A numerical Hartree self-consistent field calculation of an autoionization resonance parameters for a doubly excited $2s^2$, $3s^2$, and $4s^2$ states of He atom with a complex absorbing potential

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The self-consistent Hartree-Fock equation for the He atom is solved using the pseudospectral method. The Feshbach-type autoionization resonance parameters for doubly excited $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of He have been determined by adding a complex absorbing potential to the Hamiltonian. The Riss–Meyer iterative and Padé extrapolation methods are applied to obtain reliable values for the autoionization resonance parameters, which are compared to previous results in the literature.

Keywords: self-consistent field, Hartree–Fock equation, helium autoionization, pseudospectral method

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1. Introduction

The doubly excited states of helium atom have been of considerable interest to theoretical and experimental physicists since the first identification of these states by Madden and Codling.[1] Because these states cannot be adequately described by means of the independent-particle model, electron-electron correlation in these states makes them interesting test cases for accurate theoretical approaches. As one electron falls into available n shell below, the released energy is enough to send the other electron out from the same state or higher n shell in the continuum and then most of these state autoionize.[2]

The helium atom is an ideal system to test different theoretical and computational methods. Various methods have been employed to obtain resonance parameters for autoionizing states theoretically. Bhatia and Temkin[3,4] used a Feshbach projection formalism. Oza[5] employed the close-coupling approximation. Ho and co-workers[6–10] used a variational approach with the Hylleraas-type basis functions combined with a method of complex rotation (CR), which makes a bound state method applicable to autoionizing states. Froese–Fischer and Idrees[11] also extended a multiconfigurational Hartree–Fock method to autoionizing states of the helium. Tang *et al.*[12] employed a hyperspherical close-coupling method based on a numerical basis and Lindroth[13] applied the CR method with a finite numerical basis set built on solutions of the discretized one-particle Hamiltonian. Accurate resonance parameters for highly doubly excited S states of the He atom were also obtained with variational method combined with the CR technique by Bürgers *et al.*[14]

Moreover, Zdanska and Moiseyev[15] used a complex-scaled configuration interaction ((CS)CI) method to obtain resonance parameter. Sajeev *et al.*[16] employed a reflection-free complex absorbing potential (CAP) method with Gaussian basis set. Bravaya *et al.*[17] used a complex-scaled equation-of-motion coupled-cluster ((CS)EOM-CC) method, and a complex-scaled multiconfigurational time-dependent Hartree–Fock (CMCTDHF) method has been used by Liang and Yeager.[18] Kapralova-Zdanska and Smydke[19] also gave results for Feshbach-type autoionization resonances for highly excited states of helium atom using complex-scaled full CI method with Gaussian basis sets.

In this work we want to implement the Hartree–Fock (HF) method combined with CAP for the autoionization resonance parameters for doubly excited $2s^2$, $3s^2$, and $4s^2$ ^{1}S states for the He atom and compare our results with previous results. The reason why we implement a CAP for these resonances are as follows: (i) Zdanska and Moiseyev[15] discussed that a width of an autoionization resonance for the $2s^2$ state from the HF calculation with CR 'collapses' to zero, however, we want to see that whether this width from the HF calculation with CAP 'collapses' again to zero or not; (ii) to our knowledge, CAP has not applied for these autoionization resonances, yet.

We implement the Riss–Meyer iterative method[20] and the Padé approximation and extrapolation of a strength parameter η of a CAP[21–25] to obtain a reliable (accurate) values of the resonance parameters.

The paper is organized as follows. In Section 2 we discuss the fundamental procedures for the determination of bound and resonance states for the He atom. In Section 3 we present and discuss our results. Then a conclusion follows.

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2. Theory

In the SCF calculation for the He atom we assume that each of the electrons is governed by an atomic orbital ψ, then the complete wave function for ground $1s^2$ and doubly excited $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of the He atom can be written as

$$\Psi = \frac{1}{\sqrt{2}}\psi_i(1)\psi_i(2)\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}, \quad (i=1,2,3,4), \tag{1}$$

where α and β are single-electron spin wave functions; these may, however, be omitted from henceforward, since they play no role further part in the energy calculations, and $\psi_i(1)$ and $\psi_i(2)$ are the i-th orbital for electron 1 and electron 2, and values $i=1,2,3$ and 4 correspond to the 1s, 2s, 3s, and 4s orbitals, i.e., the $1s^2$, $2s^2$, $3s^2$, and $4s^2$ configurations, respectively.

Since the two electrons in these four configurations are distinguished by their spins, we have $\psi_i(1)=\psi_i(2)=\psi_i$ $(i=1,2,3,4)$. Atomic units ($\hbar=e=m_e=1$) are used throughout.

The orbitals ψ_i are determined as a solution of the Hartree–Fock equation

$$[H(\boldsymbol{r})+G_i(\boldsymbol{r})]\psi_i(\boldsymbol{r})=\varepsilon\psi_i(\boldsymbol{r}), \tag{2}$$

where ε is an orbital energies and the Hamiltonian $H(\boldsymbol{r})$ is a one-electron Hamiltonian given by

$$H=-\frac{1}{2}\nabla^2-\frac{Z}{r}, \tag{3}$$

where $Z=2$ for helium atom.

The interelectronic Coulomb potential $G_i(\boldsymbol{r})$ satisfies the Poisson equation

$$\nabla^2 G_i(\boldsymbol{r})=-4\pi\rho(\boldsymbol{r}), \tag{4}$$

where $\rho(\boldsymbol{r})$ is the single-electron density, $\rho=|\psi_i|^2$ $(i=1,2,3,4)$. Then the Hartree–Fock equation (2) is solved (self-consistently) iteratively together with the Poisson equation (4) for a chosen electronic configuration.

The total energy for the $1s^2$, $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of the He atom in the Hartree–Fock approximation can be found as follows:

$$E=2\varepsilon-\langle V_{\rm ee}\rangle, \tag{5}$$

where $\langle V_{\rm ee}\rangle$ is the electron–electron repulsion interaction given by

$$\langle V_{\rm ee}\rangle=\iint\frac{\rho(1)\rho(2)}{r_{12}}\,{\rm d}v_1\,{\rm d}v_2. \tag{6}$$

We note that since we only consider completely symmetric states, we would take half the electron density to remove the self-interaction in our SCF calculation.

In the central-field model for atoms, the spatial orbital $\psi(\boldsymbol{r})$ for the electron with three quantum numbers n,l, and m can be written as

$$\psi(\boldsymbol{r})=R_{nl}(r)\mathrm{Y}_{lm}(\theta,\varphi). \tag{7}$$

Since we consider only the ^{1}S states ($L=0$) in which both electrons occupy the same hydrogenic level, using the form (7) for the i-th orbital ψ_i, we can define $\psi_i\equiv\psi_{n00}\equiv\psi_{ns}$ $(i=\{nlm\}=\{n00\}=\{ns\})$, that is, ψ_{1s} now corresponds to 1s orbital for $1s^2$ configuration, etc.

Using the usual substitutions for the radial orbital $R_{ns}(r)$ and $G_{ns}(\boldsymbol{r})$

$$R_{ns}(r)=\frac{u_{ns}(r)}{r}, \quad G_{ns}(\boldsymbol{r})=\frac{\varphi_{ns}(r)}{r}, \quad (n=1,2,3,4), \tag{8}$$

equations (2) and (4) reduce to

$$\Big[-\frac{1}{2}\frac{{\rm d}^2}{{\rm d}r^2}-\frac{Z}{r}+\varphi_{ns}(r)\Big]u_{ns}(r)=\varepsilon u_{ns}(r) \tag{9}$$

for $n=1,2,3,4$, and

$$\frac{{\rm d}^2\varphi_{ns}(r)}{{\rm d}r^2}=-4\pi r\rho. \tag{10}$$

We employ a Legendre pseudospectral method to solve Eqs. (9) and (10). In this method we approximate $\psi(r)$ by $\psi_N(r)$:

$$\psi(r)\approx\psi_N(r)=\sum_{i=0}^{N}\varphi(r_i)g_i[x(r)], \tag{11}$$

In Eq. (11), $g_i[x(r)]$ is the cardinal function defined as

$$g_i(x)=-\frac{1}{N(N+1)\mathrm{P}_N(x_i)}\frac{(1-x^2)\mathrm{P}'_N(x)}{x-x_i}, \tag{12}$$

and it has the unique property $g_i(x_j)=\delta_{i,j}$, which makes the matrix calculation easy.

The semi-infinite domain $r\in[0,\infty]$ is mapped according to $r(x)=0.5(1+x)b$, where $x\in[-1,1]$ and b is a mapping range parameter (typically: $b=60$ a.u.).

We choose the Legendre–Gauss–Lobatto points which take into account both points $x_0=-1$ and $x_{N+1}=1$, and the internal points are determined by the roots of the first derivative of the Legendre polynomial, $\mathrm{P}'_N(x_i)=0$. After applying this grid technique, the discretized eigenvalue and boundary value problems can be implemented directly:

$$\sum_{j=1}^{N}\Big[-\frac{1}{2}T_{ij}-\frac{Z}{r_i}\delta_{ij}+\varphi_{ns}(r_i)\delta_{ij}\Big]u_{ns}(r_j)=\varepsilon u_{ns}(r_i) \tag{13}$$

for $n=1,2,3,4$, and

$$T_{ij}\varphi_{ns}(r_i)=-4\pi r_i\rho_i. \tag{14}$$

Here, the partial matrix T_{ij} has form $T_{ij} = (4/b^2)d_{ij}d_{ij}$, where d_{ij} is the first order differentiation matrix using the Legendre–Gauss–Lobatto points $x(r_i)$, and can be found in a simple closed form.[26,27] By solving Eqs. (13) and (14) iteratively, one can obtain the HF orbitals and orbital energies and then can obtain a total energy using Eq. (5). This pseudospectral technique was also previously implemented for a two-dimensional problem.[28]

We add an artificial CAP[20,28] to Hamiltonian (3) in order to avoid the calculation of outgoing waves in our resonance calculation. We choose this CAP as the following form

$$H_{\mathrm{CAP}} = H - \mathrm{i}\eta W, \quad W(r) = \Theta(r - r_{\mathrm{c}})(r - r_{\mathrm{c}})^2, \tag{15}$$

where Θ is the Heaviside step function, η is a small positive parameter and r_{c} determines region, outside of which the CAP dampens the outgoing wave in the asymptotic region. This means that the eigenfunction of the resonance state can be solved for in a square-integrable basis, that is, one solves an eigenvalue problem to find complex energy eigenvalues, whose real part yields the resonance position, and the inverse of the imaginary part is associated with the lifetime of that state.[28]

While using a finite basis set, ideally we want η to be small to be a small artifact. However, when the parameter η tends to zero, the computational representation error increases. Thus, we want η to not be too small to have an easier or more accurate calculation. Then, we want to remove the artifact due to the CAP. This can be done by the iterative correction method of Riss and Meyer,[20] or by Padé extrapolation method.[21–25] Following Ref. [20], we have

$$E^{(n)} = E^{(n)}(\tilde{\eta}) = E_{\mathrm{fb}}(\tilde{\eta}) + \sum_{j=1}^{n} \frac{(-\tilde{\eta})^j}{j!} \frac{\mathrm{d}^j E_{\mathrm{fb}}}{\mathrm{d}\eta^j}\Big|_{\eta=\tilde{\eta}}, \tag{16}$$

where $\tilde{\eta}$ is an optimal value found by the condition[20]

$$\Big|\frac{\eta^{n+1}}{(n+1)!} \frac{\mathrm{d}^{n+1} E_{\mathrm{fb}}}{\mathrm{d}\eta^{n+1}}\Big|_{\eta=\tilde{\eta}} = \min, \quad n = 0,1,2,3. \tag{17}$$

Here E_{fb} stands for finite-basis eigenvalues calculated on an η-grid.

Following Eq. (5) in Ref. [23], (cf. Ref. [21]) a Padé approximant for $E_{\mathrm{fb}}(\tilde{\eta})$ is obtained from

$$E_{\mathrm{Padé}}(\eta) = \frac{\sum_{i=0}^{N_1} p_i \eta^i}{1 + \sum_{j=1}^{N_1+1} q_j \eta^j}, \tag{18}$$

where p_i and q_j are complex coefficients, and $N_p = 2(N_1 + 1)$ is the number of points used in the approximant. We found that $N_p = 4$ yielded reasonable extrapolations to $\eta = 0$. In the present work we found that the Riss–Meyer method with order $n = 1$ and the extrapolation method gives very consistent results.

3. Results and discussion

In our calculations we solve first the Poisson equation to obtain the interelectronic Coulomb potential (Eq. (4)). For the given single-electron density, ρ, we have analytic solutions for the ns^2 ($n = 1,2,3,4$) configurations of He atom (see Appendix A) and using them we check numerical results for the Poisson equation in an initial step of the self-consistent calculation.

In Fig. 1(a) we present the cardinal function $g_i(x)$ for $N = 8$. In Fig. 1(b) we show the error, $||\phi(r) - \phi_{\mathrm{exact}}(r)||_\infty$, for a numerical solution for the Poisson equation for the ns^2 ($n = 1,2,3,4$) configurations of He as a function of a number of grid point N. For $N = 256$ and $b = 60$ a.u. the maximum error of the solution for the Poisson equation is of the order 10^{-14}.

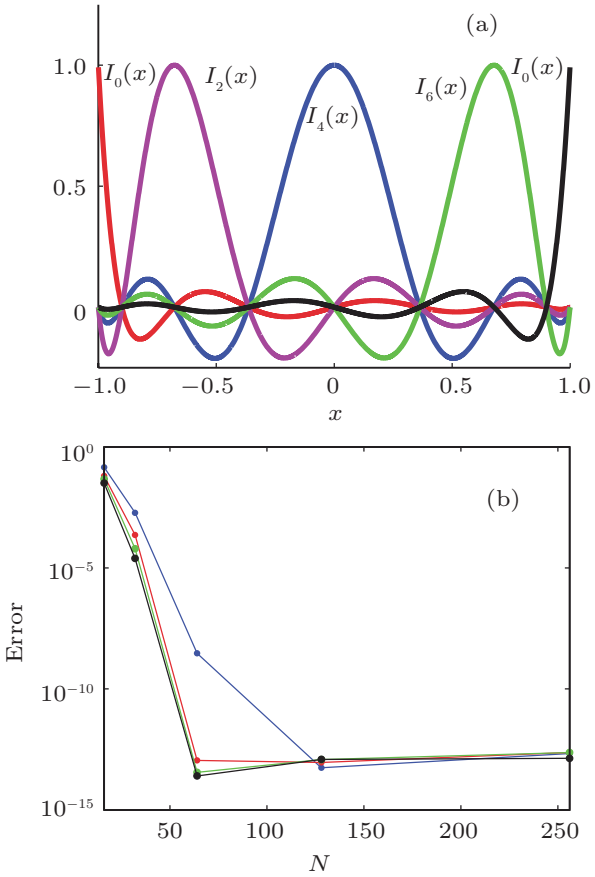


Fig. 1. (color online) Plots of a cardinal function $g_i(x)$ with $N = 8$ (a), and an error for a numerical solution for the Poisson equation (b). In panel (b), blue, red, green, and black curves correspond to the $1s^2$, $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of the He atom, respectively. Computational parameter $b = 60$ a.u.

In Table 1 we show some HF solutions for the ground $1s^2$ and a doubly excited $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of the He atom and their comparisons with those in the literature.[29–31] For a doubly excited states, the values from Ref. [31] are obtained from a spin-dependent HF calculation. Our numerical results are in good agreement with the values in Refs. [29], [30], and [31]. The convergence criterion in the interelectronic potential is set to $\Delta\langle V_{\mathrm{ee}}\rangle = 10^{-8}$ a.u. and 12 iterations are needed to achieve this criterion.

Table 1. Some HF solutions for the ground $1s^2$ and a doubly excited $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of the He atom. Computational parameters are $N = 256$ and $b = 60$ a.u.

States	Ref.	ε/a.u.	E/a.u.	$\langle 1/r\rangle$/a.u.	$\langle r\rangle$/a.u.	$\langle r^2\rangle$/a.u.
$1s^2$		−0.917 956	−2.861 679 996	1.687 282	0.927 273	1.184 828
	[29]		−2.861 6800	1.68728	0.927273	1.184828
	[30]		−2.861 6799			
$2s^2$		−0.230211	−0.719676394	0.424 652	3.493 326	14.478 080
	[31]		−0.71968			
$3s^2$		−0.102036	−0.319981555	0.188 968	7.746 937	68.537 427
	[31]		−0.31996			
$4s^2$		−0.057284	−0.179980956	0.106 344	13.689 845	210.804 105
	[31]		−0.17995			

In Figs. 2(a)–2(c) we show a radial densities for the ns^2 ($n = 2,3,4$) configurations of the He atom. Dashed lines in Fig. 2 indicate positions of orbital energies, which are given in Table 1 and the Coulomb potential is shown with the black curve.

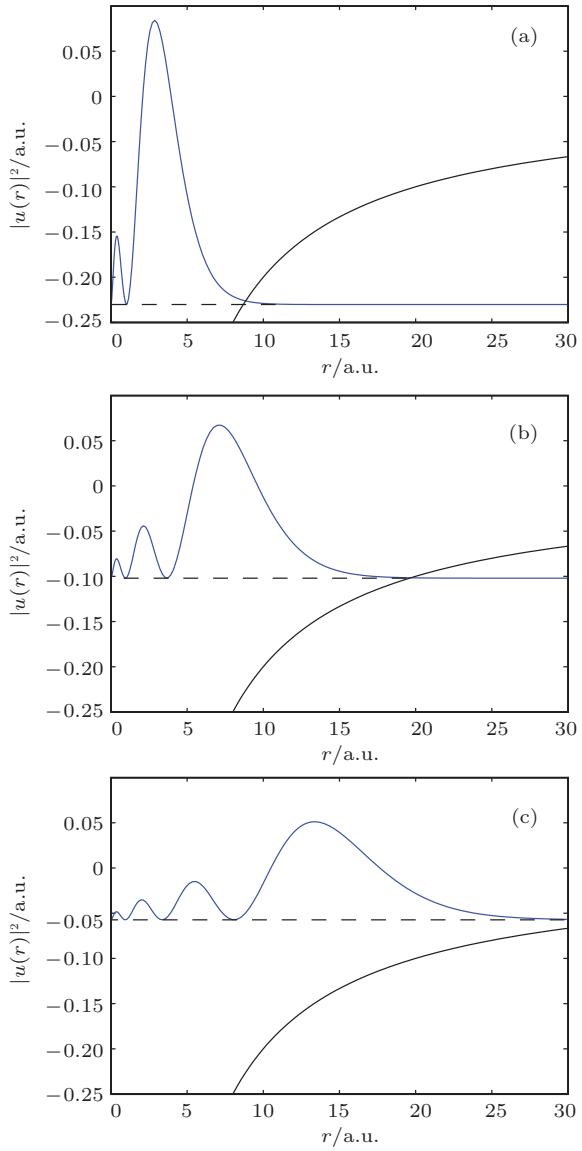


Fig. 2. (color online) Plots of $|u(r)|^2$ for the $2s^2$ (a), $3s^2$ (b), and $4s^2$ (c) ^{1}S states of the He atom. A dashed-line shows a position of an orbital energy shown in Table 1 and a black curve is the Coulomb potential. The computational parameters are $N = 256$ and $b = 60$ a.u. (panels (a), (b), and (c)).

The next step in our calculations is to obtain the autoionization resonance parameters for doubly excited $2s^2$, $3s^2$, and $4s^2$ states for the He atom. The He atom is the simplest two-electron system for which there are benchmarks values for complex eigenenergies of autoionizing states.[5,10,13–19]

In order to obtain consistent results in our calculation we need to investigate two aspects of the problem. One the one hand, the solutions of discretized problem needs to be analyzed with respect to the parameters defining the discretization. In our resonance (non-hermetain matrix) SCF calculation we employ $N = 256$ and $b = 60$ a.u. Increasing values of these parameter does not affect the results. On the other hand, in the resonance problem we are considering the analytic continuation methods introduce the artifact of complex scaling or complex absorption. It is the second issue for which we show some detailed results.[28]

There are two main methods of how to deal with removing such artifacts. The Riss–Meyer method (Eqs. (16) and (17)) is a perturbation-theory-based technique to remove the effects of the complex absorber order by order.[20] An extrapolation of complex eigenvalue trajectories as a function of the CAP strength parameter η is a more direct approach, but it requires a careful analysis to ensure that the eigenvalues used in the extrapolation are not contaminated by limitations imposed by the discretization. In principle, by making use of a CAP for which absorption sets in at large distances (analogous to exterior scaling), and where the strength parameter is usually chosen to be small, one has to represent (outgoing) oscillatory solutions at intermediate distances.[28]

First we consider the autoionization resonance problem of the $2s^2$ doubly exited state of the He atom. In our calculations we first test by varying the value of r_c. In Fig. 3 we attempt to see how resonance width depends on the value of r_c, which determines a region where a complex absorption starts. The values of r_c in Fig. 3 are 6 (a), 7.5 (b), 10 (c), and 12.5 a.u. (d), respectively. We note that each trajectory shows a turning point. As we see turning points, width changes moderately with change of r_c. However, since we only take-into account

a single-configuration in our calculation, r_c should be chosen not too large and not too small. If we reduce r_c, the CAP may not only disturb the free dynamics, but also the dynamics governed by the Coulomb potential. Note that a smaller (larger) r_c makes the optimal value $\tilde{\eta}^{(n)}$ become smaller (larger) since the wave function is absorbed over a longer (shorter) distance.

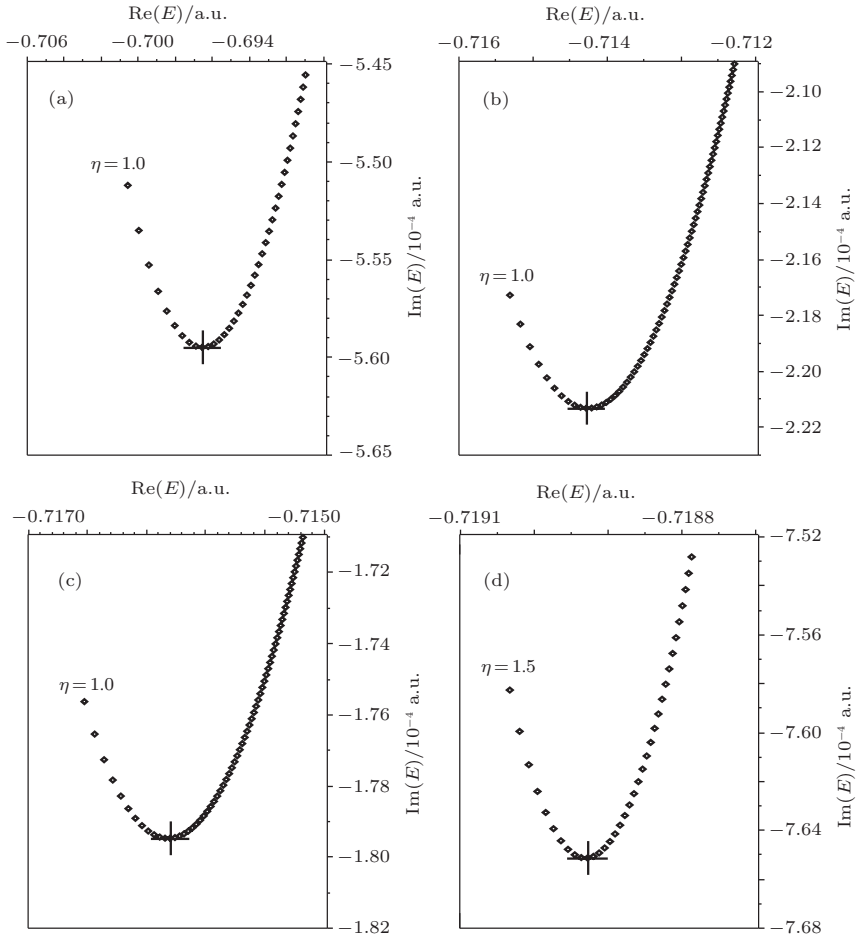


Fig. 3. The η-trajectories for $E^{(0)}$ for the $2s^2$ state of the He atom. The values of r_c are 6 (a), 7.5 (b), 10 (c), and 12.5 a.u. (d), respectively. The values of strength parameter for $\tilde{\eta}^{(0)}$ (black crosses) are 1.9 (a), 2.1 (b), 2.2 (c), and 2.5 (d), respectively. The computational parameters are $N = 256$ and $b = 60$ a.u. (panels (a), (b), (c), and (d)) and $\Delta\eta = 0.1$ (panels (a), (b), (c), and (d)).

For small $r_c = 6$ a.u. (a), the width is about 0.01 a.u., which is much larger than other values shown in panels (b), (c), and (d). This can be related to a fact that an amplitude of wave function for small r is large, which in turn may affect resonance parameters, and width is defined by a behavior of wave function in asymptotic region. For panel (d) the width is about 0.002 a.u., which is very small. This may be connected to the fact that since a large value η is required for $r_c = 13.5$ a.u., the stronger CAP causes a larger error in the asymptotic region and thus a worse imaginary part of the complex eigenvalue. Panels for $r_c = 7.5$ a.u. (b) and 10 a.u. (c) give values of 0.0044 a.u. and 0.0036 a.u. for width, respectively. Thus we now see that an intermediate distances (7.3 a.u.$< r_c <$ 8 a.u.) should be chosen in our calculations. We note that this r_c's range lies in region where an orbital energy is close to the Coulomb potential (Fig. 2(a)). This may also indicate where we need to choose r_c. The stabilized points (black crosses) in Fig. 3 are found at $\tilde{\eta}^{(0)} = 1.9$, 2.1, 2.2, and 2.5, respectively.

In Table 2 we show a complex eigenvalues calculated directly from the non-Hermitean SCF matrix problem as a function of N for three different values of $r_c = 7.4$, 7.5, and 7.8 a.u., which may work in our calculation. Value of the strength parameter of the CAP is $\eta = 2$ and $b = 60$ a.u. As $N = 256$ and the real and imaginary parts of the complex eigenvalues calculated for various r_c's values give a four and six stable digits, respectively.

Table 2. A complex eigenvalues as a function of N for the $2s^2\ ^1S$ state of the He atom for three different values of r_c. The numerical parameter $b = 60$ a.u. and $\eta = 2.0$.

N	$r_c = 7.4$ a.u.	$r_c = 7.5$ a.u.	$r_c = 7.8$ a.u.
64	−0.714183 − i0.002208	−0.714230 − i0.002206	−0.714288 − i0.002195
128	−0.714268 − i0.002212	−0.714271 − i0.002213	−0.714369 − i0.002210
256	−0.714271 − i0.002214	−0.714273 − i0.002213	−0.714372 − i0.002211

In Table 3 we show our the stabilization and extrapolation ($N_p = 4$) methods and Riss–Meyer ($n = 1$) results from the SCF calculation with a CAP for the $2s^2$ state and their comparisons with some theoretically obtained values in Refs. [11], [14]– [19]. The stabilization method is equivalent to the Riss–Meyer ($n = 0$) method.[20–22] All obtained results are consistent with each other and $r_c = 7.5$ a.u. This resonance parameter is also computed from the complex scaled SCF calculation by Zdanska and Moiseyev.[15] They showed that a width from the complex scaled SCF calculation "collapses" to zero. Their position value is shown in row 4, which is close to our position values. Zdanska and Moiseyev[15] also obtained well-converged value from a full configuration interaction calculation with the Gaussian 30s15p10d basis set. This result is shown in row 5 in Table 3. Our width is consistent with this well-converged value.[15]

Table 3. The calculated autoionization resonance parameter for the $2s^2$ ^{1}S state of the He atom using the stabilization method (SM), Padé extrapolation (PE), and the order ($n = 1$) Riss–Meyer scheme. The stabilization result (SM) is equivalent to the ($n = 0$) RM result, and the Padé extrapolation ($N_p = 4$) is based on complex eigenenergies calculated directly from the non-Hermitian matrix problem for η-values not far from the SM result η_{SM} ($\eta > \eta_{SM}$).

State		Position/a.u.	Width/a.u.
$2s^2$	SM	−0.714	0.00443
	PE ($N_p = 4$)	−0.714	0.00455
	RM ($n = 1$)	−0.714	0.00455
	(CS)SCF[15]	−0.7196	
	(CS)CI[15]	−0.778	0.00452
	CS variational[14]	−0.778	0.00454
	CAP CI[16]	−0.778	0.00494
	MCSCF scattering[11]	−0.776	0.00561
	(CS)-EOM-CC[17]	−0.778	0.00446
	CMCTDHF[18]	−0.773	0.00444
	(CS)CI[19]	−0.778	0.00454

We also place six more results for this resonance problem. Bürgers, Wintgen and Rost[14] calculated the autoionization resonance parameters for highly doubly excited S states of the helium atom to an accuracy of 10^{-10} using a complex scaled variational method. This result is shown in row 6. Sajeev, Sindelka, and Moiseyev[16] employed a reflection-free complex absorbing potential to calculate this resonance parameter using the CI method with the Gaussian basis set. This reflection-free of CAP is located close to the interaction region where the Coulomb potential is not negligible. We show their result in row 7. In row 8 of Table 3 we show the result from the multiconfigurational SCF calculation of a photoionization cross section carried by Froese–Fischer and Idrees.[11] In rows 9–10 we also show results from complex-scaled EOM-CC[17] and MCTDHF[18] calculations. In the last row of Table 3 we show results from the full CI calculation with an optimized Gaussian basis sets conducted by Kapralova–Zdanska and Smudke.[19] We want to note that they also presented values of −0.723 a.u. and 0.0024 a.u. of position and width, respectively in the s-limit calculation.

It is also interesting to note that the θ-trajectory (which is equivalent to the η-trajectory of the CAP) from the complex scaled SCF calculation in Ref. [15] shows 'width collapsing to zero' on complex energy plane, however, with our calculation we obtain the η-trajectory which clearly indicates a turning point where the points are accumulated (see Figs. 3 and 4). One may clearly think that results should be independent of r_c, however, it is also interesting to note that value of a similar parameter used in reflection-free CAP in Ref. [16] is 7.25 a.u.

Because for the first order Riss–Meyer correction ($n = 1$) the expansion error is reduced and because the basis set error decreases for growing η, the value of $\tilde{\eta}^{(1)}$ will be larger than the value of $\tilde{\eta}^{(0)}$. For large η the resonance wave function is mostly absorbed such that it becomes representable by the finite basis set on the chosen interval. For our result shown in Table 3, an optimal values of the strength parameter $\tilde{\eta}^{(0)}$ ($n = 0$) and $\tilde{\eta}^{(1)}$ ($n = 1$) are, relatively large, 2.1 and 4.7.

In Fig. 4 we show two basic methods to extract information from the complex eigenvalue trajectories for the $2s^2$ state and $r_c = 7.5$ a.u. (a) and 10 a.u. (b), respectively. Our results presented in Table 3 are based on trajectories shown in Fig. 4a. Shown as a black diamonds are the finite-basis matrix SCF eigenvalues E_{fb} (Eq. (16)) near the stabilization value η_{st} (black crosses). For η-values less than this stabilization value, the trajectory displays erratic behavior, since the numerical method cannot handle the demand to compute an outgoing oscillatory solution. When using $N_p = 4$ consistent eigenvalues from $\eta > \eta_{st}$, a Padé approximation equation (18) is calculated, and this functional is extrapolated to $\eta = 0$. These analytic η-trajectories are shown as green curves.

Also shown in panels (a) and (b) are results from the first order of the Riss–Meyer iterative correction scheme (Eqs. (16) and (17)). The trajectories $E^{(1)}(\eta)$ are shown parametrically as a blue diamonds, and it is evident that on the scale of the graphs they have accumulation points, and that the complex energy values at the accumulation points are very close, and the blue crosses at $\tilde{\eta}^{(1)}$ for $n = 1$ deviate from the stabilization points ($n = 0$). The proximity to the Padé extrapolation results is also evident. We note that in our calculations the Padé extrapolation with orders $N_p = 2$ and 4 gives a consistent results. Such as, the Padé extrapolation with order $N_p = 2$ and $r_c = 7.5$ a.u. for $2s^2$ give values of 0.714 a.u. and 0.00454 a.u. for position and width, respectively, which are consistent with the values shown in row 2 of Table 3.

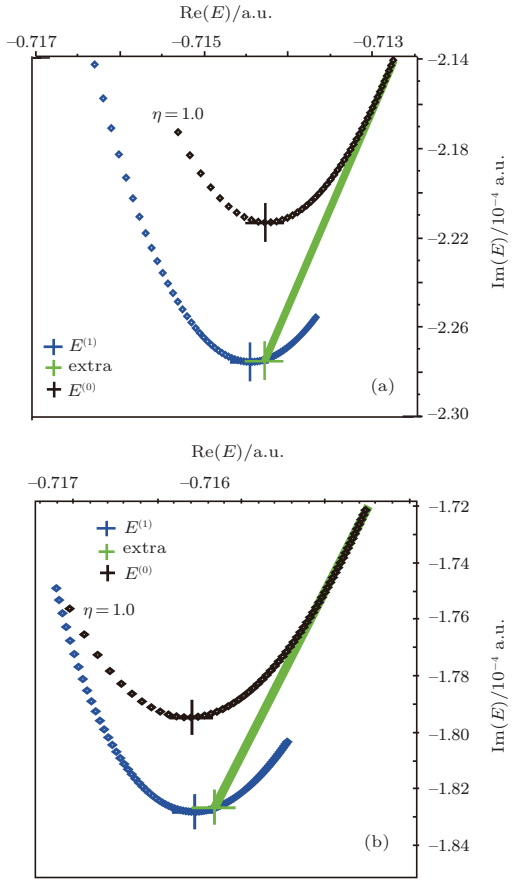


Fig. 4. (color online) The η-trajectories for $E^{(0)}$ (black diamonds) and $E^{(1)}$ (blue diamonds) for the $2s^2$ state of the He atom. Crosses are for $E^{(0)}(\tilde{\eta}^{(0)})$ and $E^{(0)}(\tilde{\eta}^{(1)})$ and the Padé extrapolated values (end point of the green line), respectively. The computational parameters are $N = 256$, $b = 60$ a.u. (panels (a) and (b)), and $r_c = 7.5$ a.u. (a) and 10 a.u. (b), respectively. The values of strength parameter for $\tilde{\eta}^{(0)}$ (black crosses) are 2.1 (a) and 2.2 (b), respectively. The $\tilde{\eta}^{(1)}$ (blue crosses) are 4.7 (a) and 5 (b), respectively and $\Delta\eta = 0.1$ (panels (a) and (b)).

When $r_c = 10$ a.u., we obtain values of 0.0036 a.u. and 0.0037 a.u. for the width from the Riss–Meyer ($n = 0$) and the Padé extrapolation ($N_p = 4$), respectively (Fig. 4(b)). In this case the Riss–Meyer ($n = 1$) calculation gives the same value of the width as the Padé extrapolation gave. These values for width are slightly smaller than those shown in Table 3. All three calculations with $r_c = 10$ a.u. give a consistent value of −0.716 a.u. for position.

With increasing order n, the data are based on $E_{fb}(\eta)$ values calculated at larger η. For $n = 1$ (blue symbols), the results come from the $\eta = 1.7, \ldots, 7.9$ range (a) and from the $\eta = 1.2, \ldots, 10$ range (b), respectively. The Padé extrapolated results were based upon $\eta = 4.5, 5.3, 6.1$, and 6.9 (a) and $\eta = 3.8, 4.1, 4.4$, and 4.7 (b), respectively. We note that these input points for the Padé approximant are taken from the stable parts in the stabilization plots. The strength of the $n = 1$ calculations comes, therefore, from the effective removal of the complex-absorber artifacts while using larger values of η. At these larger η-values the solution of the discretized complex Schrödinger problem is closer to the continuum limit, since it involves more localized wavefunctions which are more amenable to a finite representation.[20,28]

To further test our approach we continued our calculation for doubly excited $3s^2$ and $4s^2$ ^1S states of the helium atom. We have not as yet found other SCF calculations for resonance problems for these states. In Table 4 we present our results and compared them with previously obtained accurate values by a variational[14] and full CI[19] methods combined with complex scaling. Width is consistent with previously obtained accurate values[14,19] and $r_c = 13.75$ a.u., which also lies in the region where an orbital energy is close to the Coulomb potential (Fig. 2(b)). Our values from the complex SCF calculations made within the range $13.65 < r_c < 13.8$ (in unit a.u.) agree with each other as we discussed before. The values of the $\tilde{\eta}^{(0)}$ ($n = 0$) and $\tilde{\eta}^{(1)}$ ($n = 1$) are 0.24 and 0.55.

Table 4. The same as in Table 3, but for the $3s^2$ state.

State		Position/a.u.	Width/a.u.
$3s^2$	SM	−0.316	0.00289
	PE ($N_p = 4$)	−0.317	0.00297
	RM ($n = 1$)	−0.317	0.00297
	CS variational[14]	−0.354	0.00301
	(CS)CI[19]	−0.354	0.00301

In Table 5 we show our result for doubly excited $4s^2$ state and compare them with previously obtained values.[14,19] The width from our calculation is consistent with the more accurate values in Refs. [14] and [19] and $r_c = 22.5$ a.u. (Fig. 2(c)). The real and imaginary parts of the complex SCF calculations made within the range $22.0 < r_c < 23.0$ (in unit a.u.) are checked within four- and six-figure accuracies, respectively. The values of the $\tilde{\eta}^{(0)}$ ($n = 0$) and $\tilde{\eta}^{(1)}$ ($n = 1$) are 0.05 and 0.12, respectively.

Table 5. The same as in Table 3, but for the $4s^2$ state.

State		Position/a.u.	Width/a.u.
$4s^2$	SM	−0.178	0.00189
	PE ($N_p = 4$)	−0.178	0.00192
	RM ($n = 1$)	−0.178	0.00194
	CS variational[14]	−0.201	0.00194
	(CS)CI[19]	−0.201	0.00194

From our calculations for the autoionization resonance parameters for doubly excited $2s^2$, $3s^2$, and $4s^2$ states we see that the SCF calculations with a CAP are able to give consistent values for resonance widths compared with more accurate values.[14] However, position values obtained show an absolute percentage deviations of 8.23, 10.45, and 11.44 for doubly excited $2s^2$, $3s^2$, and $4s^2$ states with respect to the accurate values[14] shown in Tables 3–5, respectively. To obtain consistent values for positions and have a less dependent on r_c, one should take into account more configurations[11] in the complex SCF calculation. Such as, for the case of $2s^2$ (resonance)

calculation, a heavy mixing between the $2s^2$ and $2p^2$ which is based on degeneracy of the 2s and 2p orbitals should be at least taken into account, and for the $3s^2$ (resonance) calculation one needs to take into account a strong mixing of $3s^2$, $3p^2$, and $3d^2$, and so fourth.

We note that since we employ the CAP in our resonance calculation, we do not deal with a continuum wave, that is, the use of the CAP enables us to avoid the scattering calculation.[32] This is an advantage of the use of the CR,[9,33] and CAP[20,34,35] methods.

We also mention that Riss and Meyer[20] obtained a qualitatively correct value for a shape resonance for the N_2^- ion from an SCF calculation with a CAP using a Gaussian basis set.

In Fig. 5 we show the η-trajectories for $E^{(0)}$ and $E^{(1)}$ for the the $3s^2$ (a) and $4s^2$ (b) ^{1}S states of the He atom. Our results presented in Tables 4 and 5 are based on trajectories in shown Fig. 5. For $n = 1$ (blue symbols), the results come from the $\eta = 0.14, \ldots, 1.18$ range (a), and from the $\eta = 0.03, \ldots, 0.59$ range (b), respectively. The Padé extrapolated ($N_p = 4$) results were based upon $\eta = 0.60, \ldots, 0.63$ (a), and $\eta = 0.45, 0.49, 0.53$, and 0.57 (b), respectively.

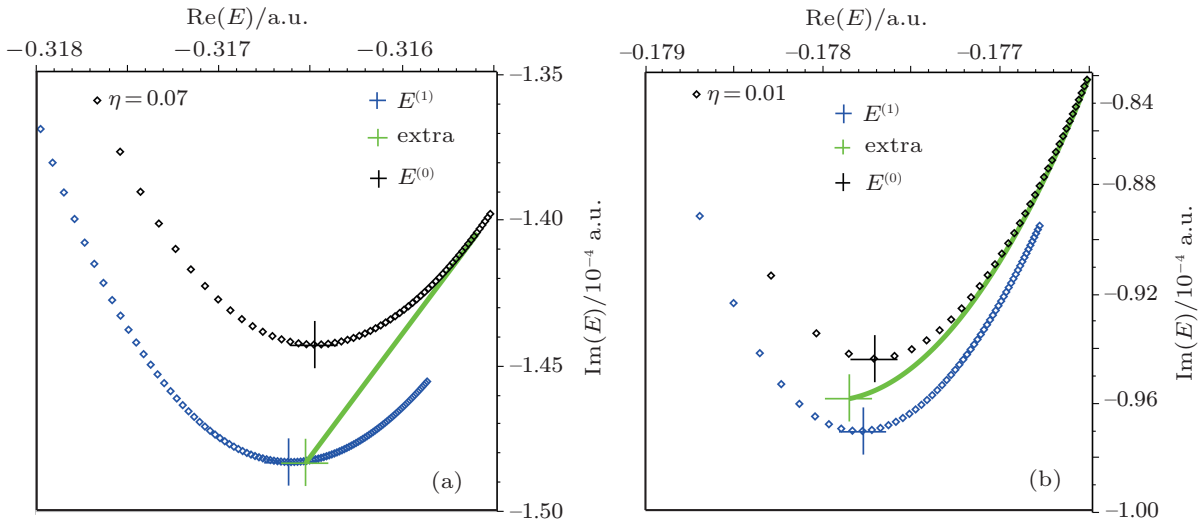


Fig. 5. (color online) The η-trajectories for $E^{(0)}$ (black diamonds) and $E^{(1)}$ (blue diamonds) for the $3s^2$ (a) and $4s^2$ (b) ^{1}S states of the He atom. Crosses are for $E^{(0)}(\tilde{\eta}^{(0)})$ and $E^{(0)}(\tilde{\eta}^{(1)})$ and the Padé extrapolated values (end point of the green line), respectively. The computational parameters are $N = 256$, $b = 60$ a.u. (panels (b) and (c)) and 13.75 (a) and 22.5 (b), respectively. The values of strength parameter for $\tilde{\eta}^{(0)}$ (black crosses) are 0.24 (a) and 0.05 (b), respectively. The $\tilde{\eta}^{(1)}$ (blue crosses) are 0.55 (a) and 0.12 (b), respectively and $\Delta\eta = 0.01$ (panels (b) and (c)).

4. Conclusions

In this work, we have applied the pseudospectral method to obtain an SCF solutions for the ground $1s^2$ and doubly excited $2s^2$, $3s^2$, and $4s^2$ ^{1}S states of the He atom. The Feshbach-type autoionization resonance parameters for the $2s^2$, $3s^2$, and $4s^2$ states are obtained by using Padé extrapolation and the Riss–Meyer iterative correction scheme to a complex self-consistent eigenvalues obtained from an SCF calculation combined with a CAP. The obtained results for resonance width are consistent with other more accurate values in the literature. However, values of position show deviations from these accurate values. This shows that the SCF calculations are not enough to obtain good values for positions and one needs to do a multi-configurational calculation to obtain a good value for positions. A natural extension of this work would be the multi-configurational SCF calculation combined with CAP for resonance problem of many-electron systems.

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Appendix A

The radial orbitals R_{ns} for the ns^2 ($n = 1,2,3,4$) configurations for atom with nuclear charge Z can be written as:

$$R_{1s}(r) = 2Z^{3/2}\,\mathrm{e}^{-Zr}, \tag{A1}$$

$$R_{2s}(r) = 2\left(\frac{Z}{2}\right)^{3/2}\left(1-\frac{Zr}{2}\right)\mathrm{e}^{-Zr/2}, \tag{A2}$$

$$R_{3s}(r) = 2\left(\frac{Z}{3}\right)^{3/2}\left(1-\frac{2Zr}{3}+\frac{2(Zr)^2}{27}\right)\mathrm{e}^{-Zr/3}, \tag{A3}$$

$$R_{4s}(r) = \frac{Z^{3/2}}{96}\left(24-18Zr+3(Zr)^2-\frac{(Zr)^3}{8}\right)\mathrm{e}^{-Zr/4}. \tag{A4}$$

An analytic solutions for the Poisson equation with $\rho = |\psi_{ns}|^2$, $(n = 1,2,3,4)$ are

$$\varphi_{1s}(r) = 1-\mathrm{e}^{-2Zr}-Zr\mathrm{e}^{-2Zr}, \tag{A5}$$

$$\varphi_{2s}(r) = 1-\mathrm{e}^{-Zr}-\frac{3}{4}Zr\mathrm{e}^{-Zr}-\frac{1}{4}(Zr)^2\mathrm{e}^{-Zr} - \frac{1}{8}(Zr)^3\mathrm{e}^{-Zr}, \tag{A6}$$

$$\varphi_{3s}(r) = 1-\mathrm{e}^{-(2/3)Zr}-\frac{5}{9}Zr\mathrm{e}^{-(2/3)Zr} - \frac{4}{27}(rZ)^2\mathrm{e}^{-(2/3)Zr}-\frac{4}{81}(Zr)^3\mathrm{e}^{-(2/3)Zr}$$

$$+\frac{4}{729}(Zr)^4\,\mathrm{e}^{-(2/3)Zr}-\frac{4}{2187}(Zr)^5\,\mathrm{e}^{-(2/3)Zr}, \quad \text{(A7)}$$

$$\begin{aligned}\varphi_{4s}(r)=1&-\mathrm{e}^{-(1/2)Zr}-\frac{7}{16}Zr\,\mathrm{e}^{-(1/2)Zr}\\&-\frac{3}{32}(rZ)^2\,\mathrm{e}^{-(1/2)Zr}-\frac{3}{128}(Zr)^3\,\mathrm{e}^{-\frac{1}{2}Zr}\\&+\frac{1}{256}(Zr)^4\,\mathrm{e}^{-(1/2)Zr}-\frac{3}{2048}(Zr)^5\,\mathrm{e}^{-(1/2)Zr}\\&+\frac{5}{36864}(Zr)^6\,\mathrm{e}^{-(1/2)Zr}\\&-\frac{1}{147456}(Zr)^7\,\mathrm{e}^{-(1/2)Zr}. \quad \text{(A8)}\end{aligned}$$

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