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High-order perturbed corrections with scaling transformation*

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The performance of the so-called superconvergent quantum perturbation theory (Wenhua Hai *et al* 2000 *Phys. Rev.* A **61** 052105) is investigated for the case of the ground-state energy of the helium-like ions. The scaling transformation $r \to r/Z$ applied to the Hamiltonian of a two-electron atomic ion with a nuclear charge Z (in atomic units). Using the improved Rayleigh–Schrödinger perturbation theory based on the integral equation to helium-like ions in the ground states and treating the electron correlations as perturbations, we have performed a third-order perturbation calculation and obtained the second-order corrected wavefunctions consisting of a few terms and third-order energy corrections. We find that third-order and higher-order energy corrections are improved with decreasing nuclear charge. This result means that the former is quadratically integrable and the latter is physically meaningful. The improved quantum perturbation theory fits the higher-order perturbation case. This work shows that it is a development on the quantum perturbation problem of helium-like systems.

Keywords: integral equation, scaling transformation, higher-order perturbation
PACC: 0365, 3165

1. Introduction

Since the Rayleigh–Schrödinger (RS) perturbation theory was first introduced in quantum mechanics,[1] it has had a long and distinguished history as a powerful and versatile approximation method.[2] For a number of reasons, however, the central issue of the convergence properties of the RS perturbation expansions has been customarily ignored in most applications, and thus the foundations of RS convergence theory, although laid early,[3] were not developed[4,5] and extended to quantum mechanics problem until fairly recently.[4−8] In practice, the general convergence theory is cumbersome to apply and has yielded disappointingly poor estimates of the convergence of selected RS perturbation expansions.[4−8] Finally, the earlier application of RS perturbation theory seldom went beyond first or, at most, second order in the eigenvalue because of the computational difficulties of evaluating the infinite summations which appear in the conventional for the higher-order terms, but for such lower-order expansions the question of perturbation convergence is hardly acute. Hyllerass–Scherr–Knight (HSK)[9−11] developed a variational-perturbation procedure which opened the door to higher-order RS perturbation expansions for both ground states and excited states.[12] There have been many papers[9−22] for the RS $1/Z$ hydrogenic expansions of the nonrelativistic electronic states of N-electron atomic isoelectronic sequences, such as $1/Z$ expansions initially obtained to lower order[10,13−16] and quite higher order[11,17] for the ground states and several excited states of N=2, 3, 4 sequences.[17−21] In view of the $1/Z$ hydrogenic expansions and their considerable advantages[23] over other types of RS expansions for atomic isoelectronic sequences, the question of their perturbation convergence has become an important issue. Recently pessimistic theoretical predictions for N=3 sequence[6] have suggested divergence of the $1/Z$ expansions for the low-lying states for all Z of interest. Further, in the HSK calculation for the N=4 sequences,[22] it was found that the $1/Z$ eigenvalue expansions for the states $1s^2 2s^2\,{}^1S$, $1s^2 2s2p\,{}^1P$ and $1s^2 2p^2\,{}^1S$ diverged for $Z < 5$. Such divergence

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may be an artifact of the calculations. Though in RS perturbation theory there has been the divergence problem, in other approximation methods the problem exists also. However, for the most physically interesting systems the Schrödinger equations are not exactly soluble,[24] hence some approximation methods, such as the semi-classical approximation, variational method and Rayleigh–Schrödinger quantum perturbation theory, have been developed. In many cases a system of interest differs from an exactly soluble system by only a small disturbance, so that the first-order and second-order perturbed solutions are in good agreement with the corresponding experimental results. Therefore, the quantum perturbation theory has been applied widely to various physical systems.[25−31] But a divergence difficulty of the perturbed series solutions exists in quantum mechanics and quantum field theory as shown in Refs.[32]–[40]. Particularly, in the standard quantum perturbation theory, the infinite square integrals of the corrected wavefunctions appear in calculations for the higher-order perturbed corrections of the Coulomb systems.[32,41,42] Tremendous effort has been devoted to improve the quantum perturbation techniques for different systems.[41−53] For the atom helium and helium-like ion systems, the $1/Z$ perturbation expansion has long been used in calculations of the energy and state corrections, and the convergence radius of the perturbation series was found.[9,54−56]

Recently Hai *et al*[51] advanced an improved Rayleigh–Schrödinger perturbation method based on an integral equation for suppressing the divergences and numerical instabilities in nonrelativistic quantum mechanics, and proved that an integral equation is equivalent to the Schrödinger equations and some boundary conditions of wavefunctions. Using the equation and conditions, they found that the divergences in the pervious perturbation theory originate from expanding the corrected wavefunctions in Hilbert space. Using the integral equation can produce the convergence Rayleigh series. In order to test the validity of the Rayleigh–Schrödinger perturbation theory for the Coulomb systems, it is necessary and important that we investigated the third-order perturbed corrections of the helium-like ion systems by using the improved Rayleigh–Schrödinger perturbation method. In this paper, the scaling transformation $r \to r/Z$ is applied to the Hamiltonian of a two-electron atomic ion with a nuclear charge Z (in atomic units). Applying the improved RS perturbation theory based on integral equation to helium-like ions in the ground-states and treating the electron correlations as perturbations, we have computed the second-order corrected wavefunctions and third-order energy corrections in the ground states of helium-like ions, and have obtained the quadratically integrable corrected states consisting of a few terms and the rational energy corrections. The results clear off the previous distrust[24,32] to the quantum perturbation theory further for the higher-order perturbation case and shows a reciprocal development on the quantum perturbation problem in the ground states of helium-like systems.

2. Scaling transformation and second-order perturbation

In atomic units, the Schrödinger equation governing the helium-like ions 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 and second electrons are labelled by the subscripts 1 and 2; $1/r_{12}$ is the electron–electron interaction and z is the number of nucleus charge. For the Hamiltonian of a two-electron atomic ion with a nuclear charge Z, using the scaling transformation $r \to r/Z$, this yields the scaled Hamiltonian

$$Z^2\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{zr_{12}}\right). \quad (2)$$

Hence RS perturbation theory can be applied to the Hamiltonian by the unperturbed Hamiltonian

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2}; \quad (3)$$

the perturbation Hamiltonian reads

$$H' = \frac{1}{Zr_{12}}. \quad (4)$$

An eigenvalue $E(1/Z)$ and an eigenfunction $\psi(1/Z)$ of $H = H_0 + H'$ can be expressed as power series in $1/Z$

$$E\left(\frac{1}{Z}\right) = \sum_{n=0}^{\infty}\frac{E_n}{Z^n}, \quad \psi\left(\frac{1}{Z}\right) = \sum_{n=0}^{\infty}\frac{\psi_n}{Z^n}. \quad (5)$$

Kato[6] proved that these series have a nonzero radius of convergence.

We only consider the ground states of helium-like ions with main quantum number $n = 1$ and angular one $l = 0$. Using the improved Rayleigh–Schrödinger perturbation theory,[51] we take the electron–electron

interaction as perturbation Hamiltonian H' and make use of the expansion formulae.[57−58] When $r_1 \leq r_2$

$$H'(r_1, r_2) = \frac{1}{Zr_2} \sum_{l=0}^{\infty} \left(\frac{r_1}{r_2}\right)^l p_l(\cos\theta_{12}) = \frac{1}{Zr_2}. \quad (6)$$

When $r_2 \leq r_1$

$$H'(r_1, r_2) = \frac{1}{Zr_1} \sum_{l=0}^{\infty} \left(\frac{r_2}{r_1}\right)^l p_l(\cos\theta_{12}) = \frac{1}{Zr_1}. \quad (7)$$

Setting the radial wavefunction in the form

$$\psi(r_1, r_2) = \frac{\chi(r_1, r_2)}{r_1 r_2}, \quad (8)$$

the ground state energy and normalized wavefunction of the unperturbed electrons have the forms

$$\begin{aligned} E_k^{(0)} =& -\frac{1}{2n^2}, \chi^{(0)}(r_1, r_2) \\ =& \chi^{(0)}(r_1)\chi^{(0)}(r_2), \end{aligned} \quad (9)$$

$$\begin{aligned} \chi^{(0)}(r_k) =& 2r_k \mathrm{e}^{-r_k}, \tilde{\chi}^{(0)}(r_k) \\ =& \chi^{(0)} \int [\chi^{(0)}]^{-2} \mathrm{d}r_k. \end{aligned} \quad (10)$$

Apply the formulae of ith-order perturbation functions $\bar{\chi}^{(i)}(r_{k)}$ and the corrected energies $E^{(i)}$ and ith-order perturbed solution[51]

$$\begin{aligned} \bar{\chi}^{(i)}(r_{k)} =& \tilde{\chi}^{(0)}(r_k) \int_{C_i}^{r_k} \chi^{(0)}(r_k)\varepsilon^{(i)}(r_k)\mathrm{d}r_k \\ & - \chi^{(0)}(r_k) \int_{D_i}^{r_k} \tilde{\chi}^{(0)}(r_k)\varepsilon^{(i)}(r_k)\mathrm{d}r_k; \end{aligned} \quad (11)$$

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

$$\begin{aligned} E^{(i)} =& \int_0^{\infty}\int_0^{\infty} \chi^{(0)}(r_1, r_2)\Big[H'\chi^{(i-1)}(r_1, r_2) \\ & - \sum_{j=1}^{i-1} E^{(j)}\chi^{(i-j)}(r_1, r_2)\Big]\mathrm{d}r_1\mathrm{d}r_2; \end{aligned} \quad (13)$$

$$\begin{aligned} &\chi(r_1, r_2) = \sum_{i=0}^{\infty} \chi^{(i)}(r_1, r_2), \\ &\chi^{(i)}(r_1, r_2) = \begin{cases} \chi^{(0)}(r_1)\chi^{(i)}(r_2), & r_1 \leq r_2, \\ \chi^{(0)}(r_2)\chi^{(i)}(r_1), & r_2 \leq r_1. \end{cases} \end{aligned} \quad (14)$$

It is clear that we can construct any ith-order corrected wavefunction and can obtain any ith-order energy correction. Obviously, for $i = 1$ Eqs.(12) and (13) imply $E^{(1)} = 5/(8Z)$ and $\varepsilon^{(1)}(r_k) = 4Z^{-1}r_k(1/r_k - 5/8)\mathrm{e}^{-r_k}$ for $r_l \leq r_k,\ k, l = 1, 2$. Combining Eqs.(12) with Eqs.(13) and (14) yields the first-order corrected wavefunctions as

$$\begin{aligned} \chi^{(1)}(r_1, r_2) =& \frac{1}{2Z} r_1 r_2 \exp^{-(r_1+r_2)} \\ & \times \left[5r_2 - 3\ln r_2 + \frac{3}{2r_2} + A\right], \\ & r_1 \leq r_2,\ r_2 \neq 0; \end{aligned} \quad (15)$$

$$\begin{aligned} \chi^{(1)}(r_1, r_2) =& \frac{1}{2Z} r_1 r_2 \exp^{-(r_1+r_2)} \\ & \times \left[5r_1 - 3\ln r_1 + \frac{3}{2r_1} + A'\right], \\ & r_1 \geq r_2,\ r_1 \neq 0. \end{aligned} \quad (16)$$

Here $A = A'$ is a normalization constant, and another integral constant being proportional to the unbounded function $\tilde{\chi}^{(0)}(r_k)$ in Eqs.(11) has been taken as zero such that the first-order corrected wavefunction vanishes at the infinite boundary. Applying Eqs.(9), (10), (12) and (14) to the first-order normalization conditions, we have

$$\int_0^{\infty}\int_0^{\infty} \chi^{(0)}(r_1, r_2)\chi^{(1)}(r_1, r_2)\mathrm{d}r_1\mathrm{d}r_2 = 0; \quad (17)$$

the constant A is given as

$$A = -3\mathrm{EulerGamma} - \frac{468}{64} = -9.04415. \quad (18)$$

Inserting Eqs.(9), (15) and (16) into Eqs.(13) produces the second-order corrected energy

$$\begin{aligned} E^{(2)} =& \int_0^{\infty} \mathrm{d}r_2 \Big[\int_0^{r_2} \chi^{(0)}\chi^{(1)}(r_1 \leq r_2) r_2^{-1}\mathrm{d}r_1 \\ & + \int_{r_2}^{\infty} \chi^{(0)}(r_1, r_2)\chi^{(1)}(r_1 \geq r_2) r_1^{-1}\mathrm{d}r_1\Big] \\ =& -\frac{0.0354622}{Z^2} + \frac{0.00608789}{Z^2} - \frac{0.0415501}{Z^2} \\ =& -\frac{0.0709244}{Z^2}, \end{aligned} \quad (19)$$

where second-order energies correction differs with Ref.[51], since we have adopted the more accurate constant A of Eq.(18) and mathematica calculation tools. The total energy of the system with number Z of nucleus charge is

$$\begin{aligned} E =& Z^2(E_1^{(0)} + E_2^{(0)} + E^{(1)} + E^{(2)}) \\ =& -Z^2 + \frac{5Z}{8} - 0.0709244. \end{aligned} \quad (20)$$

3. Third-order perturbation

Given $\chi^{(1)}(r_1,r_2)$ in Eqs.(12) and $E^{(2)}$ in Eqs.(13), we can calculate the second-order corrected wavefunction and the third-order energy correction. Inserting Eqs.(6), (7), (10), (15) and (16) into Eqs.(14), we obtain the perturbation functions

$$\varepsilon^{(2)}(r_2) = \frac{2}{Zr_2}\bar{\chi}^{(1)}(r_2) - 2E^{(1)}\bar{\chi}^{(1)}(r_2) - 2E^{(2)}\bar{\chi}^{(0)}(r_2), \quad r_1 \le r_2; \tag{21}$$

$$\varepsilon^{(2)}(r_1) = \frac{2}{Zr_1}\bar{\chi}^{(1)}(r_1) - 2E^{(1)}\bar{\chi}^{(1)}(r_1) - 2E^{(2)}\bar{\chi}^{(0)}(r_1), \quad r_2 \le r_1. \tag{22}$$

In the case $r_1 \le r_2$, Eqs.(13), (15) and (16) imply

$$\chi^{(0)}(r_2) = 2r_2\mathrm{e}^{-r_2}, \quad \chi^{(0)}(r_1) = 2r_1\mathrm{e}^{-r_1}; \tag{23}$$

$$\bar{\chi}^{(1)}(r_2) = \frac{r_2}{4Z}\mathrm{e}^{-r_2}\left[5r_2 - 3\ln r_2 + \frac{3}{2r_2} + A\right]. \tag{24}$$

Substituting them into Eqs.(12) yields

$$\varepsilon^{(2)}(r_2) = \frac{1}{4Z^2}\chi^{(0)}(r_2)\left[m_1r_2 + m_2 + \frac{m_3}{r_2} + \frac{m_4}{r_2^2} + m_5\ln(r_2) + \frac{m_6\ln r_2}{r_2}\right], \tag{25}$$

where $m_1 = -\frac{25}{8}$, $m_2 = 5 - \frac{5A}{8} - 8E^{(2)}$, $m_3 = A - \frac{15}{16z}$, $m_4 = \frac{3}{2}$, $m_5 = \frac{15}{8}$, $m_6 = -3$ are constants. Similarly, for $r_1 \ge r_2$ from Eqs.(6), (9), (11) and (19) we obtain

$$\bar{\chi}^{(1)}(r_1) = \frac{1}{4Z}r_1\exp^{-r_1}\left[5r_1 - 3\ln r_1 + \frac{3}{2r_1} + A\right] \tag{26}$$

$$\varepsilon^{(2)}(r_1) = \frac{1}{4Z^2}\chi^{(0)}(r_1)\left[m_1r_1 + m_2 + \frac{m_3}{r_1} + \frac{m_4}{r_1^2} + m_5\ln r_1 + \frac{m_6\ln r_2}{r_1}\right]. \tag{27}$$

Inserting Eq.(22) into Eq.(11) then into Eqs.(14), we obtain the second-order corrected wavefunction

$$\chi^{(2)}(r_1 \le r_2) = \frac{\chi^{(0)}(r_1,r_2)}{16Z^2}\left[n_1r_2^2 + n_2r_2 + B + \frac{n_3}{r_2} + n_4\ln r_2 + n_5r_2\ln r_2 + \frac{n_6}{r_2}\ln r_2 + n_7(\ln r_2)^2\right], \tag{28}$$

where B is a normalization constant, another integral constant has been taken as zero such that the second-order wavefunction vanishes at the infinite boundary. The coefficients n_i read $n_1 = -m_1$, $n_2 = -(3m_1 + 2m_2 + 2m_5)$, $n_3 = \frac{3m_1}{2} + m_2 + m_3 + 2m_4 + \frac{5m_5}{2} + 2m_6$, $n_4 = -(3m_1 + 2m_2 + 2m_3 + m_5)$, $n_5 = -2m_5$, $n_6 = m_5 + m_6$, $n_7 = -n_6$. Similarly, in the case $r_1 \ge r_2$, the second-order corrected wavefunction reads

$$\chi^{(2)}(r_1 \ge r_2) = \frac{\chi^{(0)}(r_1,r_2)}{16Z^2}\left[n_1r_1^2 + n_2r_1 + B' + \frac{n_3}{r_1} + n_4\ln r_1 + n_5r_1\ln r_1 + \frac{n_6}{r_1}\ln r_1 + n_7(\ln r_1)^2\right]. \tag{29}$$

The normalization constant $B = B'$ is computed by the second-order normalization condition

$$\begin{aligned}
&\int_0^\infty\int_0^\infty [2\chi^{(0)}(r_1,r_2)\chi^{(2)}(r_1,r_2) + \chi^{(1)}(r_1,r_2)\chi^{(1)}(r_1,r_2)]\mathrm{d}r_1\mathrm{d}r_2 \\
=&2\int_0^\infty \mathrm{d}r_2\left[\int_0^{r_2}\chi^{(0)}(r_1,r_2)\chi^{(2)}(r_1\le r_2)\mathrm{d}r_1 + \int_{r_2}^\infty \chi^{(0)}(r_1,r_2)\chi^{(2)}(r_1\ge r_2)\mathrm{d}r_1\right] \\
&+\int_0^\infty\left[\int_0^{r_2}\chi^{(1)}(r_1\le r_2)\chi^{(1)}(r_1\le r_2)\mathrm{d}r_1 + \int_{r_2}^\infty \chi^{(1)}(r_2\ge r_1)\chi^{(1)}(r_2\ge r_1)\mathrm{d}r_1\right]\mathrm{d}r_2 \\
=&2(G_1+G_2) + G_3 + G_4 = 0,
\end{aligned} \tag{30}$$

$$G_1 + G_2 = \frac{(0.0625B - 1.214175 + C_1 + C_2)}{Z^3}, \tag{31}$$

$$G_3 + G_4 = \frac{(0.144697 + C_3 + C_4)}{Z^2}, \tag{32}$$

where B is the undetermined normalization constant, C_i are constants given by the integrations

$$C_1 = \int_0^\infty \frac{n_7r^2}{Z^2}\mathrm{e}^{-2r}\left[\int_1^\infty r^2(\ln r)^2\mathrm{e}^{-2r}\mathrm{d}r\right]\mathrm{d}r, \tag{33}$$

$$C_2 = \int_0^\infty \frac{n_7r^2\mathrm{e}^{-2r}}{Z_2}\{\mathrm{Simpson}[f(x),x,r,1,20]\}\mathrm{d}r, \tag{34}$$

$$C_3 = \int_0^\infty \frac{9r^2\mathrm{e}^{-2r}}{4Z^2}\left[\int_1^\infty r^2(\ln r)^2\mathrm{e}^{-2r}\mathrm{d}r\right]\mathrm{d}r, \tag{35}$$

$$C_4 = \int_0^\infty \frac{9r^2\mathrm{e}^{-2r}}{4Z^2}\{\mathrm{Simpson}[f(x),x,r,1,20]\}\mathrm{d}r. \tag{36}$$

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

$\int_r^1 r^2(\ln r)^2 \mathrm{e}^{-2r}\mathrm{d}r$ is numerically approximated by the Simpson's formula

$$\begin{aligned}\int_r^1 f(x)\mathrm{d}x \approx &\mathrm{Simpson}[f(x),x,r,1,n]\\ =&\frac{1-r}{3n}\Bigg[f(x_0)+4\sum_{k=1,3,5,\ldots}^{n-1} f(x_k)\\ &+2\sum_{m=2,4,6,\ldots}^{n-2} f(x_m)+f(x_n)\Bigg],\end{aligned} \tag{37}$$

where $f(x)=x^2(\ln x)^2\mathrm{e}^{-2x}$, $n=20$. Equations (27)–(34) give the numerical integration values C_i and normalization constant

$$B=17.6598. \tag{38}$$

The substitution of Eqs.(26) and (27) with the given normalization constants into Eqs.(13), the third-order energy becomes

$$\begin{aligned}E^{(3)}=&\int_0^\infty\int_0^\infty \chi^{(0)}(r_1,r_2)[(H'(r_1,r_2)\\ &-E^{(1)})\chi^{(2)}(r_1,r_2)-E^{(2)}\chi^{(1)}(r_1,r_2)]\mathrm{d}r_1\mathrm{d}r_2\\ =&\int_0^\infty\int_0^\infty \chi^{(0)}(r_1,r_2)H'\chi^{(2)}(r_1,r_2)\mathrm{d}r_1\mathrm{d}r_2\\ &-E^{(1)}\int_0^\infty\int_0^\infty \chi^{(0)}\chi^{(2)}(r_1,r_2)\mathrm{d}r_1\mathrm{d}r_2\\ =&G_5+G_6-E^{(1)}(G_1+G_2),\end{aligned} \tag{39}$$

where G_1+G_2 is given by Eqs.(33), (35) and (36),

$$G_5+G_6=\frac{-0.7823285+0.0390625B+C_5+C_6}{z^3}, \tag{40}$$

$$C_5=\int_0^\infty \frac{n_7 r^2\mathrm{e}^{-2r}}{Z^3}\left[\int_1^\infty r(\ln r)^2\mathrm{e}^{-2r}\mathrm{d}r\right]\mathrm{d}r, \tag{41}$$

$$C_6=\int_0^\infty \frac{n_7 r^2\mathrm{e}^{-2r}}{Z^3}\{\mathrm{Simpson}[g(x),x,r,1,20]\}\mathrm{d}r, \tag{42}$$

with function $g(x)=x(\ln x)^2\mathrm{e}^{-2x}$ and Simpson $[g(x),x,r,1,20]$ obeying Eqs.(34); the calculations from Eqs.(34)–(39) give the third-order energy correction as

$$E^{(3)}=-\frac{0.027225}{Z^3}. \tag{43}$$

The total energies for helium-like ions are given by

$$\begin{aligned}E=&Z^2(E_1^{(0)}+E_2^{(0)}+E^{(1)}+E^{(2)}+E^{(3)})\\ =&-z^2+\frac{5z}{8}-0.0709244-\frac{0.027225}{Z}.\end{aligned} \tag{44}$$

The calculated results of the total energies E, second-order and third-order energy corrections $E^{(2)}$, $E^{(3)}$ are listed in Table 1, where E_{ex} denotes the experimental energy values of the helium-like ions in the ground states.[59] Comparisons between the theoretical energies E and experimental energies E_{ex} show good agreement.

Table 1. The energies of helium-like ions in ground states (a.u.).

z	$E^{(2)}$	$E^{(3)}$	E	E_{ex}
2	–0.0709244	–0.0136125	–2.83453690	–2.90378
3	–0.0709244	–0.0090750	–7.20499940	–7.28041
4	–0.0709244	–0.0068063	–13.5777307	–13.65744
5	–0.0709244	–0.0054450	–21.9513694	–22.03603
6	–0.0709244	–0.0045375	–32.3254619	–32.41733
7	–0.0709244	–0.0038893	–44.6998137	–44.80351
8	–0.0709244	–0.00340313	–59.0743275	–59.19580

4. Results and discussion

In the preceding section, the scaling transformation $r\to r/Z$ applied to the Hamiltonian of a two-electron atomic ion with a nuclear charge Z (in atomic units), and the nonrelativistic quantum perturbation theory based on integral equation is used. We constructed the convergence Rayleigh series of the wavefunction, and also we obtain the quadratically integrable corrected states consisting of a few terms and the rational energy corrections. The second-order corrected wavefunctions and third-order energy corrections of the helium-like ions in ground state are performed. Comparison between the improved quantum theory and standard quantum theories for the formulas of energy corrections shows that only the first-order correction energy given by them is certainly the same. This means that some high-order results are mathematically unbounded, which leads to the divergence of the Rayleigh series in the previous quantum perturbation theory. Because Rayleigh series are diverged, it is very difficult to calculate the ith-order ($i\geq 3$) perturbed corrections for such systems, only

the first-order and second-order energy corrections are investigated. In order to test the validity of Rayleigh–Schrödinger perturbation theory for the Coulomb systems, it is necessary and important that we investigate the third-order perturbed corrections of the helium-like ions in the ground states.

The second-order energy correction is -0.0709244, the integral constant of first-order and second-order correction wavefunctions are $A = -9.04415$, $B = 17.6598$ in this work. We found that the normalization constants A, B and the second-order correction energies of the helium atom and helium-like ions are not changed with the number of charges in helium atom and helium-like ions. The third-order correction energies are $-\dfrac{0.027225}{Z}$, they are changed with the number of charges in helium atom and helium-like ions, and the third-order and high-order energy corrections are improved with decreasing nuclear charge Z as showed in Table 1.

Particularly, in the standard quantum perturbation theory, the infinite square integrals of the corrected wavefunctions appear in calculations for the higher-order perturbed corrections of the Coulomb systems. We used the improved quantum perturbation techniques for different systems, and calculated third-order correction energies and second-order correction wavefunctions. Hyllerass[9] developed a variational-perturbation procedure to calculate numerically the coefficients E_n, E_1 is the first-order perturbation correction ($5/8 = 0.625$) and the higher E_n cannot be of closed form; using eight basis functions, he found $E_2 = -0.15744$a.u., $E_3 = 0.00876$a.u., $E_4 = -0.00274$a.u. We found that the results of third-order correction energies are of positive value in Refs.[9, 54, 55], though they obtained the radius of convergence, but the key problems are still divergences.[55] In this work we have obtained the values of third-order correction energies, which are negative, and the fourth-order, fifth-order... correction energies are also negative ones. The result is in good agrement with the experimental values. Because we used the improved quantum perturbation theory without divergences,[51,60] all correction wavefunctions are converged. We have proved the convergence of the corrected wavefunction of the helium-like ion in ground states recently.[60] The zeroth-order wavefunction, the first-order and second-order correction wavefunctions are shown in Fig.1.

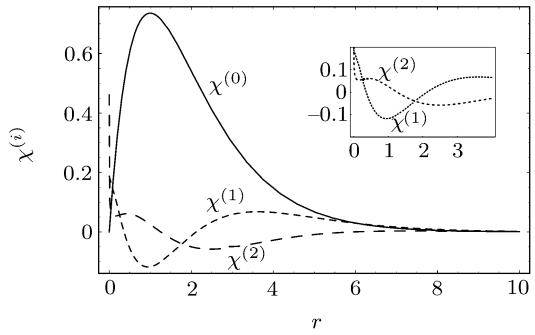


Fig.1. When Z=2, in atom units. Plots of the profiles of the lower-order wavefunction for atom helium in ground state, the first-order and second-order correction wavefunctions are amplified as in the insert. The zero-order solution is greater than the perturbation corrections for small values of the coordinate and all the wavefunctions tend to zero with r increasing 7a.u.

It is a very difficult divergence problem in the standard quantum perturbation theories. Using the improving quantum perturbation theories, the third-order and high-order perturbations are solved, all correction wavefunctions are convergent. We have calculated the second-order and third-order perturbations for the two-electron ground-state nonrelativistic energies of the helium-like ions. Based on the results, we can obtain the fourth-order perturbed corrections of the systems easily. The improving quantum perturbation method can be valid for the degenerate and near-degenerate cases, and may be widely applicable.

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