when the separation of consecutive Landau energy levels is larger than the Rydberg energy), use of this expansion leads to fast convergence. Many authors have used it to calculate energies of bound states [28–30] and binding energies and widths of autoionizing resonances associated with excited Landau states [21,22,31,32]. The coefficient functions $f(z)$ in Eq. (3) can be found by numerical integration of coupled integral equations [29] or from a variational calculation using basis sets [21,22,30].

In this work, we consider only the lowest $m = 0$, even z-parity resonance. We have chosen this state because Bhattacharya and Chu [21] reported it as the most slowly convergent one in their CCR calculation.

Since this state had already been investigated by the CCR method [21,22], we performed only a state-specific CESE calculation. This implies a choice of basis sets which are specific to the state under consideration. Our resonance is associated with the first excited Landau state. Therefore, we used the adiabatic approximation, i.e., we took only the $N = 1$ term in Eq. (3), as a zero-order description of the localized part, Ψ_0, Eq. (1). Going beyond the adiabatic approximation, we improved Ψ_0 by including the $N = 1, \ldots, 8$ Landau terms (closed channels only).

Following Vincke and Baye [22,30], we expanded the coefficients $f(z)$ of Eq. (3) in a basis of one-dimensional Slater-type orbitals (z-STO's) of the form

$$\xi_i^n(z) \equiv z^n \exp(-\beta_i|z|) . \qquad (4)$$

Since the resonance under consideration is the lowest one of $\{m = 0, \pi = 0\}$ symmetry, it does not have nodes in the z direction. Therefore, we used only nodeless, $n = 0$, z-STO's to represent the localized part of the wave function. Their nonlinear parameters were chosen to form a geometrical sequence and were optimized in a one-Landau-channel (adiabatic) calculation. In the many-Landau-channel calculation they were used unchanged. We found that 7 or 9 z-STO's are enough to obtain a converged value of the energy, for $\gamma = 2000$ or $\gamma = 10$, respectively. (The stronger the field is the more compact the wave function is.)

The ground Landau state constitutes the only open channel for the decay of the resonance. Thus, the asymptotic part of the wave function is

$$\chi_{as} = \sum_i \Phi_0^0(\rho,\varphi)\xi_i^n(ze^{-i\theta}) . \qquad (5)$$

Asymptotically free motion in the z direction is described by a basis consisting of one nodeless z-STO and several (14 in the final calculation) $n = 2$ z-STO's. Their dependence on $ze^{-i\theta}$, instead of z itself, is a consequence of regularization of the unbound asymptotic function. The exponents β of those z-STO's also formed a geometrical progression and were chosen so that the z-STO's covered the region where the localized part Ψ_0 took nonnegligible values (the most diffused z-STO was peaked beyond the average value of z resulting from Ψ_0).

TABLE II. Binding energy E_B (in Ry) and width Γ (in 10^{-2} Ry) of the lowest $m=0$ even z-parity autoionizing resonance of a hydrogen atom in a strong magnetic field.

γ	Chu and Friedrich		This work[a]		Vincke and Baye		Bhattacharya and Chu	
	E_B	$\Gamma/2$[b]	E_B	$\Gamma/2$	E_B	$\Gamma/2$	E_B	$\Gamma/2$
10	2.32	4.22	2.249	3.83				
			2.339	5.06	2.337	4.67	2.294	4.35
100	5.34	2.37	5.342	2.51				
			5.398	2.72	5.396	2.65	5.370	2.58
500	9.16	1.59	9.161	1.69				
			9.197	1.75			9.174	1.71
1000		1.33	11.378	1.40				
			11.408	1.43	11.408	1.40		
2000	14.01	1.12	14.005	1.14				
			14.029	1.16				

[a]The upper values were obtained by using the adiabatic approximation for the localized part of the wave function, Ψ_0, and the lower ones by using and eight-Landau-channel localized part.

[b]The width values recovered from the formula $\Gamma = 0.15\gamma^{-0.25}$ given by Chu and Friedrich [32].

In Table II we compare our results, obtained for several values of the field strength, with results of other authors. Our results obtained with the adiabatic Ψ_0 function for $\gamma \geq 100$, agree very well with the results obtained by Chu and Friedrich [32]. For these strengths of the field they used a two-lowest-Landau-channel expansion. We also used the same two Landau channels: the first excited one in the adiabatic Ψ_0 and the ground one in the asymptotic part. On the other hand, our results obtained by using many-Landau-channel Ψ_0 agree very well with the Vincke and Baye [22] results from the CCR method. In this case, the Landau channel expansion was of similar size in both calculations.

Similar size of the Landau-channel expansion does not mean, however, that the two calculations were of the same size and cost. In Table III we give characteristics of these two computations. Although we used nine Landau channels instead of eight, as used by Vincke and Baye [22], our computation was more economical. This is because of the following three reasons.

(i) Using nine z-STO's per Landau channel was enough in our calculation to obtain converged results. For the type of calculations done by Vincke and Baye [22], 18 z-STO's per Landau channel were needed.

(ii) The number of complex integrals which had to be evaluated for each value of complex rotation angle was much smaller in the CESE calculation than in the CCR one. This was so, not only because the smaller number of

z-STO's led to a smaller Hamiltonian matrix, but mainly because in the CESE method only $\langle \chi_{as} H \Psi_0 \rangle$ and $\langle \chi_{as} H \chi_{as} \rangle$ blocks of the Hamiltonian matrix are complex. The large (72×72) $\langle \Psi_0 H \Psi_0 \rangle$ block is real and does not change with variation of the rotation angle. Let us stress that the Coulomb interaction integrals had to be computed numerically in both methods, which is time consuming.

(iii) Since the linear coefficients of the Ψ_0 part of the wave function were found in the real energy computation, the Hamiltonian matrix was contracted before the diagonalization. Only a small, 16×16, complex matrix was diagonalized.

The convergence of our computation with respect to the asymptotic part representation is illustrated in Fig. 1. For the six-z-STO representation of the continuum, a reasonable result was obtained. The complex energy of the resonance is converged for ten z-STO's with the accuracy of four significant figures for the real part and three figures for the width. With such accuracy, the stabilization is obtained in the range $\theta = 0.8 - 1.3$. Starting from 14 z-STO's in the asymptotic part, the stabilization range is 0.5–1.4. The convergence and stabilization were also the same in our many-Landau-channel calculation for all the values of the field strength. Let us note that the stabilization range of θ in the larger size Vincke and Baye [22] and Bhattacharya and Chu [21] calculations was smaller (respectively 0.4–0.7 and 0.3–0.5).

TABLE III. Computational effort in the CCR calculation [22] and in the present CESE calculation.

	CCR	CESE
Number of Landau channels	8	9
Number of z-STO's per channel	18	9(15)[a]
Number of independent complex matrix elements	20736	1200
Size of the Hamiltonian matrix	144×144	95×95
Size of the complex diagonalization	144×144	16×16

[a]Nine z-STO's per each of the eight closed Landau channels and 15 for the open Landau channel (i.e., for the asymptotic part).
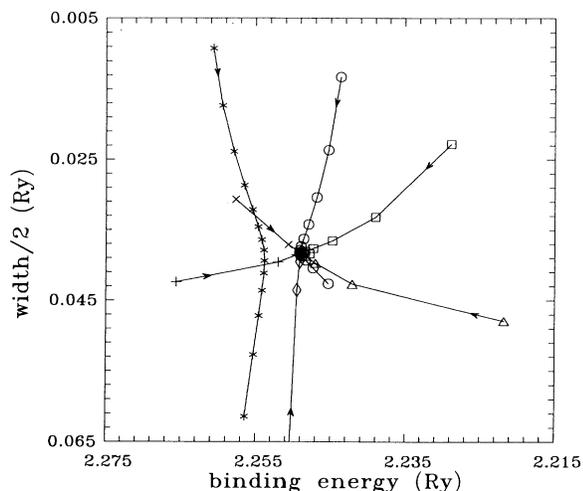
FIG. 1. Convergence and stabilization of the two-Landau-channel calculation at $\gamma = 10$. θ trajectories for various numbers of z-STO's representing the asymptotic part of the wave function: $*$, $6z$-STO's; $\bigcirc$, 8; $\square$, 10; $\triangle$, 12; $\diamond$, 14; $+$, 16; $\times$, 18. Each θ trajectory consists of 14 points corresponding to $\theta = 0.1, 0.2, \ldots, 1.4$. The arrows show the direction of increasing θ.

We have also investigated the convergence of the resonance parameters with respect to the number of Landau channels. The nine-Landau-channel results presented in Table II are converged in this sense. We do not discuss details of this convergence because it should be the same in all the calculations quoted in present paper. This is because in the CCR calculation of Bhattacharya and Chu [21] and Vincke and Baye [22], as well as in ours, the Landau states were not affected by complex rotation. Only the z coordinate was rotated either in the asymptotic function equation (5), in the CESE method, or in the

Hamiltonian, in the CCR method. It would not be the case if one had rotated all the coordinates in the Hamiltonian as was done by Delande, Bommier, and Gay [23]. In that case the Landau states would get an oscillating character and the fast convergence of the landau expansion, Eq. (3), would be lost.

IV. CONCLUSION

We have compared two approaches to the computation of resonances which employ complex coordinates. The first uses the transformation $\rho = re^{i\theta}$ in the Hamiltonian which then becomes non-Hermitian with complex eigenvalues representing the position and the total width of the resonances. The corresponding CCR computational method is formally rigorous, since it aims at the complete diagonalization of $H(\rho)$, just like the standard case of Hermitian Hamiltonians and their real eigenvalues. However, the present results, as well as previously published ones, show that the completeness requirements on the basis sets are overwhelming, especially for polyelectronic systems. Furthermore, partial widths cannot be obtained by the CCR method.

The second approach draws from the theory of electronic structure of excited states and aims at the state-specific analysis and solution of the complex eigenvalue Schrödinger equation which emerges for each system of interest after the regularizing transformation is applied to the asymptotic boundary conditions, i.e., to the unbound function of the emitted particle [9,16,17]. In this way seemingly large computational problems involving non-stationary states can be reduced to problems which can be described by physically meaningful wave functions allowing very efficient and systematic computation. Apart from the polyelectronic Coulomb and the magnetic-field problems studied here, similar results have been obtained for problems of predissociation and of polyelectronic atomic states in external dc or ac fields.

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