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Fully numerical complex-coordinate Hartree-Fock calculations for the He $2s2p\ ^{1,3}P^{\circ}$ autodetaching states

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A fully numerical multiconfiguration Hartree-Fock program has been modified for performance of calculations on atomic quasibound states using the complex-coordinate (complex dilation) technique. We present results of a lowest-order calculation of the $2s2p\ ^{1,3}P^{\circ}$ autodetaching states of He using this method, and we examine the dilational stability of our calculations. Because the numerical method exhibits a high degree of dilational stability, we need not perform auxiliary calculations to stabilize the energy with respect to the dilation parameter, as is necessary in most basis-set calculations. We also report some small-scale multiconfiguration calculations in which we account for correlation in the closed channels but attempt no improvement of the open-channel part of the wave function. As the closed-channel space is enlarged, our results show a variational collapse of the width similar to (but more pronounced than) that observed in early basis-set studies using the dilation method. The resonance position, on the other hand, is well behaved and appears to be converging to agreement with established values.

I. INTRODUCTION

The method of complex-coordinates (complex dilation method) has been widely applied in atomic self-consistent field (SCF) resonance calculations (see, for example, Ref. 1). In this procedure the complex energy $E_{\text{res}}=\varepsilon-i\gamma/2$, giving both the position ε and the width γ of the resonance, is calculated self-consistently as the complex eigenvalue of the dilated Hamiltonian, as described below. Most dilated SCF applications have been performed with basis-set expansions in which some of the difficulties of representing highly oscillatory functions are avoided by using a partially dilated basis set. As a result, the computed energies exhibit a significant dependence upon the dilation parameter ϑ. An auxiliary variational procedure is then employed in which the energy calculation is performed over a range of dilation parameters, and the resulting "ϑ trajectory" is analyzed in order to find a stationary point of the energy. This stationary value of the energy is then assumed to give the best approximation to the exact resonance energy. These problems are not encountered in the numerical scheme since it does not rely upon basis-set expansions and since all radial coordinates are dilated. The calculated energies therefore exhibit a high degree of stability in the dilation parameter, as we show here (for Feshbach resonances) and elsewhere[2] (for shape resonances).

The formal development of this technique may be found in the literature,[1] but we give a brief description of its application in the numerical scheme in Sec. II. In Sec. III the results of our calculations are presented and compared with other published results, and stability in the dilation parameter is examined.

II. NUMERICAL DILATION METHOD

The complex dilation method is applied, in practice, by replacing each radial variable r in the nonrelativistic scattering Hamiltonian with the complex coordinate $z=re^{i\vartheta}$, where $0<\vartheta<\pi/2$ is the dilation parameter. The resulting dilated Hamiltonian is non-Hermitian and possesses isolated complex eigenvalues of the form $\varepsilon-i\gamma/2$, with $\varepsilon>0$ and $\gamma>0$, corresponding to quasibound states. Since the corresponding eigenfunctions are normalizable, bound-state SCF methods may be modified for application to the study of these resonance states.

In the standard formulation of the dilated SCF method, the variational principle is applied to an energy functional constructed with the dilated Hamiltonian. Proceeding almost exactly as in the real case (that is, for bound state systems), it leads to a set of coupled, complex differential equations for the radial factors in the single-particle spin orbitals. The SCF functions determined in this way yield a stationary complex energy that approximates the eigenvalue of the dilated Hamiltonian.

In the numerical scheme the dilation method leads to dilated Hartree-Fock (HF) equations that differ in form from the real equations[3] only in that z appears in the place of r, and complex quantities replace real ones. Thus, in atomic units (used throughout unless otherwise noted), the dilated Hartree-Fock equation for the radial function $P_{nl}(z)$ is

$$\frac{d^2P_{nl}(z)}{dz^2}=\left[\frac{\lambda}{z^2}-\frac{2}{z}[Z-Y_{nl}(z)]+\varepsilon_{nl,nl}\right]P_{nl}(z)+\mathcal{G}_{nl}(z)\ , \tag{1}$$

where $\lambda=l(l+1)$, l being the angular momentum quantum number; Z is the nuclear charge; $Y_{nl}(z)$ is the nuclear screening function; and $\varepsilon_{nl,nl}$ is the (complex) diagonal Lagrange multiplier, which insures that the function $P_{nl}(z)$ satisfies the normalization condition $(P_{nl},P_{nl})=1$. The inhomogeneity $\mathcal{G}_{nl}(z)$ contains the exchange function and terms of the form $\varepsilon_{nl,n'l}P_{n'l}(z)$, where $\varepsilon_{nl,n'l}$ is the (complex) off-diagonal Lagrange multiplier, which en-

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sures satisfaction of the orthogonality condition $(P_{nl},P_{n'l})=0$, in the case of $n'\neq n$.

We rewrite the equations in the form

$$\frac{d^2P_{nl}(r;\vartheta)}{dr^2}=\left[\frac{\lambda}{r^2}-\frac{2e^{i\vartheta}}{r}[Z-Y_{nl}(r;\vartheta)]+e^{i2\vartheta}\varepsilon_{nl,nl}\right]P_{nl}(r;\vartheta)+G_{nl}(r;\vartheta)\ , \qquad (2)$$

where the notation indicates that ϑ is considered to be a parameter, and $G_{nl}=e^{i2\vartheta}\mathcal{G}_{nl}$. We have solved these equations for the He $2s2p\ {}^{1,3}P^{\circ}$ autodetaching systems using an extensively modified version of the multiconfiguration Hartree-Fock (MCHF) code of Froese Fischer.[4] The boundary conditions to be satisfied by all of the radial functions are

$$P_{nl}(0;\vartheta)=0,\quad \lim_{r\to\infty}P_{nl}(r;\vartheta)=0\ . \qquad (3)$$

In practice, the second of these conditions must be replaced by a specification of the asymptotic behavior of P_{nl} because the equation is solved only over a finite range of r. Thus, for the scattering orbital, one must consider the appropriate Siegert boundary condition

$$\lim_{r\to\infty}P_{kl}(z)\sim e^{i[kz-l\pi/2+(q/k)\ln(2kz)+\eta_l]}\ , \qquad (4)$$

where k is the (complex) outgoing wave momentum, q is the net charge of the atomic residue, and η_l is the partial-wave phase shift. For the cases examined here we use $q=1$. At no point in the calculation is it necessary to set the value of η_l or k.

III. He $2s2p\ {}^{1,3}P^{\circ}$ FESHBACH RESONANCES

The various doubly excited states that occur in helium have received much attention by theorists and have been observed in electron-scattering, photon-absorption, and ion-scattering experiments. The work presented here is a demonstration of the applicability of the dilated numerical MCHF method to the calculation of the positions and widths of Feshbach resonances, as exemplified by these states. This possibility was first suggested by McCurdy *et al.*,[5] who also demonstrated the inadequacy of the single-configuration approximation for the description of such resonances. The formation and decay of these systems is an effect of interaction of configurations, hence the lowest-order approximation to the wave function that can provide an adequate description for the He $2s2p$ systems is of the form $c_1|2s2p\rangle+c_2|1s\varepsilon p\rangle$.

The energies of these helium resonances are ordinarily referred to the ground state of the helium atom, most commonly given as the Frankowski-Pekeris[6] value $-2.903\,724\,38$ a.u.; our results are displayed in Tables I and II and are given relative to this energy. We have used $27.211\,396\,1$ as the conversion factor from a.u. to eV.

In our calculations, the dilation parameter was $\vartheta=0.05$ rad, and all radial functions were determined self-consistently except for the $1s$ function, which was held fixed. This frozen $1s$ orbital was taken from a dilated calculation of He$^+$ $1s$ at $\vartheta=0.05$ rad. It therefore gives an exact description for the target when the scattering electron is far away, but represents only a lowest-order approximation to the $1s$ function of the resonance state. The starting functions for the other bound orbitals were taken from a dilated single-configuration calculation of $2s2p\ {}^3P^{\circ}$ (which converges to a real energy). The starting function for εp was the resonance orbital from a calculation of the Be$^-$ shape resonance[2] $1s^22s^2\varepsilon p$.

In Fig. 1 we show the real parts of the direct potentials of the $2p$ and εp orbitals for the ${}^3P^{\circ}$ system; the corresponding potentials for the ${}^1P^{\circ}$ system are very similar. The real parts of the normalized $2p$ and εp functions for ${}^3P^{\circ}$ are shown in Fig. 2, and those for the ${}^1P^{\circ}$ system are shown in Fig. 3. The $2p$-εp orthogonality constraint

TABLE I. Results for the He $2s2p\ {}^3P^{\circ}$ resonance.

Study	Method	ε (eV)	γ (meV)
Present	Numerical dilated HF:		
I	two configurations	58.4992	9.88
II	three configurations	58.3643	9.68
III	four configurations	58.3086	0.40
IV	five configurations	58.3076	0.34
V	six configurations	58.3045	0.33
Ho[a]	Dilated Hylleraas basis set	58.3205	8.13
Moccia and Spizzo[b]	L^2 basis-set configuration interaction:		
	phase shift analysis	58.3097	8.18
	complex stabilization	58.3097	8.25
Bhatia and Temkin[c]	Feshbach projector	58.2937	8.90
Cederquist, Kisielinski, and Mannervik[d]	Experiment		7.12±0.12

[a] Reference 7.

[b] Reference 8.

[c] Reference 9.

[d] Reference 10.

TABLE II. Results for the He $2s2p\ {}^1P^\circ$ resonance.

Study	Method	ε (eV)	γ (meV)
Present	Numerical dilated HF:		
I	two configurations	61.0909	42.19
II	three configurations	60.2901	43.20
III	four configurations	60.2142	30.03
V	six configurations	60.1967	30.10
Ho[a]	Dilated Hylleraas basis set	60.1456	37.1
Moccia and Spizzo[b]	L^2 basis-set configuration interaction:		
	phase shift analysis	60.1542	37.0
	complex stabilization	60.1548	34.6
Bhatia and Temkin[c]	Feshbach projector	60.1450	36.3
Morgan and Ederer[d]	Experiment	60.151±0.010	38.0±2.0

[a] Reference 11.
[b] Reference 8.
[c] Reference 9.
[d] Reference 12.

affects the resonance orbital strongly in the ${}^3P^\circ$ case and results in the suppression of the εp wave function that is apparent in the vicinity of the $2p$ orbital. The constraint is much less important for ${}^1P^\circ$.

The mixing coefficients for the configurations are complex and were determined self-consistently at the following values: for ${}^3P^\circ$

$$c_1=(0.999\,91,\ 0.000\,15)\ ,$$

$$c_2=(0.016\,55,\ -0.009\,35)\ ,$$

for ${}^1P^\circ$

$$c_1=(1.000\,24,\ -0.000\,08)\ ,$$

$$c_2=(-0.003\,80,\ -0.022\,27)\ ,$$

where c_1 and c_2 satisfy $c_1^2+c_2^2=1$ in each case. (This relation is appropriate for the *non-Hermitian* dilated Hamiltonian, rather than the usual $|c_1|^2+|c_2|^2=1$.) The c_1 coefficients are much larger than the c_2 coefficients, showing the characteristic domination of the closed-channel part of the wave function over the open channels in this type of system.

Also listed in Tables I and II are the results of some small-scale multiconfiguration calculations that we performed using the following wave-function expansions:

Study	Wave function
II	$2s2p+1s\varepsilon p+2p3d$
III	$2s2p+1s\varepsilon p+2p3d+3s3p$
IV	$2s2p+1s\varepsilon p+2p3d+3s3p+3p4d$
V	$2s2p+1s\varepsilon p+2p3d+3s3p+3p4d+3d4f$

The results exhibit a "collapse" of the width that occurs with the addition of configurations (most evident in the ${}^3P^\circ$ results), while the position improves. A similar but less pronounced collapse was observed by Bain

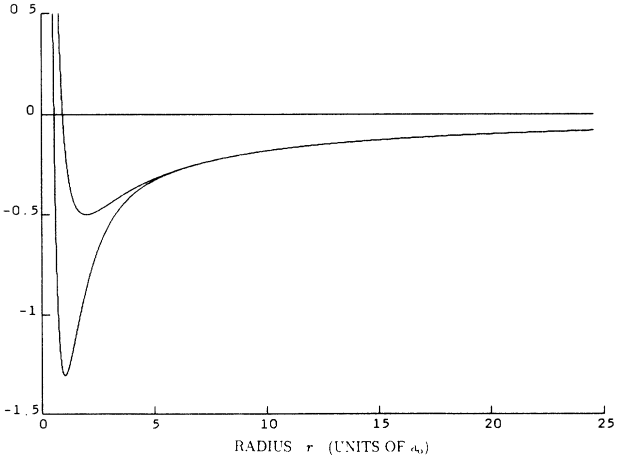

FIG. 1. Real parts of the effective direct potentials for the $2p$ orbital (deep well) and the εp orbital (shallow well) for the ${}^3P^\circ$ case. The effective direct potential is defined as the first two terms inside the large parentheses in Eq. (2). The vertical axis is marked in a.u.

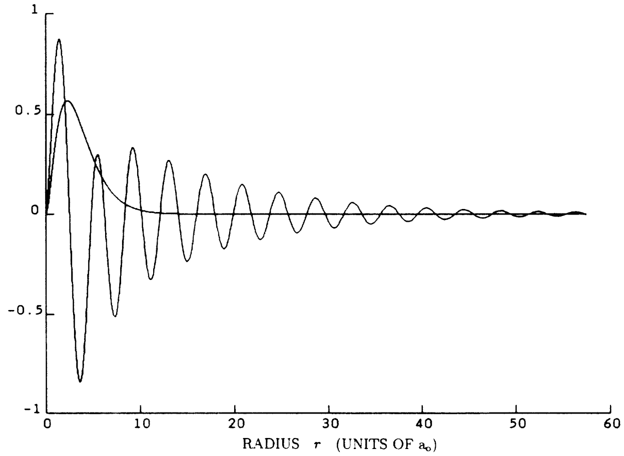

FIG. 2. Real parts of the normalized $2p$ and εp radial functions for the ${}^3P^\circ$ case. The vertical axis is marked in $a_0^{-1/2}$.

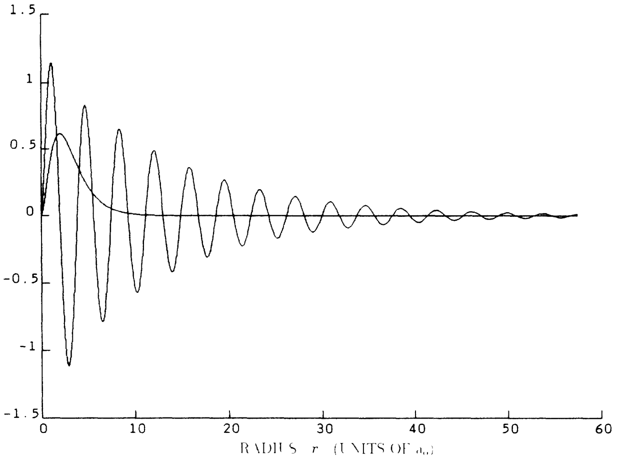

FIG. 3. Real parts of the normalized $2p$ and εp radial functions for the $^1P^\circ$ case. The vertical axis is marked in $a_0^{-1/2}$.

TABLE III. ϑ stability of the He $2s2p\ ^3P^\circ$ energy.

ϑ (rad)	ReE (a.u.)	ImE (a.u.)
0.05	−0.753 921 066 162	−0.000 181 513 806
0.10	−0.753 921 066 163	−0.000 181 513 787
0.20	−0.753 921 066 178	−0.000 181 513 782
0.30	−0.753 921 066 190	−0.000 181 513 787
0.40	−0.753 921 066 193	−0.000 181 513 796
0.50	−0.753 921 066 186	−0.000 181 513 804
0.60	−0.753 921 066 170	−0.000 181 513 806
0.70	−0.753 921 066 150	−0.000 181 513 794
0.80	−0.753 921 066 133	−0.000 181 513 768
0.90	−0.753 921 066 128	−0.000 181 513 728
1.00	−0.753 921 066 143	−0.000 181 513 680

et al.[13] in an early dilated basis-set study of the He$^-$ $1s2s^2$ Feshbach resonance; the collapse occurred during multiconfiguration improvement of the target wave function. In a report of later work on the same resonance, Junker[14] mentions unpublished studies showing that the width does not behave monotonically with the addition of configurations and is very sensitive to such changes in the wave function until a certain number of configurations have been added. Similar behavior has been noted in connection with shape resonances in a basis-set configuration interaction study of Be$^-$ $1s^22s^2\varepsilon p$ by McNutt and McCurdy[15] and in our multiconfiguration study[16] of the Li$^-$ $1s^22s\varepsilon p\ ^3P^\circ$ resonance. However, it is unlikely that our present results for the $2s2p$ width are explained by such fluctuations, since Junker demonstrated also that the collapse of the resonance width could be avoided by improving the open-channel part of the wave function. We are currently investigating the resolution of this problem in the dilated numerical method.

The dilational stability of the numerical SCF approach has been demonstrated already[2] for calculations of shape resonances. We note also that Krylstedt, Elander, and Brändas,[17] using a dilated version of the static-exchange-plus-polarization technique, have also obtained results for shape resonances that are independent of changes in the dilation parameter. In Table III we demonstrate such stability in a dilated numerical SCF calculation of a Feshbach resonance. Our results show stability through at least nine decimal places, in both the position and the width, over a range of almost 40° in ϑ. This greatly simplifies our computations by eliminating the "ϑ-trajectory" analysis that is necessary in basis-set calculations as they are usually performed (see, for example, Ref. 7).

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[1] See, for example, B. R. Junker, Adv. At. Mol. Phys. **18**, 207 (1982); for related topics, see various articles in Vol. 325 of *Lecture Notes in Physics*, edited by E. Brändas and N. Elander (Springer-Verlag, Berlin, 1989).

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