Exterior complex scaling method applied to doubly excited states of helium

Nils Elander and Evgeny Yarevsky*
Department of Physics, Stockholm University, Box 6730, S-11385 Stockholm, Sweden
(Received 18 November 1997)

We propose a technique which is suitable for calculations of resonant energies of three-body systems. It is based on a smooth exterior complex scaling procedure and the three-dimensional finite-element method. Accuracy dependencies on an exterior radius and on a curvature of the rotated path are examined. *S*-wave resonances of helium are calculated with an accuracy better than 10^{-5} a.u. [S1050-2947(98)05604-2]

PACS number(s): 31.50.+w, 02.70.Dh

I. INTRODUCTION

The complex scaling (CS) method is one of the main methods for studying resonant properties of quantum systems. Since it was proposed, a lot of papers appeared which dealt with an analytical implementation of the CS as well as with numerical realizations in molecular, atomic, and nuclear physics. The interested reader is referred to reviews and workshop proceedings treating CS-related theories and their applications [1–3].

The uniform CS method uses the coordinate transformation $\mathbf{r}\rightarrow\eta\mathbf{r}$, where η is a complex number. In many cases, however, this transformation is not applicable, e.g., in the case of potentials which are not dilation analytic [4], or when a potential is given numerically in a part of the entire coordinate space while it can be represented as an analytic function asymptotically. Even though it may be formally applied, it is unnecessary when a system decays along only one coordinate. In this case, it is natural from both physical and numerical points of view to scale only that coordinate.

To deal with these issues, the exterior CS procedure (ECS) was proposed [6]. In ECS the coordinates are only scaled outside a hypersphere of radius $|\mathbf{r}|=R_0$. This implies that one does not rotate potentials at small distances (reaction region) and, therefore, excludes the problems outlined above.

In spite of the great success in locating resonance positions, some problems are usually connected with the use of CS theories when calculating scattering data, such as cross sections [5]. Recently, however, a generalization of the CS was proposed [7,8], which can be successfully used for computing scattering amplitudes and cross sections. As this generalization is based on the ECS technique, it becomes important to have a convenient numerical method, which utilizes the idea of the exterior complex scaling.

There are a considerable number of papers [7–12] which deal with computations in the context of the ECS. However, most of them describe implementations of the one-dimensional ECS. The authors of Refs. [8,9], who used a two-dimensional method, are an exception. All these realizations are powerful enough for many practical applications, especially in molecular physics. However, even in molecular physics there exist systems, like H_3^+ or O_3, where all three interparticle distances must be scaled. Furthermore, this is a typical case for nuclear physics problems. These kinds of problems motivate the present work.

In this paper we thus describe a method which incorporates the ECS in a truly three-dimensional fashion. Numerically, our method is based on the finite-element method (FEM) [13]. The realization of the method is described in Refs. [14,15]. It was recently shown that the FEM can be used to compute energy levels of three-body systems with a very high accuracy, up to 10^{-11} [16]. Here we show that a rather high accuracy can be reached in the framework of the FEM also for resonant energies.

As a test example we have chosen the helium atom. A lot of very accurate experimental and theoretical results concerning doubly excited states in helium are available (see [17], and references therein). Thus this system is a good test case for any method, and we use it in spite of the applicability of the uniform CS for helium. For the sake of simplicity, we restrict ourselves to *S* states only despite the fact that our realization of the FEM works efficiently even for very high angular momentum, up to 40 [15].

II. THEORY

A. Complex scaling method

In a supposition of infinitely heavy nucleus, the Hamiltonian H of the helium atom for zero total angular momentum can be written as

$$H=-\sum_{i=1}^{2}\frac{1}{2r_i^2}\left(r_i\frac{\partial^2}{\partial r_i^2}r_i+\frac{\partial}{\partial c}(1-c^2)\frac{\partial}{\partial c}\right)+V(r_1,r_2,c), \tag{1}$$

where the potential energy $V(r_1,r_2,c)$ is the sum of Coulomb potentials:

$$V(r_1,r_2,c)=-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}.$$

Here r_i is the distance between the ith electron and the nucleus, $c=\cos(\vec{r_1},\vec{r_2})$, and the inter-electron distance is $r_{12}^2=r_1^2-2r_1r_2c+r_2^2$.

To calculate resonant states of the system in the CS method, we should replace the three-component vectors $\vec{r_i}$ to

*On leave of absence from Laboratory of Complex Systems Theory, Institute for Physics, St. Petersburg University, St. Petersburg, Russia.

the complex ones. In fact, only the magnitudes r_i of the vectors have to be scaled [6]. We define the transformation of r_i as [18]

$$r_i \rightarrow \phi(r_i) = r_i + \lambda g(r_i), \tag{2}$$

where $\lambda = \exp(i\theta) - 1$, and θ is a rotation angle. The function $g(r)$ describes the complex path. The formal requirements on this function are rather general and are given in Ref. [18]. It is worth noticing that $g(r) = r$ corresponds to the uniform CS. In this paper, we use the term ''smooth'' CS for the transformation when both $g(r)$ and its derivative are continuous. The term ''sharp'' CS refers to the original prescription [6] when $g'(r)$ is discontinuous. We specify our choice of $g(r)$ below. The angular variable c is obviously not changed by the transformation.

In analogy with the uniform complex scaling [4], we define the operator U_θ which scales the wave function $\Psi(r_1, r_2, c)$ as

$$U_\theta \Psi(r_1, r_2, c) = p(r_1) p(r_2) \Psi(\phi(r_1), \phi(r_2), c). \tag{3}$$

Here the function $p(r_i) = \sqrt{|J(r_i)|}$, and the Jacobians $J(r_i)$ are defined as

$$J(r_i) = \frac{d\phi(r_i)}{dr_i} = 1 + \lambda g'(r_i). \tag{4}$$

As it was suggested in Ref. [7], it is convenient to deal with the function $\Psi_\theta \equiv \Psi(\phi(r_1), \phi(r_2), c)$ without the factor $p(r_1)p(r_2)$. This has an advantage that even for the sharp exterior scaling the function Ψ_θ is continuous unlike $p(r_1)p(r_2)\Psi_\theta$ [19]. The rotated Hamiltonian $H_\theta = U_\theta H U_\theta^{-1}$ acting on the function Ψ_θ can be expressed as

$$H_\theta = -\sum_{i=1}^{2} \left[\frac{1}{2p^4(r_i)} \frac{\partial^2}{\partial r_i^2} + \left(\frac{1}{p^2(r_i)\phi(r_i)} - \frac{p'(r_i)}{p^5(r_i)} \right) \frac{\partial}{\partial r_i} + \frac{1}{2\phi^2(r_i)} \frac{\partial}{\partial c} (1 - c^2) \frac{\partial}{\partial c} \right] + V(\phi(r_1), \phi(r_2), c). \tag{5}$$

B. Finite-element method

Numerically we have treated Eq. (5) using the finite-element method. Here we outline the general ideas of this method, while one can find its detailed description elsewhere [12–14].

The three-dimensional space formed by r_1, r_2, and c is divided into some number of rectangular boxes numbered by i. The wave function Ψ_θ is expanded in a finite-element basis such that

$$\Psi_\theta = \sum_{im} v_{im} f_{im}(r_1, r_2, c). \tag{6}$$

Here, v_{im} are expansion coefficients defined in each element i and restricted through continuity conditions for the wave function and its derivatives at element boundaries. A basis function $f_{im}(r_1, r_2, c)$ has, in the finite-element algorithm, the property

$$f_{im}(r_1, r_2, c) \equiv 0 \text{ for } (r_1, r_2, c) \notin \text{element } i. \tag{7}$$

The resonant energies $z = E - i\Gamma/2$ are obtained as eigenvalues of a functional $\langle \Psi_\theta | H_\theta | \Psi_\theta \rangle$, where the rotated Hamiltonian H_θ is defined in Eq. (5). These energies are evaluated by solving a generalized eigenvalue problem:

$$\tilde{H}_\theta v = z \tilde{S} v, \tag{8}$$

where

$$(\tilde{H}_\theta)_{im,jk} = \langle f_{im} | H_\theta | f_{jk} \rangle \quad \text{and} \quad (\tilde{S})_{im,jk} = \langle f_{im} | f_{jk} \rangle.$$

The basis functions f_{im} are expressed as products of one-dimensional functions

$$f_{im}(r_1, r_2, c) = f_{im_1}(r_1) f_{im_2}(r_2) f_{im_3}(c). \tag{9}$$

Such a representation of the basis functions simplifies an evaluation of the matrix elements in Eq. (8) and reduces three-dimensional integrals of the kinetic energy to a product of one-dimensional ones. Namely, integrating Eq. (8) by parts and accounting for the smoothness of all functions, we have, for example, for a part $H_\theta^{(1)}$ which includes derivatives with respect to r_1,

$$(\tilde{H}_\theta^{(1)})_{im,jk} = \int \frac{df_{im_1}(r_1)}{dr_1} \frac{df_{jk_1}(r_1)}{dr_1} \frac{\phi^2(r_1)}{p^2(r_1)} dr_1 \times \int f_{im_2}(r_2) f_{jk_2}(r_2) \phi^2(r_2) p^2(r_2) dr_2 \times \int f_{im_3}(c) f_{jk_3}(c) dc. \tag{10}$$

Analogous expressions are obtained for the other derivatives. The only remaining three-dimensional integral is that of the potential energy.

The one-dimensional basis functions were chosen to be Legendre polynomials for the angular variable and a product of Legendre polynomials and an exponential function for the radial variables.

The generalized eigenvalue problem (8) was solved by the inverse iterations method. For solving the set of linear equations appearing, we used the block lower times upper triangular matrices (LU) factorization method.

It is well known [4] that positions and widths of resonances are independent of the rotation angle θ. However, this is true only in exact calculations. When a numerical approximation is used, resonances become θ dependent. In this case, their positions E and widths Γ are defined by means of the complex variational principle [20]:

$$\left. \frac{dE}{d\theta} \right|_{\theta_r} = 0$$

and

$$\left. \frac{d\Gamma}{d\theta} \right|_{\theta_i} = 0. \tag{11}$$

The two optimal angles θ_r and θ_i converge to one single angle as the accuracy of the calculation is increased.

III. CALCULATIONS, RESULTS, AND DISCUSSION

For our calculations we should specify a function $g(r)$ which can describe complex paths with different curvatures. Our choice

$$g(r)=\begin{cases}0, & r\leqslant R_0\\ (r-R_0)\{1-\exp[-\sigma(r-R_0)^2]\}, & r>R_0.\end{cases} \tag{12}$$

Here R_0 is the external radius and σ is the curvature parameter. Both the function and its derivative are continuous at R_0. When σ goes to infinity, $g(r)$ describes the sharp exterior CS. The case $R_0=0$ and $\sigma=\infty$ [i.e., $g(r)=r$] corresponds to the usual uniform scaling.

For our calculations we have chosen maximum radius 50 a.u. and five boxes for both r_1 and r_2 coordinates and one box for c coordinate. The box boundaries are 1.24, 4.0, 6.6, and 16.0 a.u. The number of basis functions was chosen to be 6 for the radial coordinates and 10 for the angular one. The matrix elements of the potential in Eq. (8) were calculated numerically using the 20-point Gauss-quadrature rule. This mesh yields sparse matrices of dimension 3250 with a total bandwidth of 2102. It is worth noticing that these values are very small in the context of the FEM [15,16].

As we study the accuracy dependence on the exterior scaling parameters, we use the mesh which produces relatively big errors up to 10^{-4}. To check a convergence of the results we use also a denser mesh, see below.

In Fig. 1 we present a typical behavior of real and imaginary parts of a resonance in helium. One can see that there is the definite accuracy dependence on the curvature parameter σ: the smaller σ, the better an accuracy. This fact has a natural explanation. Indeed, when σ goes to infinity, the smooth CS approaches the sharp one. It is known that for the sharp scaling both the wave function and its derivatives [19], or at least the derivatives [7], are discontinuous. For finite values of σ they are continuous but they have to change drastically on an interval $\Delta R\sim 1/\sqrt{\sigma}$ around R_0 in correspondence with the definition of $g(r)$. As in our realization of the FEM both functions and derivatives are continuous, it means that we have to use very small boxes around R_0 or very dense sets of local functions f_{im} in every box in order to approximate the wave function with a good accuracy. A similar conclusion was reported, for the sharp scaling, in Ref. [12]. When σ becomes smaller, the transition region $1/\sqrt{\sigma}$ is growing and we do not need to take special care about the vicinity of R_0.

On the other hand, σ cannot be arbitrarily small. The transition region $1/\sqrt{\sigma}$ has to be much smaller than the maximum radius of the numerical approximation: $R_{\max}-R_0\gg 1/\sqrt{\sigma}$. This means that the asymptotics $g(r)\sim r$ is already reached inside the part of the space, which is numerically approximated.

As one can see in the figure, there is no obvious accuracy dependence on the external radius R_0. The only conclusion that can be drawn is that the best results are obtained with $R_0=0$. Even in this case, the smooth CS with relatively small σ produces better results than the uniform scaling ($\sigma=\infty$) does. In the intermediate region of R_0, details of the accuracy behavior depend on a numerical realization.

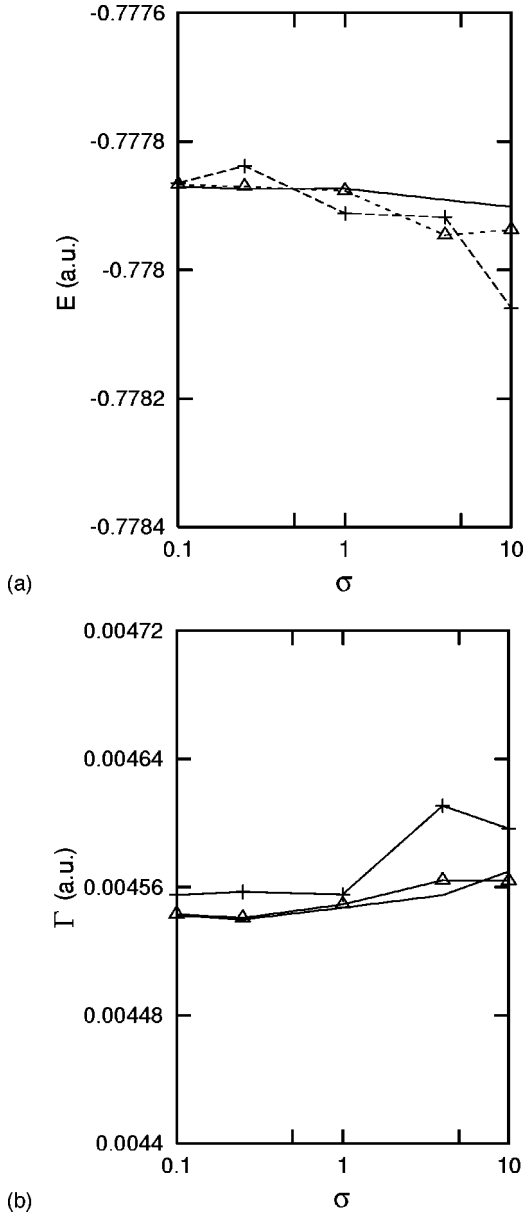

FIG. 1. Real part E (a) and width Γ (b) of a helium resonance as a function of the curvature parameter σ. The lines without symbols, with crosses, and with triangles correspond to $R_0=0.0$, 1.24, and 4.0 a.u., respectively.

Following arguments mentioned above, for calculations of other levels we have chosen the exterior scaling parameters to be $R_0=4$ a.u. and $\sigma=0.25$. The results are presented in Table I. The main aim of this work is to present and analyze a synthesis of the exterior complex scaling and our previous FEM approach. It is thus not of interest to compare our results to an extensive amount of experimental and theoretical data. Such a discussion can, for example, be found in Ref. [17]. We have rather chosen to compare our results with those of Ref. [17] since they are the most complete ones and agree with other precise calculations [21].

One can see that for the mesh mentioned above (mesh 1)

TABLE I. Energies and widths (a.u.) of S states in helium.

	Present[a]		Present[b]		Lindroth[c]	
	E	Γ	E	Γ	E	Γ
$^1S^e$ (1)	−0.77787	0.00457	−0.777870	0.004535	−0.777868	0.004541
$^1S^e$ (2)	−0.62204	0.00021	−0.621949	0.000213	−0.621926	0.000216
$^1S^e$ (1)	−0.58989	1.36×10^{-3}	−0.589895	1.36×10^{-3}	−0.58989	1.36×10^{-3}
$^1S^e$ (2)	−0.54810	7.2×10^{-5}	−0.548088	7.51×10^{-5}	−0.54809	7.62×10^{-5}
$^3S^e$ (1)	−0.60258	6.2×10^{-6}	−0.602577	6.86×10^{-6}	−0.60258	6.64×10^{-6}
$^3S^e$ (2)	−0.55975	8.6×10^{-7}	−0.559746	2.61×10^{-7}	−0.55975	2.56×10^{-7}
$^1S^e$ (1)	−0.35354	3.03×10^{-3}	−0.353539	3.01×10^{-3}	−0.35354	3.01×10^{-3}
$^1S^e$ (2)	−0.31746	6.67×10^{-3}	−0.317457	6.66×10^{-3}	−0.31745	6.67×10^{-3}

[a]Mesh 1 results.

[b]Mesh 2 results.

[c]Uniform complex scaling method, Ref. [17].

our results agree rather well except for small widths $\Gamma\lesssim10^{-4}$ a.u. The reason is that the method gives one complex number z at a time and, therefore, a relative accuracy for a small imaginary part is worse than for a bigger real part. To check a convergence, we increased the number of the local basis functions for the radial coordinates from 6 to 7 keeping other mesh parameters the same. This increased the matrix dimension up to 4530. The corresponding results are shown in Table I as results for mesh 2. One can see that they agree perfectly with the results of Ref. [17]. Indeed, comparing them with more precise Hylleraas-type calculations [21] when available, we have found a difference only a few units of 10^{-6} a.u. for all levels, except for the level with $E\simeq-0.6219$ a.u. This level experienced a slower convergence than others.

IV. CONCLUSIONS

It has been shown that the technique based on the smooth exterior complex scaling and the three-dimensional finite-element method can be successfully applied to calculations of energies of resonant states in three-body quantum systems. Guidelines for choosing the exterior scaling parameters have been presented. Our technique gives a competitive accuracy even for the helium atom despite the fact that its main implementation should be faced in molecular and nuclear physics.

ACKNOWLEDGMENT

One of us (E.Y.) is grateful for financial support from the Royal Swedish Academy of Sciences and Swedish Institute.

[1] W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982).
[2] Y. K. Ho, Phys. Rep. **99**, 1 (1983).
[3] A few articles in *Multiparticle Quantum Scattering with Applications to Nuclear, Atomic and Molecular Physics*, edited by D. G. Truhlar and B. Simon, The IMA Volumes in Mathematics and its Applications Vol. 89 (Springer, New York, 1997).
[4] M. Reed and B. Simon, *Methods of Modern Mathematical Physics* (Academic Press, New York, 1982), Vol. IV.
[5] M. Rittby, N. Elander, and E. Brändas, in *Resonances*, edited by E. Brändas and N. Elander, Lecture Notes in Physics Vol. 325 (Springer, Berlin, 1989).
[6] B. Simon Phys. Lett. **71A**, 211 (1979).
[7] T. N. Rescigno, M. Baertschy, D. Byrum, and C. W. McCurdy, Phys. Rev. A **55**, 4253 (1997).
[8] C. W. McCurdy, T. N. Rescigno, and D. Byrum, Phys. Rev. A **56**, 1958 (1997).
[9] C. W. McCurdy, C. K. Stroud, and M. K. Wisinski, Phys. Rev. A **43**, 5980 (1991).
[10] R. Lefebvre, J. Phys. Chem. **88**, 4839 (1984).
[11] N. Rom, E. Engdahl, and N. Moiseyev, J. Chem. Phys. **93**, 3413 (1990).
[12] A. Scrinzi and N. Elander, J. Chem. Phys. **98**, 3866 (1993).
[13] K. W. Morton, Comput. Phys. Rep. **6**, 1 (1987).
[14] A. Scrinzi, Comput. Phys. Commun. **86**, 67 (1995).
[15] N. Elander and E. Yarevsky, Phys. Rev. A **56**, 1855 (1997).
[16] J. Ackermann and J. Shertzer, Phys. Rev. A **54**, 365 (1996).
[17] E. Lindroth, Phys. Rev. A **49**, 4473 (1994).
[18] B. Helffer, in *Resonances*, edited by E. Brändas and N. Elander, Lecture Notes in Physics Vol. 325 (Springer, Berlin, 1989).
[19] P. B. Kurasov, A. Scrinzi, and N. Elander, Phys. Rev. A **49**, 5095 (1994).
[20] N. Moiseyev, P. R. Certain, and F. Weinhold, Mol. Phys. **36**, 1613 (1978).
[21] Y. K. Ho, Phys. Rev. A **34**, 4402 (1986).