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Boundedness and convergence of perturbed corrections for helium-like ions in ground states*

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Applying the improved Rayleigh–Schrödinger perturbation theory based on an integral equation to helium-like ions in ground states and treating electron correlations as perturbations, we obtain the second-order corrections to wavefunctions consisting of a few terms and the third-order corrections to energicity. It is demonstrated that the corrected wavefunctions are bounded and quadratically integrable, and the corresponding perturbation series is convergent. The results clear off the previous distrust for the convergence in the quantum perturbation theory and show a reciprocal development on the quantum perturbation problem of the ground state helium-like systems.

Keywords: helium-like ion, perturbation correction, boundedness, convergence
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1. Introduction

A fundamental assumption of quantum mechanics is that quantum states of microscopic systems are governed by the Schrödinger equation. So solving the Schrödinger equation is an important task for investigating the corresponding quantum system. However, for most physically interesting systems the Schrödinger equations are not exactly solvable[1] so that some approximate methods, such as the semi-classical approximation, the variational method and the quantum perturbation theory, are developed separately. In many cases a system of interest differs from an exactly solvable system by only a small disturbance, and the first-order and the second-order perturbed solutions are in good agreement with the corresponding experimental results. Therefore, the Rayleigh–Schrödinger quantum perturbation theory has been applied widely to various physical systems.[2−8] But the divergence difficulty of the perturbed series solutions exists in quantum mechanics and quantum field theory as shown by physicists Dirac, Feynman and Wigner *et al.*[9−17] Particularly, in the standard quantum perturbation theory, the infinite square integrals of the corrected wavefunctions appear in the calculations of the higher-order perturbed corrections to the Coulomb systems.[9,18,19] Tremendous efforts have been made to improve the quantum perturbation techniques for different systems.[18−31] For the atom helium and helium-like ion systems many studies have been carried out.[32−38] The $1/z$ perturbation expansion has long been used in the calculation of the corrections to the energy and the state for producing the highly accurate results; however, the perturbation series is not convergent and only the convergence radius was found.[32−35] In the previous work,[27] we have established an improved Rayleigh–Schrödinger perturbation method based on an integral equation for suppressing divergences and numerical instabilities in nonrelativistic quantum mechanics.[26] However, only the second-order energy-corrections of the helium-like ion systems are calculated as examples. In order to test the validation of the Rayleigh–Schrödinger perturbation theory for the Coulomb systems, using the improved Rayleigh–Schrödinger perturbation method to investigate the third-order corrections to the perturbed helium-like ion systems is necessary and important.

In the present paper, we use the improved Rayleigh–Schrödinger perturbation method to compute the second-order corrections to the wavefunctions

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and the third-order corrections to energies of helium-like ions in ground states, and to obtain the quadratically integrable corrected states consisting of a few terms and the rational energy corrections. According to the results we also prove the convergence of the corresponding perturbation series. The results clear off the previous distrust[1,9] of the quantum perturbation theory further for the higher-order perturbation case and show a reciprocal development on the quantum perturbation problem of helium-like systems in ground states.

2. The second-order corrections to wavefunctions and third-order corrections to energies

In atom units, the Schrödinger equation governing a helium-like ion reads

$$-\frac{1}{2}\nabla_1^2\psi-\frac{1}{2}\nabla_2^2\psi-\frac{z}{r_1}\psi-\frac{z}{r_2}\psi+\frac{1}{r_{12}}\psi=E\psi, \quad (1)$$

where the coordinates of the first electron and the second electron are labelled by subscripts 1 and 2 respectively, $1/r_{12}$ denotes the electron–electron interaction, E is the total energy and z the number of nucleus charges. We consider only the ground states of helium-like ions with main quantum number $n=1$ and angular one $l=0$. The first approximations to wavefunctions and the second-order corrections to the energies of the systems have been derived from the improved Rayleigh–Schrödinger perturbation theory.[27] Here we investigate the second-order corrections to the wavefunctions and the third-order corrections to energies.

We take the electron–electron interaction as perturbation Hamiltonian H' and make use of the expansion formulas[39,40]

$$H'(r_1,r_2)=\frac{1}{r_{12}}=\frac{1}{r_2}\sum_{l=0}^{\infty}\left(\frac{r_1}{r_2}\right)^l p_l(\cos\theta_{12})=\frac{1}{r_2}, \quad \text{for} \quad l=0, r_1\le r_2; \quad (2)$$

$$H'(r_1,r_2)=\frac{1}{r_{12}}=\frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l p_l(\cos\theta_{12})=\frac{1}{r_1}, \quad \text{for} \quad l=0, r_2\le r_1. \quad (3)$$

Setting the radial wavefunction to be in the form

$$\psi(r_1,r_2)=\frac{\chi(r_1,r_2)}{r_1r_2}, \quad (4)$$

the radial Schrödinger equation of the system becomes

$$\sum_{i=1}^{2}\left[\frac{\partial^2\chi(r_1,r_2)}{\partial r_i^2}+\frac{2z}{r_i}\right]\chi(r_1,r_2) = 2\Big[H'(r_1,r_2)-E\Big]\chi(r_1,r_2). \quad (5)$$

The corresponding integral equation reads[27,41]

$$\chi(r_1,r_2)=\chi^{(0)}(r_1,r_2)+\tilde{\chi}^{(0)}(r_l)\int_{A_l}^{r_l}\chi^{(0)}(r_l)F'\chi\mathrm{d}r_l -\chi^{(0)}(r_l)\int_{B_l}^{r_l}\tilde{\chi}^{(0)}(r_l)F'\chi\mathrm{d}r_l, \quad (6)$$

$$F'=-\frac{\partial^2}{\partial r_k^2}-\frac{2z}{r_k}+2\left[H'-E+E_l^{(0)}\right], \quad k,l=1,2;\ k\ne l, \quad (7)$$

where A_l and B_l are arbitrary constants. The ground state energy $E_l^{(0)}$ and normalized wavefunction of the unperturbed electrons have the forms

$$E_l^{(0)}=-\frac{1}{2}z^2, \quad \chi^{(0)}(r_1,r_2)=\chi^{(0)}(r_1)\chi^{(0)}(r_2), \quad (8)$$

$$\chi^{(0)}(r_l)=2z^{\frac{3}{2}}r_l\mathrm{e}^{-zr_l},$$

$$\tilde{\chi}^{(0)}(r_l)=\chi^{(0)}\int\left[\chi^{(0)}(r_l)\right]^{-2}\mathrm{d}r_l, \quad l=1,2. \quad (9)$$

Obviously, the function $\tilde{\chi}^{(0)}(r_l)$ is unbounded at the infinite boundary; so the wavefunction in Eq.(6) is bounded only if the boundedness condition $\lim\limits_{r_l\to\infty}\int_{A_l}^{r_l}\chi^{(0)}(r_l)F'\chi\mathrm{d}r_l=0$ is satisfied. Applying Eq.(7) to the boundedness condition, we arrive at the equation $\left(\dfrac{\partial^2}{\partial r_k^2}+\dfrac{2z}{r_k}+2E_k^{(0)}\right)\bar{\chi}(r_k)=\varepsilon(r_k)$ whose equivalent integral equation reads[27]

$$\bar{\chi}(r_k)=\int_0^{\infty}\chi^{(0)}(r_l)\chi(r_1,r_2)\mathrm{d}r_l = \tilde{\chi}^{(0)}(r_k)\int_C^{r_k}\chi^{(0)}(r_k)\varepsilon(r_k)\mathrm{d}r_k -\chi^{(0)}(r_k)\int_D^{r_k}\tilde{\chi}^{(0)}(r_k)\varepsilon(r_k)\mathrm{d}r_k,$$

$$\varepsilon(r_k) = 2\int_0^\infty \chi^{(0)}(r_l)\Big[H' - E + E^{(0)}\Big]\chi(r_1,r_2)\mathrm{d}r_l,$$
$$k,l = 1,2,\ k \neq l,\quad E^{(0)} = E_1^{(0)} + E_2^{(0)}. \quad (10)$$

Inserting the Rayleigh–Schrödinger perturbation expansions $\bar{\chi}(r_k) = \sum_{i=0}^{\infty}\bar{\chi}^{(i)}(r_k)$ and $E = \sum_{i=0}^{\infty}E^{(i)}$ into Eq.(10) produces the formulas of the ith-order perturbation functions $\bar{\chi}^{(i)}(r_k)$ and corrected energies $E^{(i)}$ as[27]

$$\begin{aligned}\bar{\chi}^{(i)}(r_{k)} &= \tilde{\chi}^{(0)}(r_k)\int_{C_i}^{r_k}\chi^{(0)}(r_k)\varepsilon^{(i)}(r_k)\mathrm{d}r_k \\ &\quad -\chi^{(0)}(r_k)\int_{D_i}^{r_k}\tilde{\chi}^{(0)}(r_k)\varepsilon^{(i)}(r_k)\mathrm{d}r_k, \\ \varepsilon^{(i)}(r_k) &= 2\int_0^\infty \chi^{(0)}(r_l)\Bigg[H'\chi^{(i-1)}(r_1,r_2) \\ &\quad -\sum_{j=1}^{i}E^{(j)}\chi^{(i-j)}(r_1,r_2)\Bigg]\mathrm{d}r_l, \\ &\quad k,l = 1,2,\ k \neq l; \quad (11) \\ E^{(i)} &= \int_0^\infty\int_0^\infty \chi^{(0)}(r_1,r_2)\Bigg[H'\chi^{(i-1)}(r_1,r_2) \\ &\quad -\sum_{j=1}^{i-1}E^{(j)}\chi^{(i-j)}(r_1,r_2)\Bigg]\mathrm{d}r_1\mathrm{d}r_2, \quad (12)\end{aligned}$$

where $\varepsilon^{(0)}(r_k) = 0$ and C_i, and D_i are constants. For simplicity we will set $\bar{\chi}^{(i)}(r_{k)} = \chi^{(i)}(r_{k)}$ for $i = 0,1,\cdots$ throughout the paper. Then we can expand the solution of Eq.(6) and construct any order perturbed correction as[27]

$$\chi(r_1,r_2) = \sum_{i=0}^{\infty}\chi^{(i)}(r_1,r_2),$$
$$\chi^{(i)}(r_1,r_2) = \begin{cases}\chi^{(0)}(r_1)\chi^{(i)}(r_2), & r_1 \le r_2, \\ \chi^{(0)}(r_2)\chi^{(i)}(r_1), & r_2 \le r_1.\end{cases} \quad (13)$$

It is clear that making use of Eqs.(9)–(13) we can obtain any order corrections to the wavefunction and energy. For the simple case of $i = 1$, Eqs.(12) and (11) imply $E^{(1)} = 5z/8$ and $\varepsilon^{(1)}(r_k) = 4z^{3/2}r_k(1/r_k - 5z/8)\mathrm{e}^{-zr_k}$ for $r_l \le r_k,\ k,l = 1,2$. Combining Eq.(13) with Eqs.(9)–(12) yields the first-order corrections to the wavefunctions as[27]

$$\begin{aligned}\chi^{(1)}(r_1,r_2) &= \frac{z^3}{2}r_1r_2\exp^{-z(r_1+r_2)} \\ &\quad \times\left[5r_2 - \frac{3}{z}\ln r_2 + \frac{3}{2z^2r_2} + D\right], \\ &\quad r_1 \le r_2,\quad r_2 \neq 0, \quad (14) \\ \chi^{(1)}(r_1,r_2) &= \frac{z^3}{2}r_1r_2\exp^{-z(r_1+r_2)} \\ &\quad \times\left[5r_1 - \frac{3}{z}\ln r_1 + \frac{3}{2z^2r_1} + D\right], \\ &\quad r_1 \ge r_2,\quad r_1 \neq 0. \quad (15)\end{aligned}$$

Here D is the normalization constant related to constant D_1 in Eq.(11), and another integral constant related to constant C_1 in Eq.(11) has been taken as zero such that the first order correction to the wavefunction vanishes at the infinite boundary. Applying Eqs.(8), (9), (14) and (15) to the first-order normalization conditions

$$\int_0^\infty\int_0^\infty \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1,r_2)\mathrm{d}r_1\mathrm{d}r_2 = 0, \quad (16)$$

the constant D is given as

$$D = -\frac{9.044148 + 3\ln z}{z}. \quad (17)$$

Inserting Eqs.(13), (14), (15) into Eq.(12) produces the second order correction to the energy

$$\begin{aligned}&E^{(2)} \\ &= \int_0^\infty \mathrm{d}r_2\Bigg[\int_0^{r_2}\chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1 \le r_2)r_2^{-1}\mathrm{d}r_1 \\ &\quad +\int_{r_2}^\infty \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1 \ge_2)r_1^{-1}\mathrm{d}r_1\Bigg] \\ &= -0.25 \times 0.141849 + 0.00608797 - 0.117188\ln z \\ &\quad -0.0117188(1 - 10 \times 0.577216 \\ &\quad +6 \times 1.38629 - 10\ln z) \\ &= -0.0709244. \quad (18)\end{aligned}$$

This value differs from the second-order correction to the energy in Ref.[27], for we have adopted the more accurate constant D of Eq.(17) here. Total energy of the system with number z of nucleus charges is thereby

$$\begin{aligned}E &= E_1^{(0)} + E_2^{(0)} + E^{(1)} + E^{(2)} \\ &= -z^2 + \frac{5z}{8} - 0.0709244. \quad (19)\end{aligned}$$

Given $\chi^{(1)}(r_1,r_2)$ in Eqs.(14) and (15) and $E^{(2)}$ in Eq.(18), we can calculate the second-order correction to the wave function and the third-order correction to the energy. Inserting Eqs.(2), (3), (9), (13), (14) and (15) into Eq.(11) we have the perturbation functions

$$\varepsilon^{(2)}(r_2)=\frac{2}{r_2}\chi^{(1)}(r_2)-2E^{(1)}\chi^{(1)}(r_2)-2E^{(2)}\chi^{(0)}(r_2),\quad \text{for}\quad r_1\le r_2; \tag{20}$$

$$\varepsilon^{(2)}(r_1)=\frac{2}{r_1}\chi^{(1)}(r_1)-2E^{(1)}\chi^{(1)}(r_1)-2E^{(2)}\chi^{(0)}(r_1),\quad \text{for}\quad r_2\le r_1. \tag{21}$$

In the case of $r_1\le r_2$, Eqs.(9), (13) and (14) imply

$$\begin{aligned}\chi^{(0)}(r_2)&=2z^{\frac{3}{2}}r_2\exp^{-zr_2},\\ \chi^{(0)}(r_1)&=2z^{\frac{3}{2}}r_1\exp^{-zr_1},\end{aligned} \tag{22}$$

$$\chi^{(1)}(r_2)=\frac{1}{4}z^{\frac{3}{2}}r_2\exp^{-zr_2}\times\left[5r_2-\frac{3}{z}\ln r_2+\frac{3}{2z^2r_2}+D\right]. \tag{23}$$

Substituting them into Eq.(20) yields

$$\varepsilon^{(2)}(r_2)=\frac{1}{4}\chi^{(0)}(r_2)\left[k_1r_2+k_2+\frac{k_3}{r_2}+\frac{k_4}{r_2^2}+k_5\ln(r_2)+\frac{k_6\ln r_2}{r_2}\right], \tag{24}$$

where $k_1=-\dfrac{25z}{8}$, $k_2=5-\dfrac{5zD}{8}-8E^{(2)}$, $k_3=D-\dfrac{15}{16z}$, $k_4=\dfrac{3}{2z^2}$, $k_5=\dfrac{15}{8}$, and $k_6=-\dfrac{3}{z}$ are constants. Similarly, for $r_1\ge r_2$ from Eqs.(9), (13), (15) and (21) we obtain

$$\chi^{(1)}(r_1)=\frac{1}{4}z^{\frac{3}{2}}r_1\exp^{-zr_1}\times\left[5r_1-\frac{3}{z}\ln r_1+\frac{3}{2z^2r_1}+D\right], \tag{25}$$

$$\varepsilon^{(2)}(r_1)=\frac{1}{4}\chi^{(0)}(r_1)\left[k_1r_1+k_2+\frac{k_3}{r_1}+\frac{k_4}{r_1^2}+k_5\ln r_1+\frac{k_6\ln r_2}{r_1}\right]. \tag{26}$$

Inserting Eq.(24) into Eq.(11) then into Eq.(13), we arrive at the second order correction to the wavefunction

$$\chi^{(2)}(r_1\le r_2)=\frac{\chi^{(0)}(r_1,r_2)}{16z^3}\left[m_1r_2^2+m_2r_2+B+\frac{m_3}{r_2}+m_4\ln r_2+m_5r_2\ln r_2+\frac{m_6}{r_2}\ln r_2+m_7(\ln r_2)^2\right], \tag{27}$$

where $r_2\neq 0$; B is the normalization constant related to constant D_2 in Eq.(11), and another integral constant related to constant C_2 in Eq.(11) has been taken as zero such that the second order correction to the wavefunction vanishes at the infinite boundary; the coefficients m_i read $m_1=-z^2k_1$, $m_2=-(3zk_1+2z^2k_2-2z^2k_5)$, $m_3=\dfrac{3k_1}{2z}+k_2+zk_3+2z^2k_4+\dfrac{5k_5}{2}+2zk_6$, $m_4=-(3k_1+2zk_2+2z^2k_3+zk_5)$, $m_5=-2z^2k_5$, $m_6=k_5+zk_6$ and $m_7=-zm_6$, respectively. Similarly, in the case of $r_1\ge r_2$ and $r_1\neq 0$, the second order correction to the wavefunction reads

$$\chi^{(2)}(r_1\ge r_2)=\frac{\chi^{(0)}(r_1,r_2)}{16z^3}\left[m_1r_1^2+m_2r_1+B+\frac{m_3}{r_1}+m_4\ln r_1+m_5r_1\ln r_1+\frac{m_6}{r_1}\ln r_1+m_7(\ln r_1)^2\right]. \tag{28}$$

The integration constant B can be computed from the second-order normalization condition

$$\begin{aligned}&\int_0^\infty\int_0^\infty\left[2\chi^{(0)}(r_1,r_2)\chi^{(2)}(r_1,r_2)+\chi^{(1)}(r_1,r_2)\chi^{(1)}(r_1,r_2)\right]\mathrm{d}r_1\mathrm{d}r_2\\ &=2\int_0^\infty\mathrm{d}r_2\left[\int_0^{r_2}\chi^{(0)}(r_1,r_2)\chi^{(2)}(r_1\le r_2)\mathrm{d}r_1+\int_{r_2}^\infty\chi^{(0)}(r_1,r_2)\chi^{(2)}(r_1\ge r_2)\mathrm{d}r_1\right]\\ &\quad+\int_0^\infty\left[\int_0^{r_2}\chi^{(1)}(r_1\le r_2)\chi^{(1)}(r_1\le r_2)\mathrm{d}r_1+\int_{r_2}^\infty\chi^{(1)}(r_1\ge r_2)\chi^{(1)}(r_1\ge r_2)\mathrm{d}r_1\right]\mathrm{d}r_2\\ &=2(G_1+G_2)+G_3+G_4=0,\end{aligned} \tag{29}$$

$$G_1+G_2=\frac{1}{z^3}\left[0.0625B-0.479256675z-0.273245z\ln z-0.105469z(\ln z)^2\right]+C_1'+C_2', \tag{30}$$

$$G_3+G_4=\frac{1}{z^2}\left[0.0817702+0.0814267\ln z-0.0703125(\ln z)^2\right]+C_3'+C_4', \tag{31}$$

where C_i' are constants given by the integrations

$$C_1' = \int_0^\infty \frac{9}{8} z^4 r^2 \mathrm{e}^{-2zr} \left[\int_1^\infty r^2 (\ln r)^2 \mathrm{e}^{-2zr} \mathrm{d}r \right] \mathrm{d}r, \tag{32}$$

$$C_2' = \int_0^\infty \frac{9}{8} z^4 r^2 \mathrm{e}^{-2zr} \{\mathrm{Simpson}[f(x), x, r, 1, 20]\} \mathrm{d}r, \tag{33}$$

$$C_3' = \int_0^\infty \frac{9}{4} z^4 r^2 \mathrm{e}^{-2zr} \left[\int_1^\infty r^2 (\ln r)^2 \mathrm{e}^{-2zr} \mathrm{d}r \right] \mathrm{d}r, \tag{34}$$

$$C_4' = \int_0^\infty \frac{9}{4} z^4 r^2 \mathrm{e}^{-2zr} \{\mathrm{Simpson}[f(x), x, r, 1, 20]\} \mathrm{d}r. \tag{35}$$

In the calculations, we have used $\int_r^\infty r^2 (\ln r)^2 \ \mathrm{e}^{-2zr} \mathrm{d}r = \int_r^1 r^2 (\ln r)^2 \mathrm{e}^{-2zr} \mathrm{d}r + \int_1^\infty r^2 (\ln r)^2 \mathrm{e}^{-2zr} \mathrm{d}r$ and the Simpson's rule such that the integral $\int_r^1 r^2 (\ln r)^2 \mathrm{e}^{-2zr} \mathrm{d}r$ is numerically approximated by the Simpson's formula

$$\int_r^1 f(x) \mathrm{d}x \approx \mathrm{Simpson}[f(x), x, r, 1, n] = \frac{1-r}{3n} \left[f(x_0) + 4 \sum_{k=1,3,5,\cdots}^{n-1} f(x_k) + 2 \sum_{m=2,4,6,\cdots}^{n-2} f(x_m) + f(x_n) \right], \tag{36}$$

where $f(x) = x^2 (\ln x)^2 \mathrm{e}^{-2zx}$ and $n = 20$. For $z = 2$ Eqs.(29)–(36) give the numerical integration values C_i' and normalization constant

$$B = 20.8539, \tag{37}$$

which are listed in Table 1. Similarly, for $z = 2, 3, \cdots, 8$ the normalization constants and C_i' values are computed and the results are obtained as indicated in Table 1.

Table 1. The numerical integration values C_i' and normalization constants of helium-like ions in ground states.

z	C_1'	C_2'	C_3'	C_4'	B
2	0.000544975	0.00138389	0.00108995	0.00276777	20.8539
3	0.000019024	0.00183236	0.00003805	0.00366472	39.8431
4	2.0047×10^{-6}	0.00188335	4.0094×10^{-6}	0.00376700	62.1220
5	1.6475×10^{-7}	0.00178291	3.2950×10^{-7}	0.00356582	87.0160
6	1.4819×10^{-8}	0.00163729	2.9638×10^{-8}	0.00327460	114.103
7	1.4429×10^{-9}	0.00148776	2.8858×10^{-9}	0.00297552	143.085
8	1.4646×10^{-10}	0.00134876	2.9292×10^{-10}	0.00269752	173.740

The substitution of Eqs.(27) and (28) with the normalization constant B into Eq.(12) gives the third-order correction to the energy

$$\begin{aligned} E^{(3)} &= \int_0^\infty \int_0^\infty \chi^{(0)}(r_1, r_2) \left\{ \left[H'(r_1, r_2) - E^{(1)} \right] \chi^{(2)}(r_1, r_2) - E^{(2)} \chi^{(1)}(r_1, r_2) \right\} \mathrm{d}r_1 \mathrm{d}r_2 \\ &= \int_0^\infty \int_0^\infty \chi^{(0)}(r_1, r_2) H' \chi^{(2)}(r_1, r_2) \mathrm{d}r_1 \mathrm{d}r_2 - E^{(1)} \int_0^\infty \int_0^\infty \chi^{(0)} \chi^{(2)}(r_1, r_2) \mathrm{d}r_1 \mathrm{d}r_2 \\ &= G_5 + G_6 - E^{(1)}(G_1 + G_2), \end{aligned} \tag{38}$$

where $G_1 + G_2$ is given by Eqs.(30), (32) and (33),

$$\begin{aligned} &G_5 + G_6 \\ &= \frac{1}{z^2} [0.0390625B - 0.313578z - 0.180642z \ln z \\ &\quad -0.065918z(\ln z)^2] + C_5' + C_6', \end{aligned} \tag{39}$$

$$C_5' = \int_0^\infty \frac{9}{8} z^4 r^2 \mathrm{e}^{-2zr} \left[\int_1^\infty r (\ln r)^2 \mathrm{e}^{-2zr} \mathrm{d}r \right] \mathrm{d}r, \tag{40}$$

$$C_6' = \int_0^\infty \frac{9}{8} z^4 r^2 \mathrm{e}^{-2zr} \{\mathrm{Simpson}[g(x), x, r, 1, 20]\} \mathrm{d}r \tag{41}$$

with function $g(x) = x(\ln x)^2 \mathrm{e}^{-2zx}$ and Simpson[$g(x)$, $x, r, 1, 20$] obeying Eq.(36), the values of z and B being listed in Table 1. In the case of $z = 2$, the calculations from Eqs.(38)–(41) give the third-order correction to the energy as

$$E^{(3)} = -0.00889915. \tag{42}$$

The total energies are given for a helium atom with $z = 2$ as follows:

$$\begin{aligned} E &= E_1^{(0)} + E_2^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} \\ &= -z^2 + \frac{5z}{8} - 0.0709244 - 0.00889915. \end{aligned} \tag{43}$$

For $z = 3, 4, \cdots$, the calculated results of the total energy E, the third-order energy-corrections $E^{(3)}$ and the corresponding numerical constants C_5', C_6' are listed in Table 2, where the values of E_{ex} are the experimental energy values of helium-like ions in ground states.[41,42] Although comparisons between the theoretical energies E and experimental energies E_{ex} show good agreement with each other, the results are weak up to the third-order corrections in comparison with the highly-accurate calculations for $1/z$ expansion.[32–35] But differing from the latter, our corrected solutions are bounded and our perturbed series is convergent, which will be demonstrated in the next section.

Table 2. The energies of helium-like ions in ground states (atomic units).

ions	z	C_5'	C_6'	$E^{(3)}$	E	E_{ex}
He	2	3.13173×10^{-4}	0.00363855	−0.00889915	−2.82982355	−2.90378
Li^+	3	1.90736×10^{-5}	0.00582985	−0.00593328	−7.20185766	−7.28041
Be^{++}	4	1.46006×10^{-6}	0.00719001	−0.00445156	−13.57537596	−13.65744
B^{+++}	5	1.26836×10^{-7}	0.00799284	−0.00356375	−21.94948815	−22.03603
C^{4+}	6	1.19416×10^{-8}	0.00845463	−0.00297159	−32.32389599	−32.41733
N^{5+}	7	1.18873×10^{-9}	0.00870753	−0.00254976	−44.69847416	−44.80351
O^{6+}	8	1.23352×10^{-10}	0.0088296	−0.00223362	−59.07315807	−59.19580

3. Boundedness of corrected solutions and convergence of perturbed series

In the preceding section, the improved quantum perturbation theory based on an integral equation is applied to constructing the second-order corrections to the wavefunctions and the third-order corrections to the energies for helium-like ions in ground states. From Table 1 it can be easily seen that up to the third-order approximations the energies are in good agreement with the corresponding experimental data. The integrability of the square of corrected wavefunctions has also be shown in Eqs.(16) and (29) by using the wavefunctions to directly integrate from $r_k = 0$ to $r_k = \infty$ for $k = 1, 2$. We will verify the boundedness of any order perturbed correction and the convergence of the perturbed series which is the sum of the perturbed corrections as follows.

Starting from Eq.(9) and applying the Höpital rule we have limit

$$\begin{aligned} &\lim_{r_k \to \infty} \tilde{\chi}^{(0)}(r_k) \\ &= \lim_{r_k \to \infty} \frac{\int (\chi^{(0)}(r_k))^{-2} \mathrm{d}r_k)}{(\chi^{(0)}(r_k))^{-1}} \\ &= \lim_{r_k \to \infty} \frac{\mathrm{e}^{zr_k}}{2z^{\frac{3}{2}}} = \infty. \end{aligned} \tag{44}$$

This means that the singularity of wavefunction (10) may appear only at the infinite boundary. Combining Eq.(44) with Eqs.(11) and (13) implies that the perturbed solutions is bounded at the infinite boundary if and only if the conditions

$$\begin{aligned} &\lim_{r_k \to \infty} \int_{C_i}^{r_k} \chi^0(r_k) \varepsilon^{(i)}(r_k) \mathrm{d}r_k = 0, \\ &r_k \geq r_l, \quad k, l = 1, 2, \quad k \neq l \end{aligned} \tag{45}$$

are satisfied. Noticing $\chi^{(0)}(r_l) = 0$ at the boundary $r_l = \infty$, Eq.(13) means that the boundedness of the perturbed correction is determined by the boundedness of $\chi^i(r_k)$. The latter can be proved by taking the limit from Eq.(11),

$$\lim_{r_k\to\infty}\chi^{(i)}(r_k)=\lim_{r_k\to\infty}\left\{\frac{\chi^{(0)}(r_k)\varepsilon^{(i)}(r_k)}{\left[(\tilde{\chi}^{(0)}(r_k))^{-1}\right]_{r_k}}-\frac{\tilde{\chi}^{(0)}(r_k)\varepsilon^{(i)}(r_k)}{\left[(\chi^{(0)}(r_k))^{-1}\right]_{r_k}}\right\}$$
$$=\lim_{r_k\to\infty}\left\{\frac{(\chi^{(0)}(r_k))^2\tilde{\chi}^{(0)}(r_k)\varepsilon^{(i)}(r_k)}{\left[\chi^{(0)}(r_k)\right]_{r_k}}-\frac{(\tilde{\chi}^{(0)}(r_k))^2\chi^{(0)}(r_k)\varepsilon^{(i)}(r_k)}{\left[\tilde{\chi}^{(0)}(r_k)\right]_{r_k}}\right\}$$
$$=\lim_{r_k\to\infty}\left\{\frac{\chi^{(0)}(r_k)\tilde{\chi}^{(0)}(r_k)\varepsilon^{(i)}(r_k)}{\left[\chi^{(0)}(r_k)\right]_{r_k}\left[\tilde{\chi}^{(0)}(r_k)\right]_{r_k}}\left[\chi^{(0)}(r_k)\left[\tilde{\chi}^{(0)}(r_k)\right]_{r_k}-\tilde{\chi}^{(0)}(r_k)\left[\chi^{(0)}(r_k)\right]_{r_k}\right]\right\}$$
$$=\lim_{r_k\to\infty}\left\{\frac{\chi^{(0)}(r_k)\tilde{\chi}^{(0)}(r_k)}{\left[\chi^{(0)}(r_k)\right]_{r_k}\left[\tilde{\chi}^{(0)}(r_{(k)})\right]_{r_k}}\right\}\lim_{r_k\to\infty}\varepsilon^{(i)}(r_k)$$
$$=\lim_{r_k\to\infty}\left\{\frac{\chi^{(0)}(r_k)\left[\tilde{\chi}^{(0)}(r_k)\right]_{r_k}+\left[\chi^{(0)}(r_k)\right]_{r_k}\tilde{\chi}^{(0)}(r_k)}{\left[\chi^{(0)}(r_k)\right]_{r_kr_k}\left[\tilde{\chi}^{(0)}(r_{(k)})\right]_{r_k}+\left[\chi^{(0)}(r_k)\right]_{r_k}\left[\tilde{\chi}^{(0)}(r_{(k)})\right]_{r_kr_k}}\right\}\lim_{r_k\to\infty}\varepsilon^{(i)}(r_k)$$
$$=\lim_{r_k\to\infty}\left\{\frac{\varepsilon^{(i)}(r_k)}{2\left[V(r_k)-E_k^{(0)}\right]}\right\},\tag{46}$$

where $V(r_k)=-\dfrac{z}{r_k}$ and $E_k^{(0)}=-\dfrac{1}{2}z^2$. In the calculations the Höpital rule and the Wronskian formula $\chi^{(0)}(r_k)\left[\tilde{\chi}^{(0)}(r_k)\right]_{r_k}-\left[\chi^{(0)}(r_k)\right]_{r_k}\tilde{\chi}^{(0)}(r_k)=1$ have been used. Combining Eq.(46) with Eqs.(11) and (13), we have the limit

$$\lim_{r_k\to\infty}\chi^{(i)}(r_l,r_k)=\chi^{(0)}(r_l)\lim_{r_k\to\infty}\chi^{(i)}(r_k)=\frac{1}{z^2}\chi^{(0)}(r_l)\lim_{r_k\to\infty}\varepsilon^{(i)}(r_k)$$
$$=\frac{1}{z^2}\chi^{(0)}(r_l)\lim_{r_k\to\infty}\left[H'(r_k)\chi^{(i-1)}(r_k)-\sum_{j=1}^{i}E^{(j)}\chi^{(i-j)}(r_k)\right],\quad\text{for}\quad r_k\geq r_l;\ i=1,2,\cdots.\tag{47}$$

From Eq.(9) we know $\lim_{r_k\to\infty}\chi^{(0)}(r_k)=0$ so that Eqs.(47), (2) and (3) imply $\lim_{r_k\to\infty}\chi^{(i)}(r_l,r_k)\propto\lim_{r_k\to\infty}\chi^{(0)}(r_k)=0$ for $i=1,2,\cdots$. Thus we have analytically verified the boundedness of the perturbed corrections at the infinite boundary.

Given Eq.(46), we can easily prove the convergence of the perturbation series (13) at the infinite boundary. In fact, from Eqs.(10) and (11) we can see $\sum\varepsilon^{(i)}(r_k)=\varepsilon(r_k)$ and $\sum\chi^{(i)}(r_k)=\chi(r_k)$. Therefore, summing Eq.(46) and applying Eq.(10) lead to the limit

$$\lim_{r_k\to\infty}\chi(r_k)=\lim_{r_k\to\infty}\sum\chi^{(i)}(r_k)$$
$$=\lim_{r_k\to\infty}\left\{\frac{\sum\varepsilon^{(i)}(r_k)}{2\left[V(r_k)-E_k^{(0)}\right]}\right\}$$
$$=\lim_{r_k\to\infty}\left\{\frac{\varepsilon(r_k)}{2\left[V(r_k)-E_k^{(0)}\right]}\right\}$$
$$=\lim_{r_k\to\infty}\left[\frac{H'(r_k)-E+E^{(0)}}{V(r_k)-E_k^{(0)}}\right]\lim_{r_k\to\infty}\chi(r_k)$$
$$=\left[\frac{E-E^{(0)}}{E_k^{(0)}}\right]\lim_{r_k\to\infty}\chi(r_k)\tag{48}$$

for $r_k\geq r_l;\ i=1,2,\cdots$. This equation can be satisfied if and only if

$$\lim_{r_k\to\infty}\sum\chi^{(i)}(r_k)=\lim_{r_k\to\infty}\chi(r_k)=0,\quad\text{for}\quad r_k\geq r_l;\ i=1,2,\cdots,\tag{49}$$

since $[E-E^{(0)}]/E_k^{(0)}\neq 1$. Combining this with Eqs.(13) and (4) we assert that the convergence of the perturbation series at the infinite boundary has been verified analytically. According to Eq.(12), the convergence of the perturbed wavefunctions will lead to the convergence of the energy corrections.

We now take the atom helium with $z=2$ as an example to illustrate the profiles of the radial wavefunctions from the zero-order to the second-order corrections and to prove the boundedness of the perturbed corrections numerically. We plot $\chi^{(0)}(r)$ from Eq.(9), $\chi^{(1)}(r)$ from Eqs.(23) and (17), and $\chi^{(2)}(r)$ from Eqs.(27) and (13) respectively as the solid curve, short dashed curve and long dashed curve as shown in Fig.1, where coordinate r is used instead of r_k, $k=1,2$ without the loss of generality. In this figure we show that all the wavefunctions tend to zero with r increasing to 4 a.u., so they are bounded at the infinite bound-

ary. Therefore, the convergence of perturbation series for the wave function is expectable in the numerical computations.

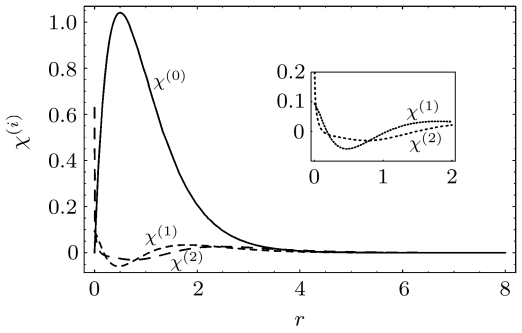


Fig.1. Plots of the profiles of the lower-order wavefunctions in atom units for an atom helium in a ground state. The first-order and the second-order corrections to the wavefunctions are amplified as shown in the inset. The zero-order solution is greater than the perturbed corrections for small values of the coordinate and all the wavefunctions tend to zero with r increasing to 4 a.u..

4. Discussion and conclusions

We well known that for a simple Coulomb system treated by the common Rayleigh–Schrödinger perturbation method[12] 'the square integral of the first approximation to the wavefunction tends to infinity' with increasing the boundary coordinate, and the energy correction is 'incorrect numerically'. Therefore, the corresponding perturbed series of the wavefunction is divergent and the energy series is meaningless. For the atom helium with $1/z$ perturbation expansion only the convergence radius of the perturbation series was found.[32−35] In the previous work,[26,27] we have adopted the improved Rayleigh–Schrödinger perturbation theory based on an integral equation to yield the new forms of the first approximations to the wavefunctions and the second approximations to the energies for perturbation systems, and found that the former are quadratically integrable and the latter are good corrections to the unperturbed energies. However, the convergence of the perturbed series is still a problem which needs to be verified. In order to prove the convergence, we are required to calculate the multi-order approximations and to show their boundedness.

In this work, we have applied the improved Rayleigh–Schrödinger perturbation theory to helium-like ions in ground states and treated the electron correlations as perturbations to obtain the second-order corrections to the wavefunctions and the third-order corrections to the energies. It is shown that the corrected wavefunctions are quadratically integrable and the energy corrections are in good agreement with the experimental data. The boundedness of any order perturbed correction and the convergence of the corresponding perturbation series are proved. The results clear off the previous distrust[12,32−35] of the convergence in the quantum perturbation theory further for the higher-order perturbation case, and show a reciprocal development on the quantum perturbation problem of ground state helium-like systems.

The improved Rayleigh–Schrödinger perturbation method can be applied more widely to various physical fields, for it holds true not only for the non-degenerate quantum systems but also for the degenerate and near degenerate systems[26,27,42] which cannot be correctly treated by the standard quantum perturbation theory usually.

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