Alternative quantum perturbation theory without divergences

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A different integral form of the Schrödinger equation and some boundedness conditions of the wave functions are proved, which exhibit the origin of some divergences in quantum mechanics. The iterations from the integral equation and the boundedness conditions lead to a method for avoiding the divergence difficulties. The result is extended to the time-dependent and the multidimensional cases. Examples of an electron in the Wigner spherical ''box'' with a $1/r$ perturbed potential, some heliumlike ions in the ground state, and the Stark effect of the hydrogen atom show that this different perturbation method can give rational multiorder corrections of the wave function and energy.

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I. INTRODUCTION

In quantum mechanics the states of a microscopic system are described by the wave functions and the latter are governed by the Schrödinger equation. Therefore, solving the Schrödinger equation is the most important task of this subject. However, this equation is not exactly soluble for the most physically interesting systems, except a few systems such as the hydrogen atom, harmonic oscillator, and rigid rotator [1–3]. For applicable purposes the quantum perturbation theories were established and developed [4–7]. In many cases the system of interest differs from an exactly soluble system by only a small disturbance, enabling an approximation to be made by the Rayleigh-Schrödinger expansions

$$\psi=\psi_k=\sum_{i=0}^{\infty}\psi_k^{(i)},$$

$$E=E_k=\sum_{i=0}^{\infty}E_k^{(i)}\quad\text{for}\ \ |\psi_k^{(i)}|\ll|\psi_k^{(i-1)}|,\tag{1}$$

$$|E_k^{(i)}|\ll|E_k^{(i-1)}|,$$

where ψ and E are the wave function and energy with the quantum number k. The expansions change the perturbed Schrödinger equation

$$\frac{1}{2}\psi_{xx}-[V(x)-E]\psi=H'(x)\psi\tag{2}$$

with potential $V(x)$ and perturbed potential $H'(x)$ into a set of nonhomogeneous ones,

$$\frac{1}{2}\psi_{k,xx}^{(i)}-[V(x)-E_k^{(0)}]\psi_k^{(i)}=\varepsilon_k^{(i)},\quad\text{for}\ \ i=0,1,2,\ldots,\infty,$$

$$\varepsilon_k^{(0)}=0,$$

$$\varepsilon_k^{(i)}=H'(x)\psi_k^{(i-1)}-\sum_{j=1}^{i}E_k^{(j)}\psi_k^{(i-j)}\quad\text{for}\ \ i=1,2,\ldots,\infty,\tag{3}$$

with $E_k^{(0)}$ being the energy eigenvalues associated with the eigenfunctions $\psi_k^{(0)}$. Equations (3) are some nonhomogeneous equations with the nonhomogeneous terms $\varepsilon_k^{(i)}$ for $i=1,2,\ldots,\infty$. The corresponding homogeneous equation is just the zeroth-order unperturbed Schrödinger equation for any i. Here the atomic unit has been adopted such that $\hbar=\mu=e=1$. Unfortunately, Eqs. (3) still are not exactly soluble for many interesting systems. Suppose that the energy eigenfunctions $\psi_k^{(0)}$ of the unperturbed equation form a complete orthonormal set in Hilbert space. The previous perturbation theories had to expand the wave function $\psi_k^{(i)}$ in terms of $\psi_k^{(0)}$ for $i,k=1,2,\ldots$. But the recent [8] and previous [9–12] works on quantum theory have shown that the Rayleigh series (1) diverges for most practically disturbed potentials in Hilbert space. This may lead to an infinite square integral of the corrected wave function. The divergence difficulties have puzzled many physicists for 60 years [8–13]. Although some large order perturbation theories for improving the results were presented [14–17], the genuine cause of the previous divergences is still not found in these works.

Recently, we gave a method for exactly solving the nonhomogeneous Schrödinger equations (3) and used the exact solutions to obtain the convergent Rayleigh series [18] and scattering amplitudes [19]. In this paper we will prove an integral equation equivalent to the Schrödinger one and some boundedness conditions of the wave function. Using the equation and conditions, we find that the divergences in the previous perturbation theory originate from expanding the corrected wave functions in Hilbert space. Avoiding the Hilbert space or using it under the boundedness conditions and making iterations from the integral equation can produce the convergent Rayleigh series. We will also extend the result to

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the time-dependent and the multidimensional systems and show that the method can be applied to degenerate and near degenerate cases. For examples we calculate the second-order energy corrections of an electron in the Wigner spherical ''box'' with a $1/r$ perturbed potential and some helium-like ions in the ground state and discuss the Stark effect of the hydrogen atom. The results show that our perturbation method can give rational multiorder perturbation results.

II. QUANTUM PERTURBATION OF THE ONE-DIMENSIONAL SYSTEMS

We have known that the function $\psi_k^{(0)}$ is a solution of the unperturbed Schrödinger equation associated with energy eigenvalue $E_k^{(0)}$. Given this solution, we construct another solution of the equation by $\tilde{\psi}_k^{(0)}=\psi_k^{(0)}\int(\psi_k^{(0)})^{-2}dx$. Making use of the two linearly independent solutions, we can easily prove that the integral equation

$$\psi=\psi_k^{(0)}+2\tilde{\psi}_k^{(0)}\int_A^x\psi_k^{(0)}(H'-E+E_k^{(0)})\psi dx -2\psi_k^{(0)}\int_B^x\tilde{\psi}_k^{(0)}(H'-E+E_k^{(0)})\psi dx \tag{4}$$

is completely equivalent to the Schrödinger one (2). Here A and B are arbitrary constants determined by the normalization and boundary conditions. From Eq. (4) we perform the calculations

$$\psi_x=\psi_{k,x}^{(0)}+2\tilde{\psi}_{k,x}^{(0)}\int_A^x\psi_k^{(0)}(H'-E+E_k^{(0)})\psi dx -2\psi_{k,x}^{(0)}\int_B^x\tilde{\psi}_k^{(0)}(H'-E+E_k^{(0)})\psi dx,$$

$$\begin{aligned}\psi_{xx}&=\psi_{k,xx}^{(0)}+2\tilde{\psi}_{k,xx}^{(0)}\int_A^x\psi_k^{(0)}(H'-E+E_k^{(0)})\psi dx-2\psi_{k,xx}^{(0)}\\&\quad\times\int_B^x\tilde{\psi}_k^{(0)}(H'-E+E_k^{(0)})\psi dx+2(\tilde{\psi}_{k,x}^{(0)}\psi_k^{(0)}\\&\quad-\psi_{k,x}^{(0)}\tilde{\psi}_k^{(0)})(H'-E+E_k^{(0)})\psi\\&=2[V(x)-E_k^{(0)}]\psi+2(H'-E+E_k^{(0)})\psi\\&=2[V(x)+H'(x)-E]\psi.\end{aligned}$$

This is just Eq. (2), as our assertion. As in Eq. (4), the general solution of the second-order ordinary differential equation (2) also contains two arbitrary constants. So the integral equation (4) is completely equivalent to the Schrödinger one (2).

Assume that the initial state is a bound state such that $\psi_k^{(0)}$ and $\psi_{k,x}^{(0)}$ vanish at the boundary points $x\to\pm\infty$. Then $\tilde{\psi}_k^{(0)}$ tends to infinity at the boundaries and does not represent any physical state. Inserting such an unbounded function into Eq. (4) shows that its solution is bounded if and only if the conditions

$$P_{\pm}(A)=\lim_{x\to\pm\infty}\int_A^x\psi_k^{(0)}(H'-E+E_k^{(0)})\psi dx=0 \tag{5}$$

are satisfied. Given Eq. (5), we can apply the l'Hospital rule to Eq. (4) producing the limit

$$\begin{aligned}\lim_{x\to\pm\infty}\psi&=\lim_{x\to\pm\infty}\left[2(H'-E+E_k^{(0)})\left(\frac{\psi_k^{(0)}\psi}{[(\tilde{\psi}_k^{(0)})^{-1}]_x}-\frac{\tilde{\psi}_k^{(0)}\psi}{[(\psi_k^{(0)})^{-1}]_x}\right)\right]\\&=2\lim_{x\to\pm\infty}[(H'-E+E_k^{(0)})\psi]\lim_{x\to\pm\infty}\left[\frac{(\psi_k^{(0)})^2\tilde{\psi}_k^{(0)}}{\psi_{k,x}^{(0)}}-\frac{(\tilde{\psi}_k^{(0)})^2\psi_k^{(0)}}{\tilde{\psi}_{k,x}^{(0)}}\right]\\&=2\lim_{x\to\pm\infty}[(H'-E+E_k^{(0)})\psi]\lim_{x\to\pm\infty}\left[\frac{\psi_k^{(0)}\tilde{\psi}_k^{(0)}}{\psi_{k,x}^{(0)}\tilde{\psi}_{k,x}^{(0)}}(\psi_k^{(0)}\tilde{\psi}_{k,x}^{(0)}-\psi_{k,x}^{(0)}\tilde{\psi}_k^{(0)})\right]\\&=2\lim_{x\to\pm\infty}[(H'-E+E_k^{(0)})\psi]\lim_{x\to\pm\infty}\left[\frac{\psi_k^{(0)}\tilde{\psi}_k^{(0)}}{\psi_{k,x}^{(0)}\tilde{\psi}_{k,x}^{(0)}}\right]\\&=2\lim_{x\to\pm\infty}[(H'-E+E_k^{(0)})\psi]\lim_{x\to\pm\infty}\left[\frac{\psi_k^{(0)}\tilde{\psi}_{k,x}^{(0)}+\tilde{\psi}_k^{(0)}\psi_{k,x}^{(0)}}{\psi_{k,xx}^{(0)}\tilde{\psi}_{k,x}^{(0)}+\psi_{k,x}^{(0)}\tilde{\psi}_{k,xx}^{(0)}}\right]\\&=\lim_{x\to\pm\infty}\left[\frac{H'-E+E_k^{(0)}}{V(x)-E_k^{(0)}}\right]\lim_{x\to\pm\infty}\psi=L\lim_{x\to\pm\infty}\psi,\end{aligned}$$

where

$$L=\lim_{x\to\pm\infty}\left[\frac{(H'-E+E_k^{(0)})}{V(x)-E_k^{(0)}}\right]\neq 1.$$

This equation cannot be satisfied unless $\lim_{x\to\pm\infty}\psi=0$. Thus we have proved the sufficiency of Eq. (5). In the calculation for limit only the second term in Eq. (4) depends on the conditions (5). Without Eq. (5), this term will tend to infinity as $x\to\pm\infty$. This is the proof for the necessity of the conditions.

In order to solve the integral equation (4) and evidence the boundedness conditions (5), we apply the Rayleigh-Schrödinger expansions (1) to Eq. (4) and equate the sum of ith-order terms for both sides, arriving at the ith-order corrected wave functions as

$$\psi_k^{(i)}=2\tilde{\psi}_k^{(0)}\left[A_k^{(i)}+\int_0^x\psi_k^{(0)}\varepsilon_k^{(i)}dx\right]-2\psi_k^{(0)}\left[B_k^{(i)}+\int_0^x\tilde{\psi}_k^{(0)}\varepsilon_k^{(i)}dx\right],\qquad(6)$$

for $i=1,2,\ldots,\infty$, where $A_k^{(i)}$ and $B_k^{(i)}$ are constants associated with the expansions of the constants A and B. Combining Eq. (5) with Eqs. (1) yields the boundedness conditions

$$P_{\pm}^{(i)}(A_k^{(i)})=\lim_{x\to\pm\infty}\left[A_k^{(i)}+\int_0^x\psi_k^{(0)}\varepsilon_k^{(i)}dx\right]=0,\quad i=1,2,\ldots,\infty\qquad(7)$$

of the solutions (6). By applying the l'Hospital rule to Eq. (6) we can readily prove their boundedness under the condition (7). For sufficiently small potential $H'(x)$ and bounded corrections of the wave function, the Rayleigh series (1) will be convergent. Applying the second of Eqs. (3) to (7), from $P_+^{(i)}-P_-^{(i)}=0$ we get

$$E_k^{(i)}=\int_{-\infty}^{\infty}\psi_k^{(0)}\left[H'(x)\psi_k^{(i-1)}-\sum_{j=1}^{i-1}E_k^{(j)}\psi_k^{(i-j)}\right]dx,\quad i=1,2,\ldots,\infty.\qquad(8)$$

These are just the formulas of the corrected energies. The corrected solution (6) is formally a general solution of the perturbed equations (3), which differ from the common solutions of the equations. In previous perturbation theory, the solutions of Eqs. (3) are expanded as

$$\psi_k^{(i)}=\sum_{n=1}^{\infty}a_{kn}^{(i)}\psi_n^{(0)}\quad\text{for}\quad a_{kn}^{(i)}=\text{const},\quad i=1,2,\ldots,\infty\qquad(9)$$

in Hilbert space. When Eqs. (3) are not exactly soluble, any series of Eq. (9) cannot be truncated as finite terms. However, it is impossible to count in infinite terms in any practical calculation. Let $\psi_k'^{(i)}$ be the finite N terms of a series in Eq. (9) for the calculation. It is certainly different from $\psi_k^{(i)}$ with infinite terms so that it may not obey the boundedness condition (7). Thus the unbounded wave functions $\psi_k'^{(i)}$ and infinite energy corrections $E_k^{(i)}$ for $i=1,2,\ldots,\infty$ are produced in the practical calculations. This may lead to the divergence of the Rayleigh series (1) in previous perturbation theory. Our results, the formal solution (6) and boundedness condition (7), have avoided the infinity and divergence. An interesting thing is that the first-order energy correction in Eq. (8) with $i=1$ agrees with the previous result. Particularly, our perturbation method is valid for the degenerate and near degenerate cases, where the previous theory failed. Therefore our method can be applied to a wider area of the scientific investigations.

As a simple example we consider the motion of a single electron in the Wigner spherical "box" with an infinite radius R and a perturbed potential $H'=-1/r$. The unperturbed Schrödinger equation has the spherically symmetric solution [9]

$$\Psi_n^{(0)}=\sin(\alpha_n r)/(Cr),\quad n=1,2,\ldots\qquad(10)$$

for the energy eigenvalues $E_n^{(0)}=\alpha_n^2/2$ and constant C. The orthonormalization conditions require that

$$\alpha_n R=n\pi,\quad C^2=2\pi R,\quad E_n^{(0)}=\alpha_n^2/2\to 0\quad\text{as}\quad R\to\infty.\qquad(11)$$

Setting $\Psi_n^{(i)}=\psi_n^{(i)}(r)/r$ for $i=0,1,2,\ldots$, then $\psi_n^{(i)}$ obey the nonhomogeneous equations (3) with the formally general solution (6) and $x\to r$, where

$$\psi_n^{(0)}=\sin(\alpha_n r)/C,$$

$$\tilde{\psi}_n^{(0)}=\psi_n^{(0)}\int(\psi_n^{(0)})^{-2}dx=-C\cos(\alpha_n r)/\alpha_n.\qquad(12)$$

Substituting Eqs. (12) into Eq. (6) arrives at the ith-order corrected wave functions

$$\Psi_n^{(i)}=\frac{\psi_n^{(i)}(r)}{r}=\frac{2}{\alpha_n r}\left[\sin(\alpha_n r)\left(B_n^{(i)}+\int_0^r\cos(\alpha_n r)\varepsilon_n^{(i)}dr\right)-\cos(\alpha_n r)\left(A_n^{(i)}+\int_0^r\sin(\alpha_n r)\varepsilon_n^{(i)}dr\right)\right]\qquad(13)$$

with $\varepsilon_n^{(i)}$ given by Eqs. (3) for $i=1,2,\ldots$. The boundary conditions

$$\lim_{r\to 0}\Psi_n^{(i)}=\text{finite value},\qquad\lim_{\alpha_n r\to\alpha_n R=n\pi}\Psi_n^{(i)}=0$$

imply that

$$\int_0^R\sin(\alpha_n r)\varepsilon_n^{(i)}dr/C=\int_0^R\psi_n^{(0)}\varepsilon_n^{(i)}dr=0,$$

$$A_n^{(i)}=0\quad\text{for}\quad\alpha_n R=n\pi,\qquad(14)$$

TABLE I. The possible energies of an electron in the $-1/r$ potential (atomic units).

n	1	2	3	4	5	6	7	8	9	10
$-B_n^{(1)}$	1.09704	0.99391	0.94556	0.91737	0.89765	0.88377	0.87321	0.86489	0.85813	0.85253
$-E_n^c$	0.50000	0.12500	0.05556	0.03125	0.02000	0.01389	0.01020	0.00781	0.00617	0.00500
$-E_n^{(2)}$	0.41051	0.17998	0.10544	0.07071	0.05142	0.03940	0.03135	0.02566	0.02147	0.01828
$\Delta E_n^{(2)}$	0.08949	0.05498	0.04988	0.03946	0.03142	0.02552	0.02115	0.01785	0.01530	0.01328

which agrees with Eqs. (7) and (8). Obviously, the first-order energy vanishes for the infinite R. Applying $A_n^{(1)}=0$, $E_n^{(1)}=0$, Eqs. (10), (13), and (3) with $i=1$ to the normalization condition yields

$$\begin{aligned}0=&\lim_{\alpha_n R\to n\pi}\int_0^R \Psi_n^{(0)}\Psi_n^{(1)}4\pi r^2 dr\\ =&\frac{8\pi}{\alpha_n C^2}\int_0^{n\pi}\sin\rho\bigg[\cos\rho\int_0^\rho \sin^2\rho'\frac{d\rho'}{\rho'}\\ &-\sin\rho\left(B_n^{(1)}+\int_0^\rho\cos\rho'\sin\rho'\frac{d\rho'}{\rho'}\right)\bigg]d\rho \qquad (15)\end{aligned}$$

in the first approximation for $n=1,2,\ldots,$ where the transformation $\rho=\alpha_n r$ has been used. These conditions give the constants $B_n^{(1)}$ as Table I. Inserting Eqs. (10), (11), (13), and (3) with $i=2$ into Eqs. (14) leads to the second-order corrections

$$\begin{aligned}E_n^{(2)}=&\lim_{\alpha_n R\to n\pi}\int_0^R \Psi_n^{(0)}H'(r)\Psi_n^{(1)}4\pi r^2 dr\\ =&\frac{4}{n\pi}\int_0^{n\pi}\sin\rho\bigg[\sin\rho\left(B_n^{(1)}+\int_0^\rho\cos\rho'\sin\rho'\frac{d\rho'}{\rho'}\right)\\ &-\cos\rho\int_0^\rho\sin^2\rho'\frac{d\rho'}{\rho'}\bigg]\frac{d\rho}{\rho} \qquad (16)\end{aligned}$$

of energy. Given $B_n^{(1)}$ by Eq. (15), from Eq. (16) the second corrected energies are evaluated numerically in Table I. The correct energy values of the system should be $E_n^c=-1/(2n^2)$, which are also shown in Table I. Setting differences between the correct energy and second energy correction as $\Delta E_n^{(2)}=|E_n^c-E_n^{(2)}|$ for any n, Table I shows $\Delta E_n^{(2)}$ being less than $E_n^{(2)}$ such that the result can be improved by the third approximation.

We know that the previous perturbation method used expansion (9) in Hilbert space and gave a meaningless wave function and inaccurate energy value for this instance [9]. Our method has greatly improved the previous result. Our result reveals that the Rayleigh-Schrödinger perturbation expansions (1) are correct, but the expansion (9) in Hilbert space may bring divergences. To overcome the divergences, we have to avoid the expansion (9) and employ the formally general solution (6) or use Eq. (9) under the boundedness condition (7). The Hilbert space is the mathematical foundation of quantum mechanics, which has been queried by the validity by the above results. Further exploration to this problem will be quite interesting.

III. QUANTUM TRANSITIONS IN OUR THEORY

Applying the above-mentioned method to the time-dependent Schrödinger equation

$$\frac{1}{2}\psi_{xx}-V(x)\psi=H'(x,t)\psi-i\partial\psi/\partial t,\quad H'=0\quad \text{for } t\leqslant t_0, \qquad (17)$$

the corresponding integral form is directly given as

$$\begin{aligned}\psi=&\psi_k^{(0)}(x)\exp(-iE_k^{(0)}t)+2\tilde{\psi}_{k'}^{(0)}(x)\int_A^x\psi_{k'}^{(0)}(x)\\ &\times[H'(x,t)+E_{k'}^{(0)}-i\partial/\partial t]\psi dx-2\psi_{k'}^{(0)}(x)\\ &\times\int_B^x\tilde{\psi}_{k'}^{(0)}(x)[H'(x,t)+E_{k'}^{(0)}-i\partial/\partial t]\psi dx, \qquad (18)\end{aligned}$$

where $\psi_k^{(0)}(x)$ and $\psi_{k'}^{(0)}(x)$, respectively, represent the initial and final states associated with $H'=0$, and A and B are two arbitrary constants. Inserting Eq. (18) into Eq. (17) can readily prove the result. As in Eq. (5), the boundedness conditions of Eq. (18) become the differential and integral equations

$$G_{\pm}(A,t)=\lim_{x\to\pm\infty}\int_A^x\psi_{k'}^{(0)}(x)[H'(x,t)+E_{k'}^{(0)}-i\partial/\partial t]\psi dx=0. \qquad (19)$$

When the perturbed potential H' is small, transition amplitude of the system can be easily obtained as follows.

(a) For the case $|E_k^{(0)}-E_{k'}^{(0)}|\gg|H'|$, we make the Rayleigh expansion

$$\psi=\sum_{i=0}\psi_k^{(i)}(x,t)\exp(-iE_k^{(0)}t)$$

$$\text{for } |\psi_k^{(i)}|\ll|\psi_k^{(i-1)}|,\quad \psi_k^{(0)}(x,t)=\psi_k^{(0)}(x) \qquad (20)$$

and substitute Eq. (20) into Eq. (19), obtaining the boundedness conditions

$$\begin{aligned}G_{\pm}^{(i)}(A_i,t)=&\lim_{x\to\pm\infty}\int_{A_i}^x\psi_{k'}^{(0)}(x)[H'(x,t)\psi_k^{(i-1)}\\ &+(E_{k'}^{(0)}-E_k^{(0)}-i\partial/\partial t)\psi_k^{(i)}]dx=0 \qquad (21)\end{aligned}$$

with A_i and B_i being constants corresponding to expansions of the constants A and B for $i=1,2,\ldots,\infty$. From $G_+^{(i)}-G_-^{(i)}=0$ we have the ith-order equations

$$i\partial\overline{\psi}_{k'k}^{(i)}(t)/\partial t-H_{k'k}'^{(i)}(t)-(E_{k'}^{(0)}-E_k^{(0)})\overline{\psi}_{k'k}^{(i)}(t)=0,$$

$$i=1,2,\ldots,\infty,$$

$$\overline{\psi}_{k'k}^{(i)}=\int_{-\infty}^{\infty}\psi_{k'}^{(0)}(x)\psi_k^{(i)}(x,t)dx,$$

$$H_{k'k}'^{(i)}=\int_{-\infty}^{\infty}\psi_{k'}^{(0)}(x)H'(x,t)\psi_k^{(i-1)}(x,t)dx. \tag{22}$$

Integrating Eqs. (22), one easily yields the functions

$$\overline{\psi}_{k'k}^{(i)}=-i\exp[-i(E_{k'}^{(0)}-E_k^{(0)})t]\times\int_{t_0}^{t}H_{k'k}'^{(i)}(t)\exp[i(E_{k'}^{(0)}-E_k^{(0)})t]dt, \tag{23}$$

If we introduce the Hilbert space as in the ordinary quantum mechanics, the function $\overline{\psi}_{k'k}^{(i)}(t)$ in Eqs. (22) is a projection of the solution $\psi_k^{(i)}(x,t)$ to the basis vector $\psi_{k'}^{(0)}(x)$ of the Hilbert space, which is just the ith-order transition amplitude from state k to k' [1–3]. The corresponding transition probability is its norm and the total probability is the sum of the norms. In the first-order approximation, the transition probability reads

$$P_{k'k}^{(1)}=|\overline{\psi}_{k'k}^{(1)}|^2=\left|\int_0^t H_{k'k}'^{(1)}(t)\exp[i(E_{k'}^{(0)}-E_k^{(0)})t]dt\right|^2, \tag{24}$$

which is in complete agreement with the previous result. The new multiorder results, of course, differ from the previous ones. Our results are certainly convergent, since they come from the boundedness conditions (19) and (21). And the previous multiorder results may contain infinity such that the corresponding Rayleigh series diverges.

(b) When $|E_k^{(0)}-E_{k'}^{(0)}|$ is in the order of $|H'(x,t)|$, inserting Eq. (20) into Eqs. (19) gives the boundedness conditions

$$G_\pm^{(i)}(A_i,t)=\lim_{x\to\pm\infty}\int_{A_i}^{x}\psi_{k'}^{(0)}(x)\{[H'(x,t)+E_{k'}^{(0)}-E_k^{(0)}]\psi_k^{(i-1)}-i\partial\psi_k^{(i)}/\partial t\}dx=0 \tag{25}$$

for $i=1,2,\ldots,\infty$. The equation $G_+^{(i)}-G_-^{(i)}=0$ becomes the ith-order ones

$$i\partial\overline{\psi}_{k'k}^{(i)}(x,t)/\partial t-H_{k'k}'^{(i)}(t)-(E_{k'}^{(0)}-E_k^{(0)})\overline{\psi}_{k'k}^{(i-1)}(t)=0,$$

$$i=1,2,\ldots,\infty. \tag{26}$$

Noticing that Eqs. (22) imply $\overline{\psi}_{k'k}^{(0)}=0$, the solutions of Eq. (26) are obviously

$$\overline{\psi}_{k'k}^{(1)}=-i\int_{t_0}^{t}H_{k'k}'^{(1)}(t)dt=-i\int_{t_0}^{t}\int_{-\infty}^{\infty}\psi_{k'}^{(0)}H'(x,t)\psi_k^{(0)}dxdt,$$

$$\overline{\psi}_{k'k}^{(i)}=-i\int_{t_0}^{t}[H_{k'k}'^{(i)}+(E_{k'}^{(0)}-E_k^{(0)})\overline{\psi}_{k'k}^{(i-1)}]dt$$

$$\text{for}\ \ i=2,3,\ldots. \tag{27}$$

The case $|E_k^{(0)}-E_{k'}^{(0)}|\approx|H'|\ll 1$ means near degenerate of the initial and final states. An interesting example of the case is the one-dimensional (1D) hydrogen atom with large quantum numbers $n=k$ and $n+1=k'$ and weak microwave field $H'(x,t)=\alpha x\cos(\omega t)$. This is a typical instance of the quantum chaos [20,21]. The previous quantum perturbation method is invalid for such problems. The above analysis has supplied a useful method for studying the quantum chaos. Making use of the above method in this instance, from Eqs. (27) we find that $\overline{\psi}_{k'k}^{(i)}$ consists of the terms proportional to $[\alpha^j(\Delta E_{k'k}^{(0)})^{i-j}/\omega^i]$ for $\Delta E_{k'k}^{(0)}=|E_k^{(0)}-E_{k'}^{(0)}|$ and $j=1,2,\ldots,i$. The total transition probability from state k to k' therefore reads

$$P_{k'k}=\sum_{i=1}^{\infty}|\overline{\psi}_{k'k}^{(i)}|^2=\sum_{i=1}^{\infty}\left[\sum_{j=1}^{i}b_i(t)\alpha^j(\Delta E_{k'k}^{(0)})^{i-j}/\omega^i\right]^2, \tag{28}$$

where $b_i(t)$ are some periodic functions of time t. Equation (28) denotes a polynomial of α and ω^{-1} that possess many different extreme points on the (α,ω) plane. An important property is that the probability at the resonance frequency $\omega=\Delta E_{k'k}^{(0)}$ may get less than one at $\omega<\Delta E_{k'k}^{(0)}$ for some times. These qualitatively agree with the previous results on the multiphoton ionization and excitation of the hydrogen atom [22]. Further work along this line will give a fully quantum-mechanical explanation to the chaotic behavior of the highly excited atoms and the multiphoton ionization and excitation.

IV. THE CORRESPONDING MULTIDIMENSIONAL RESULTS

Let us extend the above results to spatially three-dimensional (3D) case with the perturbed potential H' being a 3D function. For convenience sake, we take perturbed hydrogen atom as an example to discuss the problem. Adopting the spherical coordinates (r,θ,φ), the Schrödinger equation of the system is

$$\left[\frac{1}{2}\nabla^2+\frac{1}{r}+E\right]\psi=H'(r,\theta,\varphi)\psi. \tag{29}$$

Setting $\psi=r^{-1}\chi(r,\theta,\varphi)$ and inserting it into Eq. (29) yields the equation

$$\frac{\partial^2\chi(r,\theta,\varphi)}{\partial r^2}+\left[2\left(E_n^{(0)}+\frac{1}{r}\right)-\frac{l(l+1)}{r^2}\right]\chi(r,\theta,\varphi)=Q\chi(r,\theta,\varphi), \tag{30a}$$

$$Q=[\hat{L}^2(\theta,\varphi)-l(l+1)]r^{-2}+2[E_n^{(0)}-E+H'(r,\theta,\varphi)], \tag{30b}$$

with the angular momentum operator $\hat{L}$. When the right-hand side of Eq. (30a) is equal to zero, the equation agrees with the unperturbed radial equation, which has the two fundamental solutions, bounded $\chi_{nl}^{(0)}$ and unbounded $\tilde{\chi}_{nl}^{(0)}$,

$$\chi_{nl}^{(0)}(r)=rR_{nl}^{(0)}(r),$$

$$\tilde{\chi}_{nl}^{(0)}(r)=\chi_{nl}^{(0)}\int(\chi_{nl}^{(0)})^{-2}dr=r\tilde{R}_{nl}^{(0)}(r) \tag{31}$$

for the energy eigenvalue $E_n^{(0)}$. The similarity of Eqs. (30) to Eq. (2) leads the integral equation associated with Eqs. (30) to the form of Eq. (4), namely,

$$\chi_{nlm}^{\lambda}=\chi_{nlm}^{\lambda(0)}+\tilde{\chi}_{nl}^{(0)}(r)\int_A^r R_{nl}^{(0)}(r)Q\chi_{nlm}^{\lambda}rdr$$
$$-\chi_{nl}^{(0)}(r)\int_B^r \tilde{R}_{nl}^{(0)}(r)Q\chi_{nlm}^{\lambda}rdr,$$

$$\chi_{nlm}^{\lambda(0)}=\sum_{l'=0}^{n-1}\sum_{m'=-l'}^{l'}a_{l'm'}^{\lambda}r\psi_{nl'm'}^{(0)}(r,\theta,\varphi),$$

$$l=0,1,\ldots,(n-1),\quad m=0,\pm1,\ldots,\pm l, \tag{32}$$

where we have considered the degeneracy of the states and set the initial state $\chi_{nlm}^{\lambda(0)}$ as a linear superposition of $\psi_{nl'm'}^{(0)}(r,\theta,\varphi)$. For fixed principal quantum number n, the λ describes different initial states and A and B are arbitrary boundary constants. The expansion coefficients are thus selected,

$$a_{l'm'}^{\lambda}=\pm1/n,\quad \lambda=1,2,\ldots,\lambda_n,\quad \lambda_n=\sum_{l'=0}^{n-1}(2l'+1)=n^2 \tag{33}$$

that the initial states are orthonormalized for all of λ. Here we have assumed the system with the same probability density $(a_{l'm'}^{\lambda})^2$ in state $\psi_{nl'm'}^{(0)}$ for any set of l',m'. Two boundedness conditions of Eq. (32) are the coefficient functions of the unbounded function $\tilde{\chi}_{nl}^{(0)}(r)$ equating to zero at its two singular points $r=0,\infty$. Using Eqs. (30), from the difference of the two conditions we have the equation

$$\int_0^\infty R_{nl}^{(0)}\{[\hat{L}^2-l(l+1)]r^{-2}$$
$$+2[E_n^{(0)}-E+H'(r,\theta,\varphi)]\}\chi_{nlm}^{\lambda}rdr=0. \tag{34}$$

Applying the angular momentum operator to Eq. (34) gives the two-dimensional (2D) equations

$$\left[-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{m^2}{\sin^2\theta}-l(l+1)\right]\Theta_{nlm}^{\lambda}$$
$$=\left(\frac{m^2-\hat{l}_z^2}{\sin^2\theta}\right)\Theta_{nlm}^{\lambda}+\varepsilon_{nlm}^{\lambda},$$

$$\Theta_{nlm}^{\lambda}=\int_0^\infty R_{nl}^{(0)}(r)\chi_{nlm}^{\lambda}r^{-1}dr,$$

$$\varepsilon_{nlm}^{\lambda}=2\int_0^\infty[E-E_n^{(0)}-H'(r,\theta,\varphi)]R_{nl}^{(0)}\chi_{nlm}^{\lambda}rdr. \tag{35}$$

Equating the left-hand side of first in Eqs. (35) to zero results in an associated Legendre equation with the two linearly independent solutions

$$\Theta_{lm}^{(0)}=(-1)^m\sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}P_l^m(\cos\theta),$$

$$\tilde{\Theta}_{lm}^{(0)}=-\Theta_{lm}^{(0)}\int\frac{d\theta}{(\Theta_{lm}^{(0)})^2\sin\theta}. \tag{36}$$

Here $P_l^m(\cos\theta)$ is the associated Legendre polynomial and $\tilde{\Theta}_{lm}^{(0)}$ has the singular points $\theta=0,\pi$. The integral equation corresponding to the first of Eq. (35) therefore is constructed as

$$\Theta_{nlm}^{\lambda}(\theta,\varphi)=\tilde{\Theta}_{lm}^{(0)}\int_C^\theta\Theta_{lm}^{(0)}[(m^2-\hat{l}_z^2)\Theta_{nlm}^{\lambda}(\theta,\varphi)/\sin\theta$$
$$+\varepsilon_{nlm}^{\lambda}(\theta,\varphi)\sin\theta]d\theta-\Theta_{lm}^{(0)}$$
$$\times\int_D^\theta\tilde{\Theta}_{lm}^{(0)}[(m^2-\hat{l}_z^2)\Theta_{nlm}^{\lambda}(\theta,\varphi)/\sin\theta$$
$$+\varepsilon_{nlm}^{\lambda}(\theta,\varphi)\sin\theta]d\theta \tag{37}$$

with C,D being arbitrary constants. At the singular points of the unbounded function $\tilde{\Theta}_{lm}^{(0)}$, there exist two boundedness conditions. Their difference gives the 1D equation

$$(m^2-\hat{l}_z^2)\Phi_{nlm}^{\lambda}(\varphi)=\overline{\varepsilon_{nlm}^{\lambda}}(\varphi),\quad \hat{l}_z=-i\partial/\partial\varphi,$$

$$\Phi_{nlm}^{\lambda}=\int_0^\pi\Theta_{lm}^{(0)}\Theta_{nlm}^{\lambda}(\theta,\varphi)(\sin\theta)^{-1}d\theta,$$

$$\overline{\varepsilon_{nlm}^{\lambda}}(\varphi)=-\int_0^\pi\Theta_{lm}^{(0)}\varepsilon_{nlm}^{\lambda}(\theta,\varphi)\sin\theta d\theta. \tag{38}$$

One thing apparent from Eqs. (38) and (35) is that the functions $\Phi_{nlm}^{\lambda}(\varphi)$ and $\overline{\varepsilon_{nlm}^{\lambda}}(\varphi)$ of φ contain functionals of the solution χ_{nlm}^{λ} of Eq. (32). If $H'(r,\theta,\varphi)$ includes periodic functions of the variable φ, Eq. (38) becomes a modified Mathieu equation of these functionals. However, we are unable to solve this severe equation analytically. Numerical and perturbed solutions of this equation should be important.

We are interested in determining the perturbed solution of Eq. (38) for the small H'. Setting $\psi_k=\chi^{\lambda}_{nlm}, E_k=E^{\lambda}_{nlm}$, and substituting the Rayleigh expansions (1) into Eqs. (38) yields

$$[\partial^2/\partial\varphi^2+m^2]\Phi^{\lambda(i)}_{nlm}(\varphi)=\overline{\varepsilon}^{\lambda(i)}_{nlm}(\varphi),\quad i=1,2,\ldots,\infty,$$

$$\overline{\varepsilon}^{\lambda(i)}_{nlm}(\varphi)=-2\int_0^\infty\int_0^\pi R^{(0)}_{nl}\Theta^{(0)}_{lm}\times\left[\sum_{j=1}^{i}E^{\lambda(j)}_{nlm}\chi^{\lambda(i-j)}_{nlm}-H'\chi^{\lambda(i-1)}_{nlm}\right]r\sin\theta d\theta dr. \tag{39}$$

Here $\overline{\varepsilon}^{\lambda(i)}_{nlm}(\varphi)$ are only some nonhomogeneous terms and $\Phi^{\lambda(i)}_{nlm}(\varphi)$ comes from Eqs. (38) with $\chi^{\lambda(i)}_{nlm}$ instead of χ^{λ}_{nlm}. The general solutions of Eqs. (39) are known in the form

$$\Phi^{\lambda(i)}_{nlm}(\varphi)=\frac{i}{2m}e^{-im\varphi}\int_{C_i}^{\varphi}\overline{\varepsilon}^{\lambda(i)}_{nlm}(\varphi)e^{im\varphi}d\varphi-\frac{i}{2m}e^{im\varphi}\int_{D_i}^{\varphi}\overline{\varepsilon}^{\lambda(i)}_{nlm}(\varphi)e^{-im\varphi}d\varphi. \tag{40}$$

Here C_i and D_i are arbitrary boundary constants. Given Eqs. (40), the periodicity condition $\Phi^{\lambda(i)}_{nlm}(2\pi)-\Phi^{\lambda(i)}_{nlm}(0)=0$ leads to the new formulas of energy corrections

$$\int_0^{2\pi}\overline{\varepsilon}^{\lambda(i)}_{nlm}(\varphi)\sin(m\varphi)d\varphi=0,\quad i=1,2,\ldots,\infty. \tag{41}$$

Combining Eqs. (39) with Eq. (32) yields the first-order perturbed function

$$\overline{\varepsilon}^{\lambda(1)}_{nlm}=-2\int_0^\pi\sin\theta d\theta\int_0^\infty R^{(0)}_{nl}\Theta^{(0)}_{lm}[E^{\lambda(1)}_{nlm}-H'(r,\theta,\varphi)]\times\sum_{l'm'}a^{\lambda}_{l'm'}\psi^{(0)}_{nl'm'}r^2dr, \tag{42}$$

where $a^{\lambda}_{l'm'}$ are given by Eqs. (33). Inserting Eq. (42) into Eqs. (40) and (41) can produce evident forms of the first-order corrections of the wave function and energy. Only the first-order energy corrections agree with the previous results. In order to obtain any order corrections, we sometimes could combine these results with the expansion in Hilbert space under the boundedness conditions. In some cases, the perturbed potential H' does not contain one or two of the variables (r,θ,φ) such that the problems can be simplified into one or two-dimensional ones. The following simple examples could be helpful for understanding these complex results.

V. SECOND-ORDER ENERGY CORRECTION OF THE HELIUMLIKE IONS

For simplicity we only consider the heliumlike ions under ground state with the main quantum number $n=k=1$ and angular one $l=0$. First-order corrected energy of the system has been derived from the previous perturbation theory. But to obtain second-order energy correction is difficult from the previous theory. Our method will simplify this work and make possibility to produce multiorder results. Taking the electron-electron interaction as perturbation, we have the expansion formula [1]

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

$$H'(r_1,r_2)=\frac{1}{r_{12}}=\frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l p_l(\cos\theta_{12})=\frac{1}{r_1}\quad\text{for } r_1\geqslant r_2,\quad l=0, \tag{43}$$

where $p_l(\cos\theta_{12})=[4\pi/(2l+1)]\Sigma^{l}_{m=-l}Y^{*}_{lm}(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2)=1$ for $l=0$ with (r_i,θ_i,φ_i) being coordinates of the electron i. Setting the radial wave function in the form $\psi(r_1,r_2)=R(r_1,r_2)=\chi(r_1,r_2)/(r_1r_2)$, the Schrödinger equation of the system is only the radial one

$$\sum_{i=1}^{2}\frac{\partial^2\chi(r_1,r_2)}{\partial r_i^2}+2\left(E+\frac{Z}{r_i}\right)\chi(r_1,r_2)=2H'(r_1,r_2)\chi(r_1,r_2) \tag{44}$$

with Z being the number of nuclear charges. As in Eqs. (32) the corresponding integral equation is

$$\chi(r_1,r_2)=\chi^{(0)}(r_1,r_2)+\tilde{\chi}^{(0)}(r_\alpha)\int_A^{r_\alpha}\chi^{(0)}(r_\alpha)Q'\chi dr_\alpha-\chi^{(0)}(r_\alpha)\int_B^{r_\alpha}\tilde{\chi}^{(0)}(r_\alpha)Q'\chi dr_\alpha,$$

$$Q'(r_1,r_2)=-\frac{\partial^2}{\partial r_\beta^2}-\frac{2Z}{r_\beta}+2[H'(r_1,r_2)-E+E^{(0)}_\alpha]\quad\text{for }\alpha,\beta=1,2,\quad\alpha\neq\beta. \tag{45}$$

Here A and B are arbitrary constants, $E^{(0)}_\alpha=-\frac{1}{2}Z^2$ is the ground-state energy of an unperturbed electron and the functions

$$\chi^{(0)}(r_1,r_2)=\chi^{(0)}(r_1)\chi^{(0)}(r_2),\quad\chi^{(0)}(r_\alpha)=2Z^{3/2}r_\alpha e^{-Zr_\alpha},$$

$$\tilde{\chi}^{(0)}(r_\alpha)=\chi^{(0)}(r_\alpha)\int[\chi^{(0)}(r_\alpha)]^{-2}dr_\alpha \tag{46}$$

for $\alpha=1,2$ denote the solutions of Eq. (44) at $H'=0$. Because $\tilde{\chi}^{(0)}(r_\alpha)$ is an unbounded function with the singular points $r_\alpha=0,\infty$, the boundedness conditions of Eqs. (45) which are similar to Eq. (34) leads to

$$\int_0^\infty \chi^{(0)}(r_\alpha)\left[-\frac{\partial^2}{\partial r_\beta^2}-\frac{2Z}{r_\beta}+2(H'(r_1,r_2)-E+E_\alpha^{(0)})\right]\times\chi(r_1,r_2)dr_\alpha=0. \tag{47}$$

Setting

$$\overline{\chi(r_\beta)}=\int_0^\infty \chi^{(0)}(r_\alpha)\chi(r_1,r_2)dr_\alpha. \tag{48}$$

Equation (47) can be written as

$$\left[\frac{\partial^2}{\partial r_\beta^2}+\frac{2Z}{r_\beta}+2E_\beta^{(0)}\right]\overline{\chi(r_\beta)}=\varepsilon(r_\beta),$$

$$\varepsilon(r_\beta)=2\int_0^\infty \chi^{(0)}(r_\alpha)[H'(r_1,r_2)-E+E_\alpha^{(0)}+E_\beta^{(0)}]\chi(r_1,r_2)dr_\alpha. \tag{49}$$

Its equivalent integral equation reads

$$\overline{\chi(r_\beta)}=\tilde{\chi}^{(0)}(r_\beta)\int_C^{r_\beta}\chi^{(0)}(r_\beta)\varepsilon(r_\beta)dr_\beta-\chi^{(0)}(r_\beta)\int_D^{r_\beta}\tilde{\chi}^{(0)}(r_\beta)\varepsilon(r_\beta)dr_\beta. \tag{50}$$

Applying the Rayleigh-Schrödinger expansions (1) to Eq. (50) gives the solutions

$$\overline{\chi^{(i)}}(r_\beta)=\tilde{\chi}^{(0)}(r_\beta)\int_{C_i}^{r_\beta}\chi^{(0)}(r_\beta)\varepsilon^{(i)}(r_\beta)dr_\beta-\chi^{(0)}(r_\beta)\int_{D_i}^{r_\beta}\tilde{\chi}^{(0)}(r_\beta)\varepsilon^{(i)}(r_\beta)dr_\beta \tag{51}$$

for $i=1,2,\ldots,\infty;\alpha,\beta=1,2$ and $\alpha\neq\beta$ with the perturbed functions

$$\varepsilon^{(i)}(r_\beta)=2\int_0^\infty \chi^{(0)}(r_\alpha)\left[H'(r_1,r_2)\chi^{(i-1)}(r_1,r_2)-\sum_{j=1}^{i}E^{(j)}\chi^{(i-j)}(r_1,r_2)\right]dr_\alpha. \tag{52}$$

The boundedness conditions of Eq. (51) give the energy formulas

$$E^{(i)}=2\int_0^\infty\int_0^\infty \chi^{(0)}(r_1,r_2)\left[H'(r_1,r_2)\chi^{(i-1)}(r_1,r_2)-\sum_{j=1}^{i-1}E^{(j)}\chi^{(i-j)}(r_1,r_2)\right]dr_1dr_2 \tag{53}$$

for $i=1,2,\ldots,\infty$. By substituting Eqs. (43) and (46) into Eq. (53), we easily get the first-order energy correction $E^{(1)}=5Z/8$ that agrees with the previous result [1,23–25].

When $r_1\leqslant r_2$ in Eqs. (43), from Eqs. (45) and (48) we can take

$$\chi(r_1,r_2)=\chi^{(0)}(r_1)\chi(r_2)=\chi^{(0)}(r_1)\overline{\chi}(r_2),$$

$$\chi^{(i)}(r_1,r_2)=\chi^{(0)}(r_1)\overline{\chi^{(i)}}(r_2). \tag{54}$$

Combining Eqs. (54) with Eq. (51) results in

$$\begin{aligned}\chi^{(i)}(r_1r_2)&=\chi^{(0)}(r_1)\left[\tilde{\chi}^{(0)}(r_2)\int_{C_i}^{r_2}\chi^{(0)}(r_2)\varepsilon^{(i)}(r_2)dr_2-\chi^{(0)}(r_2)\int_{D_i}^{r_2}\tilde{\chi}^{(0)}(r_2)\varepsilon^{(i)}(r_2)dr_2\right]\\&=\chi^{(0)}(r_1)\chi^{(0)}(r_2)\int_{D_i}^{r_2}[\chi^{(0)}(r_2)]^{-2}\times\left[\int_{C_i}^{r_2}\chi^{(0)}(r_2)\varepsilon^{(i)}(r_2)dr_2\right]dr_2\\&\quad\text{for }\ i=1,2,\ldots,\end{aligned} \tag{55}$$

where C_i and D_i are constants, $\varepsilon^{(i)}$ is given by Eqs. (52), (54), and (43) as

$$\varepsilon^{(i)}(r_2)=\frac{2}{r_2}\overline{\chi^{(i-1)}}(r_2)-2\sum_{j=1}^{i}E^{(j)}\overline{\chi^{(i-j)}}(r_2). \tag{56}$$

Let us consider the simplest case $i=1$. Combining Eqs. (55) and (56) with Eqs. (54) and (46) yields

$$\begin{aligned}\varepsilon^{(1)}(r_1,r_2)&=2\left[\frac{1}{r_2}-E^{(1)}\right]\chi^{(0)}(r_1,r_2)\\&=8Z^3r_1r_2\left[\frac{1}{r_2}-\frac{5Z}{8}\right]e^{-Z(r_1+r_2)},\end{aligned} \tag{57}$$

$$\begin{aligned}\chi^{(1)}(r_1,r_2)&=\chi^{(1)}(r_1\leqslant r_2)\\&=\frac{Z^3}{2}r_1r_2e^{-Z(r_1+r_2)}\times\left[5r_2-\frac{3}{Z}\ln r_2+\frac{3}{2Z^2r_2}+D_1'\right],\end{aligned} \tag{58}$$

where D_1' is a normalization constant associated with D_1. Another integration constant has been taken as zero such that the first-order wave function converges at the infinite boundary. Supposing that the two electrons cannot simultaneously reach zero point, we have $r_2\neq 0$ in Eq. (58).

Similarly, in the case $r_1\geqslant r_2$ of Eqs. (43), we have the first-order wave function

$$\chi^{(1)}(r_1 \geqslant r_2) = \frac{Z^3}{2} r_1 r_2 e^{-Z(r_1+r_2)} \times \left[5r_1 - \frac{3}{Z}\ln r_1 + \frac{3}{2Z^2 r_1} + D_1' \right], \quad \text{for } r_1 \neq 0. \tag{59}$$

In the first-order approximation, the normalization conditions means that

$$\int_0^\infty \int_0^\infty \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1,r_2)dr_1 dr_2 = \int_0^\infty dr_2 \left[\int_0^{r_2} \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1 \leqslant r_2) dr_1 + \int_{r_2}^\infty \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1 \geqslant r_2) dr_1 \right] = 0. \tag{60}$$

Applying Eqs. (46), (58), and (59) to Eq. (60), the long calculation produces the constant

$$D_1' = -(9.0448 + 3\ln Z)/Z. \tag{61}$$

The substitution of Eqs. (43) and (60) into Eq. (53) gives the second-order energy correction

$$E^{(2)} = \int_0^\infty \int_0^\infty \chi^{(0)}(r_1,r_2)[H'(r_1,r_2) - E^{(1)}] \times \chi^{(1)}(r_1,r_2) dr_1 dr_2 = \int_0^\infty dr_2 \left[\int_0^{r_2} \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1 \leqslant r_2) r_2^{-1} dr_1 + \int_{r_2}^\infty \chi^{(0)}(r_1,r_2)\chi^{(1)}(r_1 \geqslant r_2) r_1^{-1} dr_1 \right]. \tag{62}$$

Inserting Eqs. (46), (58), (59), and (61) into Eq. (62) numerically arrives at the corrected energy value

$$E^{(2)} = 0.6612 + \frac{15}{64}\ln Z + \frac{5}{64} Z D_1' = -0.045\,43. \tag{63}$$

Up to second-order we have the total energy

$$E = E_1^{(0)} + E_2^{(0)} + E^{(1)} + E^{(2)} = -Z^2 + 5Z/8 - 0.045\,43. \tag{64}$$

The result is in good agreement with the previous experimental data, which is shown in Table II. In this table, we also exhibit the corresponding result of the variation method [1]. Although the perturbation result up to second order is not as good as that of the variation method, the ith-order energy corrections for $i>2$ i in Eqs. (53) can further improve the result.

TABLE II. Energies of the heliumlike ions in the ground state [1,26] (atomic units). E_e represents the experimental values; E_{p1} represents $-Z^2+5Z/8$; E_{p2} represents $-Z^2+5Z/8-0.4543$; and E_v represents results of the variation method.

Ions	Z	$-E_e$	$-E_{p1}$	$-E_{p2}$	$-E_v$
He	2	2.9037	2.7500	2.7954	2.8476
Li^+	3	7.3087	7.1250	7.1704	7.2226
Be^{++}	4	13.6557	13.5000	13.5454	13.5975
B^{+++}	5	22.0232	21.8750	21.9204	21.9725
C^{4+}	6	32.4098	32.2500	32.2954	32.3474
N^{5+}	7	44.7887	44.6250	44.6704	44.8707
O^{6+}	8	59.1696	59.0000	59.0454	59.0972

VI. FIRST-ORDER STARK EFFECT IN THE HYDROGEN ATOM

Consider a hydrogen atom interacting with an electric field that leads to the Stark effect. In this case, the perturbed potential reads

$$H' = \alpha r \cos\theta, \quad \text{for } |\alpha| \ll 1, \tag{65}$$

which is independent of the variable φ. Therefore, we can set the wave functions in the separated forms

$$\psi_{nlm}^\lambda(r,\theta,\varphi) = r^{-1}\chi_{nlm}^\lambda(r,\theta,\varphi) = r^{-1}\chi_{nlm}^\lambda(r,\theta)\Phi_m^{(0)}(\varphi), \tag{66}$$

$$\Theta_{nlm}^\lambda(\theta,\varphi) = \Theta_{nlm}^\lambda(\theta)\Phi_m^{(0)}(\varphi),$$

$$\varepsilon_{nlm}^\lambda(\theta,\varphi) = \varepsilon_{nlm}^\lambda(\theta)\Phi_m^{(0)}(\varphi). \tag{67}$$

Inserting Eqs. (66) and (67) into Eqs. (37) and (35) yields

$$\Theta_{nlm}^\lambda(\theta) = \tilde{\Theta}_{lm}^{(0)} \int_C^\theta \Theta_{lm}^{(0)} \varepsilon_{nlm}^\lambda(\theta) \sin\theta d\theta - \Theta_{lm}^{(0)} \int_D^\theta \tilde{\Theta}_{lm}^{(0)} \varepsilon_{nlm}^\lambda(\theta) \sin\theta d\theta = \int_0^\infty R_{nl}^{(0)}(r)\chi_{nlm}^\lambda(r,\theta) r^{-1} dr, \tag{68}$$

$$\varepsilon_{nlm}^\lambda(\theta) = 2\int_0^\infty [E - E_n^{(0)} - H'(r,\theta)] R_{nl}^{(0)}(r)\chi_{nlm}^\lambda(r,\theta) r dr. \tag{69}$$

Using the Rayleigh-Schrödinger expansions

$$E = E_{nlm}^\lambda = E_n^{(0)} + \sum_{i=1}^\infty E_{nlm}^{\lambda(i)}, \quad \chi_{nlm}^\lambda(r,\theta) = \sum_{i=0}^\infty \chi_{nlm}^{\lambda(i)}(r,\theta) \tag{70}$$

to Eqs. (68) and (69), we arrive at

$$\Theta_{nlm}^{\lambda(i)}(\theta)=\tilde{\Theta}_{lm}^{(0)}(\theta)\int_{C_i}^{\theta}\Theta_{lm}^{(0)}(\theta)\varepsilon_{nlm}^{\lambda(i)}(\theta)\sin\theta d\theta$$
$$-\Theta_{lm}^{(0)}(\theta)\int_{D_i}^{\theta}\tilde{\Theta}_{lm}^{(0)}(\theta)\varepsilon_{nlm}^{\lambda(i)}(\theta)\sin\theta d\theta$$
$$=\int_0^\infty R_{nl}^{(0)}(r)\chi_{nlm}^{\lambda(i)}(r,\theta)r^{-1}dr$$
$$=\int_0^\infty R_{nl}^{(0)}(r)\psi_{nlm}^{\lambda(i)}(r,\theta)dr, \tag{71}$$

$$\varepsilon_{nlm}^{\lambda(i)}(\theta)=2\int_0^\infty\left[\sum_{j=1}^{i}E_{nlm}^{\lambda(j)}\chi_{nlm}^{\lambda(i-j)}(r,\theta)-H'(r,\theta)\chi_{nlm}^{\lambda(i-1)}(r,\theta)\right]R_{nl}^{(0)}(r)rdr. \tag{72}$$

From the two equations we can derive the corrected wave functions. On the other hand, given Eqs. (67), the boundedness conditions (38) become

$$\overline{\varepsilon_{nlm}^{\lambda}}=-\int_0^\pi\Theta_{lm}^{(0)}(\theta)\varepsilon_{nlm}^{\lambda}(\theta)\sin\theta d\theta=0. \tag{73}$$

Combining Eqs. (70) with Eq. (73) results in

$$\overline{\varepsilon_{nlm}^{\lambda(i)}}=-\int_0^\pi\Theta_{lm}^{(0)}(\theta)\varepsilon_{nlm}^{\lambda(i)}(\theta)\sin\theta d\theta=0 \quad \text{for } i=1,2,\ldots,\infty, \tag{74}$$

which implies the formulas of energy corrections.

Let us take the degenerate case $i=1$ and $n=2$, where Eqs. (66), (32), and (33) give the orthonormalized initial states

$$\psi_{2lm}^{1(0)}(r,\theta)=\frac{1}{2}\psi_{200}^{(0)}(r,\theta)+\frac{1}{2}\psi_{210}^{(0)}(r,\theta)+\frac{1}{2}\psi_{21-1}^{(0)}(r,\theta)+\frac{1}{2}\psi_{211}^{(0)}(r,\theta), \tag{75}$$

$$\psi_{2lm}^{2(0)}(r,\theta)=\frac{1}{2}\psi_{200}^{(0)}(r,\theta)-\frac{1}{2}\psi_{210}^{(0)}(r,\theta)+\frac{1}{2}\psi_{21-1}^{(0)}(r,\theta)-\frac{1}{2}\psi_{211}^{(0)}(r,\theta), \tag{76}$$

$$\psi_{2lm}^{3(0)}(r,\theta)=-\frac{1}{2}\psi_{200}^{(0)}(r,\theta)+\frac{1}{2}\psi_{210}^{(0)}(r,\theta)+\frac{1}{2}\psi_{21-1}^{(0)}(r,\theta)-\frac{1}{2}\psi_{211}^{(0)}(r,\theta), \tag{77}$$

$$\psi_{2lm}^{4(0)}(r,\theta)=-\frac{1}{2}\psi_{200}^{(0)}(r,\theta)-\frac{1}{2}\psi_{210}^{(0)}(r,\theta)+\frac{1}{2}\psi_{21-1}^{(0)}(r,\theta)+\frac{1}{2}\psi_{211}^{(0)}(r,\theta), \tag{78}$$

where $\psi_{2lm}^{(0)}(r,\theta)=\psi_{2lm}^{(0)}(r,\theta,\varphi)/\Phi_m^{(0)}(\varphi)=R_{2l}^{(0)}(r)\Theta_{lm}^{(0)}(\theta)$. For $i=1$ Eqs. (71), (72), and (74) read

$$\Theta_{nlm}^{\lambda(1)}(\theta)=\tilde{\Theta}_{lm}^{(0)}(\theta)\int_{C_1}^{\theta}\Theta_{lm}^{(0)}\varepsilon_{nlm}^{\lambda(1)}(\theta)\sin\theta d\theta$$
$$-\Theta_{lm}^{(0)}(\theta)\int_{D_1}^{\theta}\tilde{\Theta}_{lm}^{(0)}\varepsilon_{nlm}^{\lambda(1)}(\theta)\sin\theta d\theta$$
$$=\int_0^\infty R_{nl}^{(0)}(r)\chi_{nlm}^{\lambda(1)}(r,\theta)r^{-1}dr$$
$$=\int_0^\infty R_{nl}^{(0)}(r)\psi_{nlm}^{\lambda(1)}(r,\theta)dr, \tag{79}$$

$$\varepsilon_{nlm}^{\lambda(1)}(\theta)=2\int_0^\infty[E_{nlm}^{\lambda(1)}-\alpha r\cos\theta]\psi_{nlm}^{\lambda(0)}(r,\theta)R_{nl}^{(0)}(r)r^2dr, \tag{80}$$

$$\int_0^\pi\Theta_{lm}^{(0)}(\theta)\sin\theta d\theta\int_0^\infty[E_{nlm}^{\lambda(1)}-\alpha r\cos\theta]\times\psi_{nlm}^{\lambda(0)}(r,\theta)R_{nl}^{(0)}(r)r^2dr=0. \tag{81}$$

The substitutions of Eqs. (75)–(78) into Eq. (81) produce the first-order corrected energies

$$E_{200}^{1(1)}=-E_{200}^{2(1)}=-E_{200}^{3(1)}=E_{200}^{4(1)}=E_{210}^{1(1)}=-E_{210}^{2(1)}=-E_{210}^{3(1)}=E_{210}^{4(1)}=3\alpha,$$
$$E_{211}^{\lambda(1)}=E_{21-1}^{\lambda(1)}=0,\quad \lambda=1,2,3,4, \tag{82}$$

which agree with the previous results [1]. To construct the first-order solution $\chi_{nlm}^{\lambda(1)}(r,\theta)$, we could expand it in terms of $R_{nl}^{(0)}$ under the boundedness conditions, that is

$$\psi_{nlm}^{\lambda(1)}(r,\theta)=\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}b_{n'l'm}^{\lambda(1)}(\theta)r^2R_{n'l'}^{(0)}(r). \tag{83}$$

Applying Eqs. (83), (82), and (80) to Eqs. (79), we obtain the coefficient functions

$$b_{n'l'm}^{\lambda(1)}(\theta)=\Theta_{n'l'm}^{\lambda(1)}(\theta)$$
$$=\tilde{\Theta}_{l'm}^{(0)}(\theta)\int_{C_1}^{\theta}\Theta_{l'm}^{(0)}(\theta)\varepsilon_{n'l'm}^{\lambda(1)}(\theta)\sin\theta d\theta$$
$$-\Theta_{l'm}^{(0)}(\theta)\int_{D_1}^{\theta}\tilde{\Theta}_{l'm}^{(0)}(\theta)\varepsilon_{n'l'm}^{\lambda(1)}(\theta)\sin\theta d\theta. \tag{84}$$

Substituting Eqs. (36), (80), and (75)–(78) into Eqs. (84) and (83), one can get an obvious form of the first-order correction of wave function. Because $\tilde{\Theta}^{(0)}_{l'm}(\theta)$ has the singular points $\theta=0,\pi$, Eq. (84) implies that if the boundedness conditions

$$\lim_{\theta\to 0,\pi}\int_{C_1}^{\theta}\Theta^{(0)}_{l'm}(\theta)\varepsilon^{\lambda(1)}_{n'l'm}(\theta)\sin\theta d\theta=0 \tag{85}$$

are satisfied, the corrected wave functions and energies are certainly bounded. This can be realized through selections of the constant C_1 and energy correction $E^{(1)}_{n'l'm}$, say selecting $C_1=0$ and $E^{(1)}_{n'l'm}$ to obey Eq. (81). Knowing the first order result, the above method can give the second-order one. Any ith-order result is proportional to α^i for $\alpha\ll 1$ that leads to a converdent Rayleigh series. The detailed calculations will be made in further work.

VII. CONCLUSIONS AND DISCUSSIONS

In conclusion, we have proved an integral equation that is completely equivalent to the Schrödinger one. The boundedness conditions of the solution are given as a complex equation of functionals of the wave function. The Rayleigh-Schrödinger perturbation method and the iterations from the integral equation lead to the corrected wave functions, which may contain some nonintegrable terms. Their boundedness conditions are just the formulas of energy corrections. Under the boundedness conditions we have constructed the convergent Rayleigh series of the wave function and energy. Comparison between the new and old formulas of energy corrections shows that only the first-order-corrected energy given by them is certainly same. This means that some high-order results are mathematically unbounded, which leads to the divergence of the Rayleigh series in the previous perturbation theory. The result implies that, given the appropriate perturbations, atoms may automatically tend to stability by changing their energy. On the other hand, we also can control the states of atoms by setting and adjusting some controllable perturbations to fit the boundedness conditions. The examples of hydrogen atoms with (1+1)D space-time and 3D spatial perturbations reveal that this method is valid for the degenerate and near degenerate cases. The second-order corrections of energies for an electron in the Wigner spherical ''box'' and some heliumlike ions are calculated and the first-order Stark effect of hydrogen atom is investigated. Good agreement is found between the analytical results and experimental ones. The results supply a quantum perturbation theory without divergences.

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