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Equal-factors method for solutions of the extended Schrödinger equation for $(Zns)^2$ states of heliumlike ions

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An approximate method using iterative techniques developed for solving the extended Schrödinger equation is applied to principles of the first and second kind of balance theory and an example for $(Zns)^2$ heliumlike ions is presented. The implementation of the equal-factors method presented here, which leads to a series of self-consistent equations, has advantages that provide the results for an entire series of energy levels and an entire isoelectronic sequence in a single calculation. Results for all two-electron ions for the ground-state energies for $Z=1$ to 10 are tabulated and compared with other results for these systems. Theoretical predictions of energy levels for $(Z2s)^2$ to $(Z11s)^2$, excited autoionizing states of heliumlike ions with $Z=1,10$, are tabulated as well. [S1050-2947(96)06512-2]

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I. INTRODUCTION

Suppose we have an unperturbed subsystem

$$H_0(c)\Psi_n^{(0)}(\vec{r},c)=E_n^{\langle 0\rangle}(c)\Psi_n^{(0)}(\vec{r},c), \tag{1}$$

where c is a structure constant that is contained in the unperturbed Hamiltonian $H_0(C)$. As a perturbing potential H' imposes a force [1] on the unperturbed system, the unperturbed subsystem will vary its structure to generate a resistance that balances the external force. After a very short period, the total system stabilizes at the energy minimum. In other words, a certain forming process of H_0+H' exists if a perturbing potential H' is present. In this formation period, both the Hamiltonians H_0, H', and the corresponding wave functions $\Psi_n^{(0)}(\vec{r},c)$ and $\phi^p(\vec{r},c)$ are varying [1]:

$$H_0(c)\rightarrow H_0(\alpha), \tag{2}$$

$$H'\rightarrow H_1(\alpha), \tag{3}$$

and

$$\Psi_n^{(0)}(\vec{r},c)\rightarrow\Psi_n^{(0)}(\vec{r},\alpha), \tag{4}$$

$$0\rightarrow\phi^{\,p}(\vec{r},\alpha), \tag{5}$$

where α is a varying structure parameter, $\phi^{\,p}(\vec{r},\alpha)$ is a perturbing wave function.

Clearly, if the perturbing potential does not exist ($H'=0$), then both $H_1(\alpha)$ and $\phi^{\,p}(\vec{r},\alpha)$ vanish and the varying structure parameter α takes a constant value c. If H' does exist, then a ‘‘forming process’’ of H_0+H' takes place. After a very short period of time this forming process finishes and the system $H=H_0+H'$ becomes stable. This phenomenon is quite similar to the deformation of a body in classical mechanics.

Based on these ideas, the forming process of H_0 and H' has been investigated and a principles of the first and second kind of balance (PFSKB) theory is developed here as in previous [1] work. We assume that the wave functions of the total system $\mathcal{H}$ in the short period of time of this forming process can be described in PFSKB theory by the extended Schrödinger equation [1]:

$$\mathcal{H}\Psi_n(\vec{r},\alpha)=E_n(\alpha)\Psi_n(\vec{r},\alpha), \quad \subset\vec{x}\oplus\vec{\pi}\ \text{space}, \tag{6}$$

and

$$\Psi_n(\vec{r},\alpha)=\Psi_n^{(0)}(\vec{r},\alpha)+\phi^p(\vec{r},\alpha), \tag{7}$$

where $\Psi_n(\vec{r},\alpha)$ and $\mathcal{H}$ are wave functions with a varying parameter and total Hamiltonian [1]:

$$\mathcal{H}=H_0(\alpha)+H_1(\alpha), \tag{8}$$

and [1]

$$H_0(\alpha)=H_0(c)+\Delta H_0, \tag{9}$$

$$H_1(\alpha)=H'-\Delta H_0, \tag{10}$$

$$\Delta H_0=H_0(\alpha)-H_0(c). \tag{11}$$

We notice that the extended total Hamiltonian $\mathcal{H}$ remains invariant, because we merely add or subtract suitable terms in a standard Hamiltonian, namely

$$\begin{aligned}\mathcal{H}&=H_0(c)+H'\\&=H_0(\alpha)+H_1(\alpha)\\&=H,\end{aligned} \tag{12}$$

where H is the original Hamiltonian. But we observe that interesting changes of wave function [1] are taking place:

$$\Psi_n(\vec{r},c)\rightarrow\Psi_n^{(0)}(\vec{r},\alpha)+\phi^p(\vec{r},\alpha). \tag{13}$$

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In fact, the wave functions with varying parameter play essential roles in the beginning of the forming process. We consider the orthonormal condition for these functions:

$$\langle \Psi_n^{(0)}(\vec{r},\alpha)|\Psi_n(\vec{r},\alpha)\rangle = 1, \tag{14}$$

which means that the perturbing wave function $\phi^p(\vec{r},\alpha)$ is orthogonal to $\Psi_n^{(0)}(\vec{r},\alpha)$ for varying parameter α. Thus we obtain the varying energy of the total system in the early part of the forming process [1]:

$$E_n(\alpha) = \langle \Psi_n^{(0)}(\vec{r},\alpha)|\mathcal{H}|\Psi_n(\vec{r},\alpha)\rangle, \tag{15}$$

or

$$E_n(\alpha) = \frac{\langle \Psi_n(\vec{r},\alpha)|\mathcal{H}|\Psi_n(\vec{r},\alpha)\rangle}{\langle \Psi_n(\vec{r},\alpha)|\Psi_n(\vec{r},\alpha)\rangle}. \tag{16}$$

Obviously, this forming process will be ended at the point α^* and the energy in Eqs. (15) and (16) is a minimum at that point:

$$E_n(\alpha^*) = \min_{\alpha=\alpha^*}\{E_n(\alpha)\}. \tag{17}$$

The perturbed wave function in balance positions of the total system is

$$\Psi_n(\vec{r},\alpha^*) = \Psi_n(\vec{r},\alpha)|_{\alpha=\alpha^*}, \tag{18}$$

so both energies and wave functions of the system $\mathcal{H}$ are obtained in Eqs. (17) and (18).

II. THEORY

Suppose we have the extended Schrödinger equation for a quantum system of charge Z:

$$H\Psi_{Zn}^{\text{exc}}(\vec{r},\alpha) = E_{Zn}^{\text{exc}}(\alpha)\Psi_{Zn}^{\text{exc}}(\vec{r},\alpha), \tag{19a}$$

$$H = H_0(\alpha) + H_1(\alpha), \tag{19b}$$

$$H_0(\alpha)\Psi_n^{(0)}(\vec{r},\alpha) = E_n^{\langle 0\rangle}(\alpha)\Psi_n^{(0)}(\vec{r},\alpha), \tag{19c}$$

where the exact wave functions are

$$\Psi_{Zn}^{\text{exc}}(\vec{r},\alpha) = \Psi_n^{(0)}(\vec{r},\alpha) + \phi^p(\vec{r},\alpha). \tag{20}$$

We rewrite the orthonormal condition:

$$\langle \Psi_n^{(0)}(\vec{r},\alpha)|\Psi_{Zn}^{\text{exc}}(\vec{r},\alpha)\rangle = 1, \tag{21}$$

which means that a perturbing wave function $\phi^p(\vec{r},\alpha)$ is orthonormal to $\Psi_n^{(0)}(\vec{r},\alpha)$ for the varying parameter α.

In general, the wave function can be expanded in a complete set $\{\Psi_n^{(0)}(\vec{r},\alpha)\}$ of eigenfunctions of $H_0(\alpha)$:

$$\Psi_{Zn}^{\text{exc}}(\vec{r},\alpha) = \Psi_n^{(0)}(\vec{r},\alpha) + \sum_{i\neq n}^{\infty} C_{ni}^{\text{exc}}(Z)\Psi_i^{(0)}(\vec{r},\alpha). \tag{22}$$

At this point we have not found a general means to determine the coefficients $C_{ni}^{\text{exc}}(Z)$. But for some specific cases the coefficients $C_{ni}^{\text{exc}}(Z)$ can be obtained in practice.

The method of ''equal factors'' is developed in the PFSKB theory for solving the extended Schrödinger equation (6) in some specific cases under investigation. Suppose we have a subset in a complete set of orthonormal eigenfunctions. This subset $\{\Psi_{n\beta}^{(0)}(\vec{r},\alpha)\}$ is defined by operator $\hat{\mathcal{L}}$:

$$\hat{\mathcal{L}}\Psi_{n\beta}^{(0)}(\vec{r},\alpha) = L_\beta \Psi_{n\beta}^{(0)}(\vec{r},\alpha), \tag{23}$$

where L_β is a eigenvalue of $\hat{\mathcal{L}}$. We assume that the solutions we are looking for belong to this subspace; namely, they have common eigenvalues L_β:

$$\hat{\mathcal{L}}\Psi_{Zn\beta}^{\text{exc}}(\vec{r},\alpha) = L_\beta \Psi_{Zn\beta}^{\text{exc}}(\vec{r},\alpha). \tag{24}$$

Thus the solutions $\Psi_{Zn\beta}^{\text{exc}}(\vec{r},\alpha)$ can be expanded in the subspace:

$$\Psi_{Zn\beta}^{\text{exc}}(\vec{r},\alpha) = \Psi_{n\beta}^{(0)}(\vec{r},\alpha) + \sum_{i\neq n}^{\infty} C_{ni}^{\text{exc}}(Z)\Psi_{i\beta}^{(0)}(\vec{r},\alpha). \tag{25}$$

As mentioned above in Eqs. (15) and (17):

$$E_{Zn\beta}^{\text{exc}}(\alpha) = \langle \Psi_{n\beta}^{(0)}(\vec{r},\alpha)|H|\Psi_{Zn\beta}^{\text{exc}}(\vec{r},\alpha)\rangle \tag{26}$$

and

$$\begin{aligned} E_{Zn\beta}^{\text{exc}}(\alpha^*) &= \min_{\alpha=\alpha^*}\{E_{Zn\beta}^{\text{exc}}(\alpha)\} \\ &= F[C_{ni}^{\text{exc}}(Z)]. \end{aligned} \tag{27}$$

Thus

$$\alpha^* = \Lambda[C_{ni}^{\text{exc}}(Z)], \tag{28}$$

if $C_{ni}^{\text{exc}}(Z)$ is known, where ''exc'' means exact, and F and Λ are some analytic functions. We assume that exact coefficients $C_{ni}^{\text{exc}}(Z)$ can be approached by the mth-order approximation:

$$C_{ni}^{\text{exc}}(Z) = \lim_{m\to\infty} C_{ni}^{\langle m-1\rangle}(Z) \tag{29}$$

and

$$|C_{ni}^{\text{exc}}(Z) - C_{ni}^{\langle m-1\rangle}(Z)| < |C_{ni}^{\text{exc}}(Z) - C_{ni}^{\langle m-2\rangle}(Z)|. \tag{30}$$

We define the $(m-1)$th-order approximation of coefficients as follows:

$$C_{ni}^{\langle m-1\rangle}(Z) = \begin{cases} C_{ni}^{\langle m-2\rangle}(Z) + \Delta C_{ni}^{(m-1)}(Z), \quad m \geqslant 3 & \text{(31a)} \\ C_{ni}^{\langle 1\rangle}(Z), \quad m = 2, & \text{(31b)} \end{cases}$$

where $C_{ni}^{\langle m-2\rangle}(Z)$ is the (m-2)th-order approximation, namely

$$C_{ni}^{\langle m-1\rangle}(Z) = C_{ni}^{\langle 1\rangle}(Z) + \Delta C_{ni}^{(2)}(Z) + \cdots + \Delta C_{ni}^{(m-1)}(Z), \tag{32}$$

where

$$|\Delta C_{ni}^{(m-1)}(Z)| < |\Delta C_{ni}^{(m-2)}(Z)|. \tag{33}$$

Thus, we rewrite Eqs. (27) and (28) for the mth-order approximation:

$$\begin{aligned} E_{Zn}^{\langle m\rangle}(\alpha^{(m)}) &= \min_{\alpha=\alpha^{(m)}} \{E_{Zn}^{\langle m\rangle}(\alpha)\} \\ &= F[C_{ni}^{\langle m-1\rangle}(Z)] \\ &= F[C_{ni}^{\langle 1\rangle}(Z)+\Delta C_{ni}^{(2)}(Z)+\cdots+\Delta C_{ni}^{(m-1)}(Z)] \end{aligned} \tag{34}$$

and

$$\begin{aligned} \alpha^{(m)} &= \Lambda[C_{ni}^{\langle m-1\rangle}(Z)] \\ &= \Lambda[C_{ni}^{\langle 1\rangle}(Z)+\Delta C_{ni}^{(2)}(Z)+\cdots+\Delta C_{ni}^{(m-1)}(Z)], \end{aligned} \tag{35}$$

and we define the mth-order energy-level difference:

$$\begin{aligned} \Delta E_{Zn}^{(m)} &= E_{Zn}^{\langle m\rangle}(\alpha^{(m)}) - E_{Zn}^{\langle m-2\rangle}(\alpha^{(m-2)}) \\ &= F[C_{ni}^{\langle m-1\rangle}(Z)] - F[C_{ni}^{\langle m-3\rangle}(Z)] \\ &= \Delta F[\Delta C_{ni}^{(m-1)}(Z)]. \end{aligned} \tag{36}$$

We notice the following relations:

$$E_{Zn}^{\langle m\rangle}(\alpha^{(m)})|_{\Delta C_{ni}^{(m-1)}(Z)\equiv 0} = E_{Zn}^{\langle m-1\rangle}(\alpha^{(m-1)}), \tag{37}$$

$$\alpha^{(m)}|_{\Delta C_{ni}^{(m-1)}(Z)\equiv 0} = \alpha^{(m-1)}, \tag{38}$$

and

$$\Delta E_{Zn}^{(m)}|_{\Delta C_{ni}^{(m-1)}(Z)\equiv 0} + E_{Zn}^{\langle m-2\rangle}(\alpha^{(m-2)}) = E_{Zn}^{\langle m-1\rangle}(\alpha^{(m-1)}). \tag{39}$$

Suppose that relations between coefficients $C_{ni}^{\langle m-1\rangle}(Z)$ and $C_{ni}^{\langle m-1\rangle}(Z=1)$ for charge Z and $Z=1$ quantum systems by separation of variables are

$$\Delta C_{ni}^{(m-1)}(Z) = g_j^{(m-1)}(Z)\Delta C_{ni}^{(m-1)}(1), \quad m \geqslant 3 \tag{40a}$$

and

$$C_{ni}^{\langle 1\rangle}(Z) = g_j^{(1)}(Z) C_{ni}^{\langle 1\rangle}(1), \quad m=2, \tag{40b}$$

where $g_j^{(m-1)}(1)=1$ and $g_j^{(1)}(1)=1$ for charge $Z=1$ quantum system and $i<n,\ j=i;\ i>n,\ j=i-1$ are conventions.

We now rewrite Eqs. (34) and (36) as follows:

$$\begin{aligned} E_{Zn}^{\langle m\rangle}(\alpha^{(m)}) = F[&g_j^{(1)}(Z) C_{ni}^{\langle 1\rangle}(1) + g_j^{(2)}(Z)\Delta C_{ni}^{(2)}(1) + \cdots \\ &+ g_j^{(m-1)}(Z)\Delta C_{ni}^{(m-1)}(1)] \end{aligned} \tag{41}$$

and

$$\Delta E_{Zn}^{(m)} = \Delta F[g_j^{(m-1)}(Z)\Delta C_{ni}^{(m-1)}(1)]. \tag{42}$$

So if m is odd,

$$E_{Zn}^{\langle m\rangle}(\alpha^{(m)}) = E_{Zn}^{\langle 1\rangle} + \Delta E_{Zn}^{(3)} + \cdots + \Delta E_{Zn}^{(m)}, \tag{43a}$$

and if m is even,

$$E_{Zn}^{\langle m\rangle}(\alpha^{(m)}) = E_{Zn}^{\langle 2\rangle} + \Delta E_{Zn}^{(4)} + \cdots + \Delta E_{Zn}^{(m)}, \tag{43b}$$

where $E_{Zn}^{\langle 1\rangle}$ is the first-order approximate energy that can be obtained [1]:

$$E_{Zn}^{\langle 1\rangle}(\alpha^{(1)}) = \min_{\alpha=\alpha^{(1)}} \{\langle \Psi_n^{(0)}(\vec{r},\alpha)|H|\Psi_n^{(0)}(\vec{r},\alpha)\rangle\}. \tag{44}$$

First we observe that the energy expression (41) in the second-order approximation for charge Z systems is

$$E_{Zn}^{\langle 2\rangle} = F[g_j^{(1)}(Z) C_{ni}^{\langle 1\rangle}(1)]. \tag{45}$$

Assumption I. We assume that the first-order approximate coefficients $C_{ni}^{\langle 1\rangle}(1)$ for the charge $Z=1$ system have equal-factor relations with the second-order approximate energy levels of the neutral quantum system of charge Z^*, namely,

$$C_{ni}^{\langle 1\rangle}(1) = f_n^{(1)} E_{Z^*j}^{\langle 2\rangle} \quad \text{if } i<n,\ j=i, \quad i>n, \quad j=i-1, \tag{46}$$

where the first-order approximate energy levels should be nondegenerate in Eq. (44) because the one-to-one relations are required in Eq. (46) and $f_n^{(1)}$ is the corresponding first-order equal factor, meaning that they are the same factor for all energy levels in the second-order approximation.

Substituting the coefficient $C_{ni}^{\langle 1\rangle}(1)$ in Eq. (46) into Eq. (45)

$$E_{Zn}^{\langle 2\rangle} = F[g_j^{(1)}(Z) f_n^{(1)} E_{Z^*j}^{\langle 2\rangle}]. \tag{47a}$$

We notice that if charge Z takes the value of Z^* on the left-hand side of Eq. (47a), the set $\{E_{Z^*n}^{\langle 2\rangle}\}$ and $\{E_{Z^*j}^{\langle 2\rangle}\}$ on both sides become the same; i.e., Eq. (47a) now is a self-consistent equation:

$$E_{Z^*n}^{\langle 2\rangle} = F[g_j^{(1)}(Z^*) f_n^{(1)} E_{Z^*j}^{\langle 2\rangle}], \tag{47b}$$

which can be solved in an exact manner with Hartree-Fock self-consistent-field calculations [2].

If a reasonable equal factor $f_n^{(1)}$ is determined by any means, the second-order approximate energy levels for the neutral system $\{E_{Z^*n}^{\langle 2\rangle}\}$ will be obtained by an iterative technique using the method of successive approximations. However, if the second-order approximate energy levels set $\{E_{Z^*n}^{\langle 2\rangle}\}$ is known, we consider the third-order approximation energy-level difference:

$$\Delta E_{Zn}^{(3)} = \Delta F[g_j^{(1)}(Z) f_n^{(1)} E_{Z^*j}^{\langle 2\rangle} + g_j^{(2)}(Z)\Delta C_{ni}^{(2)}(1)]. \tag{48}$$

Assumption II. We assume that the second-order approximate coefficient difference $\Delta C_{ni}^{(2)}(1)$ has equal-factor relations with the third-order approximate energy-level difference set $\{\Delta E_{Z^*j}^{(3)}\}$ for the neutral system with charge Z^*, namely,

$$\Delta C_{ni}^{(2)}(1) = f_n^{(2)} \Delta E_{Z^*j}^{(3)} \quad \text{if } i<n, \quad j=i; \quad i>n, \quad j=i-1. \tag{49}$$

As mentioned above, Eq. (48) becomes the self-consistent equation:

$$\Delta E^{(3)}_{Z^*n}=\Delta F[g^{(1)}_j(Z^*)f^{(1)}_n E^{\langle 2\rangle}_{Z^*j}+g^{(2)}_j(Z^*)f^{(2)}_n\Delta E^{(3)}_{Z^*j}]. \tag{50a}$$

Thus we can solve these equations by an iterative technique and third-order approximate energy levels:

$$E^{\langle 3\rangle}_{Z^*n}=\Delta E^{(3)}_{Z^*n}+E^{\langle 1\rangle}_{Z^*n}. \tag{50b}$$

We repeat this routine for the mth-order energy-level difference:

$$\Delta E^{(m)}_{Zn}=\Delta F[g^{(m-1)}_j(Z)\Delta C^{(m-1)}_{ni}(1)]. \tag{51}$$

Assumption III. We assume that the $(m-1)$th-order approximate coefficient difference set $\{\Delta C^{(m-1)}_{ni}(1)\}$ has equal-factor relations with the mth-order approximation of energy-level difference set $\{\Delta E^{(m)}_{Z^*j}\}$ of the neutral quantum system with charge Z^*, namely,

$$\begin{aligned}&\Delta C^{(m-1)}_{ni}(1)\\ &\quad =f^{(m-1)}_n\Delta E^{(m)}_{Z^*j}\quad \text{if } i<n,\quad j=i;\quad i>n,\quad j=i-1.\end{aligned} \tag{52}$$

Thus Eq. (51) becomes a self-consistent equation, as Z takes the value Z^*. Finally we obtain

$$E^{\langle m\rangle}_{Z^*n}=\Delta E^{(m)}_{Z^*n}+E^{\langle m-2\rangle}_{Z^*n}, \tag{53}$$

and the isoelectronic sequence $E^{\langle m\rangle}_{Zn}$ as well.

In summary the equal-factors assumption yields:

$$\begin{aligned}C^{\langle m-1\rangle}_{ni}(1)&=f^{(1)}_nE^{\langle 2\rangle}_{Z^*j}+f^{(2)}_n\Delta E^{(3)}_{Z^*j}+\cdots+f^{(m-1)}_n\\ &\quad\times\Delta E^{(m)}_{Z^*j}\quad \text{if } i<n,\quad j=i;\quad i>n,\quad j=i-1,\end{aligned} \tag{54}$$

where the first-order approximate energy-level set $\{E^{\langle 1\rangle}_{Zn}\}$ in Eq. (44) should be nondegenerate because one-to-one relations between sets $\{\Delta C^{\langle m-1\rangle}_{ni}(1)\}$ and $\{\Delta E^{(m)}_{Z^*j}\}$ are required.

The so-called equal factor $f^{\langle m-1\rangle}_n$ means that it is a constant factor for the corresponding set $\{\Delta E^{(m)}_{Z^*j}\}$.

III. CALCULATIONS

As an example of applying the equal-factors method, we investigate the specific case in which both electrons are in the same shell for S-wave states in heliumlike ions. The nonrelativistic extended Schrödinger equation for $(Zns)^2$ states of two-electron ions in a forming process that lasts a very short time in the PFSKB theory is, on neglecting the motion of the nucleus, given by

$$\mathcal{H}\Psi_{(Zns)^2}(\alpha,\vec{r}_1,\vec{r}_2)=E_{(Zns)^2}(\alpha)\Psi_{(Zns)^2}(\alpha,\vec{r}_1,\vec{r}_2), \tag{55}$$

and [3–5]

$$\begin{aligned}\mathcal{H}&=H_0(c)+H'\\ &=H_0(\alpha)+H_1(\alpha),\end{aligned} \tag{56a}$$

$$H_0(\alpha)=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{\alpha}{r_1}-\frac{\alpha}{r_2}, \tag{56b}$$

$$H_1(\alpha)=\frac{1}{r_{12}}-\frac{Z-\alpha}{r_1}-\frac{Z-\alpha}{r_2}, \tag{56c}$$

where α is the varying effective nuclear charge when two electrons are in the same shells and S-wave state. We shall always employ the conventions that

$$|\alpha ns\rangle=R_{\alpha ns}Y_{00}, \tag{57}$$

$$\langle(\alpha ns)(\alpha ns)|(\alpha js)(\alpha js)\rangle=\delta nj, \tag{58}$$

$$J_{(ns)^2}(\alpha)=\left\langle(\alpha ns)(\alpha ns)\left|\frac{1}{r_{12}}\right|(\alpha ns)(\alpha ns)\right\rangle=j_{(ns)^2}\alpha, \tag{59}$$

$$\begin{aligned}K_{(ns)(js)}(\alpha)&=\left\langle(\alpha ns)(\alpha js)\left|\frac{1}{r_{12}}\right|(\alpha js)(\alpha ns)\right\rangle\\ &=k_{(ns)(js)}\alpha,\end{aligned} \tag{60}$$

where $J_{(ns)^2}(\alpha)$ and $K_{(ns)(js)}(\alpha)$ are Coulomb and exchange integrals, respectively. The $j_{(ns)^2}$ and $k_{(ns)(js)}$ are both proportional coefficients and are listed in Table I [6].

We consider the specific cases in which a subset $\{\Psi^{(0)}_{n\beta}(\alpha,\vec{r}_1,\vec{r}_2)\}$ of the complete set of orthonormal eigenfunctions of $H_0(\alpha)$ is defined by angular-momentum operators $\hat{L}_1^2$ and $\hat{L}_2^2$:

$$\hat{L}_1^2\Psi^{(0)}_{n\beta}=l_1(l_1+1)\Psi^{(0)}_{n\beta}, \tag{61}$$

$$\hat{L}_2^2\Psi^{(0)}_{n\beta}=l_2(l_2+1)\Psi^{(0)}_{n\beta}, \tag{62}$$

where eigenvalues $l_1=0$ and $l_2=0$ are required. In other words, the subset $\{(ns)(ns),(n's)(n''s)\}$ defines a subspace charactered by common eigenvalues $l_1=0$ and $l_2=0$, namely, the electrons remain in the S_1 orbital and the S_2 orbital separately.

Solutions for $(Zns)^2$ states can be divided into two parts:

$$\Psi_{(Zns)^2}(\alpha,\vec{r}_1\vec{r}_2)=\Psi^{(0)}_{(Zns)^2}(\alpha,\vec{r}_1,\vec{r}_2)+\phi^p(\alpha,\vec{r}_1,\vec{r}_2). \tag{63}$$

In general, the perturbing wave $\phi^p(\alpha,\vec{r}_1,\vec{r}_2)$ may contain such terms $(ns)(n'p),(ns)(n''d),(np)^2,(nd)^2,\ldots$. But under such considerations, $(Zns)^2$ states are perfectly spherically symmetric in $\vec{R}_1$ and $\vec{R}_2$; the possible terms are only the terms $(ns)(ns),(n's)(n''s)$. We notice that as the two electrons are in different shells n' and n''; the corresponding α' and α'' will differ from α:

$$\alpha'\neq\alpha''\neq\alpha, \tag{64a}$$

so

$$\langle(\alpha ns)(\alpha ns)|(\alpha' n's)(\alpha'' n''s)\rangle\neq 0. \tag{64b}$$

According to the orthonormal condition Eq. (14), the terms $(n's)(n''s)$ drop out as well.

Finally we obtain the $(m-1)$th-order approximate wave functions for the $(Zns)^2$ state in the forming process:

TABLE I. Coefficients of $J(\alpha)$ and $K(\alpha)$; $j_{(ns)^2}$ in diagonal positions and $k_{(ns)(is)}$ in nondiagonal positions for $n=1$ to 11, $i=1$ to 12, respectively. The accuracy is estimated to be ±1 in the last digit (in a.u.). Numbers in square brackets indicate powers of 10.

is \ *ns*	1*s*	2*s*	3*s*	4*s*	5*s*	6*s*	7*s*	8*s*	9*s*	10*s*	11*s*
1*s*	5/8	0.219 478 7[−1]	0.576 782 3[−2]	0.233 963 6[−2]	0.117 683 0[−2]	0.674 577 4[−3]	0.422 388 3[−3]	0.281 924 6[−3]	0.197 505 5[−3]	0.143 722 2[−3]	0.107 837 0[−3]
2*s*	0.219 478 7[−1]	77/512	0.747 601 3[−2]	0.239 349 6[−2]	0.109 830 0[−2]	0.601 155 6[−3]	0.366 495 9[−3]	0.240 519 0[−3]	0.166 588 3[−3]	0.120 250 9[−3]	0.896 947 6[−4]
3*s*	0.576 782 4[−2]	0.747 601 3[−2]	0.663 992 8[−1]	0.377 503 1[−2]	0.132 711 6[−2]	0.650 426 0[−3]	0.374 186 3[−3]	0.237 196 2[−3]	0.160 619 0[−3]	0.114 131 2[−3]	0.841 807 5[−4]
4*s*	0.233 963 6[−2]	0.239 349 6[−2]	0.377 503 1[−2]	0.372 360 4[−1]	0.227 753 0[−2]	0.849 063 7[−3]	0.432 434 5[−3]	0.256 660 7[−3]	0.167 101 2[−3]	0.115 772 9[−3]	0.838 792 5[−4]
5*s*	0.117 683 0[−2]	0.109 830 0[−2]	0.132 711 7[−2]	0.227 753 0[−2]	0.238 288 8[−1]	0.152 068 4[−2]	0.584 434 9[−3]	0.307 463 3[−3]	0.187 262 3[−3]	0.124 381 7[−3]	0.875 853 0[−4]
6*s*	0.674 577 4[−3]	0.601 155 6[−3]	0.650 426 0[−3]	0.849 063 7[−3]	0.152 068 4[−2]	0.165 316 4[−1]	0.108 800 6[−2]	0.429 936 1[−3]	0.230 298 0[−3]	0.142 991 6[−3]	0.964 737 9[−4]
7*s*	0.422 388 2[−3]	0.366 495 9[−3]	0.374 186 3[−3]	0.432 434 5[−3]	0.584 434 8[−3]	0.108 800 6[−2]	0.121 378 0[−1]	0.816 903 4[−3]	0.329 458 7[−3]	0.179 010 3[−3]	0.112 841 6[−3]
8*s*	0.281 924 6[−3]	0.240 519 0[−3]	0.237 196 2[−3]	0.256 660 7[−3]	0.307 463 4[−3]	0.429 936 1[−3]	0.816 903 4[−3]	0.929 397 5[−2]	0.635 645 7[−3]	0.253 542 6[−3]	0.143 271 4[−3]
9*s*	0.197 505 5[−3]	0.166 588 3[−3]	0.160 619 0[−3]	0.167 101 2[−3]	0.187 262 3[−3]	0.230 298 0[−3]	0.329 458 7[−3]	0.635 645 7[−3]	0.733 769 1[−2]	0.508 868 7[−3]	0.210 871 6[−3]
10*s*	0.143 722 2[−3]	0.120 250 9[−3]	0.114 131 2[−3]	0.115 753 8[−3]	0.124 395 2[−3]	0.142 991 6[−3]	0.179 010 3[−3]	0.259 542 6[−3]	0.508 868 7[−3]	0.594 763 2[−2]	0.416 231 3[−3]
11*s*	0.107 837 0[−3]	0.896 937 3[−4]	0.841 892 0[−4]	0.838 733 1[−4]	0.875 852 9[−4]	0.964 688 9[−4]	0.112 847 1[−3]	0.143 281 9[−3]	0.210 865 9[−3]	0.416 231 3[−3]	0.491 331 3[−2]
12*s*	0.829 778 9[−4]	0.687 090 7[−4]	0.639 545 3[−4]	0.628 978 2[−4]	0.643 471 4[−4]	0.688 023 1[−4]	0.770 041 2[−4]	0.911 317 1[−4]	0.117 241 7[−3]	0.173 438 4[−3]	0.347 247 2[−3]

$$\Psi^{\langle m-1\rangle}_{(Zns)^2}(\alpha,\vec{r}_1,\vec{r}_2)=|(\alpha ns)(\alpha ns)\rangle+\sum_{j\neq n}^{\infty}C^{\langle m-1\rangle}_{Zns,js}|(\alpha js)(\alpha js)\rangle. \quad (65)$$

If one is only interested in energy levels up to M $(M\gg m)$, then the mth-order approximate wave functions for $(Zns)^2$ states can be expanded in M terms:

$$\Psi^{\langle m-1\rangle}_{(Zns)^2}(\alpha,\vec{r}_1,\vec{r}_2)=|(\alpha ns)(\alpha ns)\rangle+\sum_{j\neq n}^{M+1}C^{\langle m-1\rangle}_{Zns,js}|(\alpha js)(\alpha js)\rangle, \quad (66)$$

where an infinite series of energy levels is truncated at M terms $(M\gg m)$ under an approximation. Thus the mth-order approximate varying energy levels at short times can be obtained:

$$E^{\langle m\rangle}_{(Zns)^2}(\alpha)=-\frac{\alpha^2}{n^2}-\frac{2(Z-\alpha)\alpha}{n^2}+\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}C^{\langle m-1\rangle}_{Zns,js}k_{(ns)(js)}\right]\alpha. \quad (67)$$

Recalling the principle of the second kind of balance in the PFSKB theory [1], the condition of the second kind of balance for $(Zns)^2$ orbitals is carried out by

$$\frac{d}{d\alpha}E^{\langle m\rangle}_{(Zns)^2}(\alpha)=\frac{2\alpha}{n^2}-\frac{2Z}{n^2}+\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}C^{\langle m-1\rangle}_{Zns,js}k_{(ns)(js)}\right]=0 \quad (68)$$

and the second kind of balance pointing to the mth-order approximation is found:

$$\alpha^{(m)}_{(Zns)^2}=Z-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}C^{\langle m-1\rangle}_{Zns,js}k_{(ns)(js)}\right], \quad (69)$$

and the mth-order approximate energy levels for the Schrödinger equation for $(Zns)^2$ states are obtained:

$$E^{\langle m\rangle}_{(Zns)^2}=E^{\langle m\rangle}_{(Zns)^2}(\alpha)|_{\alpha=\alpha^{(m)}_{(Zns)^2}}=-\left\{Z-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}C^{\langle m-1\rangle}_{Zns,js}k_{(ns)(js)}\right]\right\}^2\bigg/ n^2. \quad (70)$$

TABLE II. Coefficients of 1/Z expansion for Z heliumlike ions up to the fourth-order approximation.

Z	1	2	3	4	5	6	7	8	9	10
$U^{(1)}(Z)$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$U^{(2)}(Z)$	5.75	−0.069	−1.144	−2.0	−2.0	−2.0	−2.0	−2.0	−2.0	−2.0
$U^{(3)}(Z)$	−3.6	−6.0	−0.10	−274.5	−55.0	88.0	190.0	264.0	325.0	370.0

We consider that the coefficient $C^{\langle m-1\rangle}_{Zns,js}$ can be expanded in terms of

$$C^{\langle m-1\rangle}_{Zns,js}=C^{\langle 1\rangle}_{Zns,js}+\Delta C^{(2)}_{Zns,js}+\cdots+\Delta C^{(m-1)}_{Zns,js}, \tag{71}$$

as mentioned above in Eq. (32). Hence Eqs. (69) and (70) can be rewritten as follows:

$$\alpha^{(m)}_{(Zns)^2}=Z-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}[C^{\langle 1\rangle}_{Zns,js}+\Delta C^{(2)}_{Zns,js}+\cdots+\Delta C^{(m-1)}_{Zns,js}]k_{(ns)(js)}\right], \tag{72}$$

and

$$E^{\langle m\rangle}_{(Zns)^2}=-\left\{Z-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}[C^{\langle 1\rangle}_{Zns,js}+\Delta C^{(2)}_{Zns,js}+\cdots+\Delta C^{(m-1)}_{Zns,js}]k_{(ns)(js)}\right]\right\}^2\Big/ n^2. \tag{73}$$

It is easy to verify the following relationships:

$$\alpha^{(m-1)}_{(Zns)^2}=\alpha^{(m)}_{(Zns)^2}\big|_{\Delta C^{(m-1)}_{Zns,js}\equiv 0}, \tag{74}$$

and

$$E^{\langle m-1\rangle}_{(Zns)^2}=E^{\langle m\rangle}_{(Zns)^2}\big|_{\Delta C^{(m-1)}_{Zns,js}\equiv 0}. \tag{75}$$

Furthermore, we calculate the difference of energy levels between the mth-order and $(m-2)$th-order approximations

$$\begin{aligned}\Delta E^{(m)}_{(Zns)^2}&=E^{\langle m\rangle}_{(Zns)^2}-E^{\langle m-2\rangle}_{(Zns)^2}\\&=\left\{Z-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j\neq n}^{M+1}C^{\langle m-3\rangle}_{Zns,js}k_{(ns)(js)}\right]-\frac{n^2}{4}\left[\sum_{j\neq n}^{M+1}(\Delta C^{(m-2)}_{Zns,js}+\Delta C^{(m-1)}_{Zns,js})k_{(ns)(js)}\right]\right\}\\&\quad\times\left\{\sum_{j\neq n}^{M+1}(\Delta C^{(m-2)}_{Zns,js}+\Delta C^{(m-1)}_{Zns,js})k_{(ns)(js)}\right\},\end{aligned} \tag{76}$$

where

$$C^{\langle m-3\rangle}_{Zns,js}=C^{\langle 1\rangle}_{Zns,js}+\Delta C^{(2)}_{Zns,js}+\cdots+\Delta C^{(m-3)}_{Zns,js}. \tag{77}$$

Now we consider the 1/Z expansion [7–11] for the cases of nuclear charge $Z\geqslant 2$ heliumlike ions. According to relations (40),

$$\Delta C^{(m-1)}_{Zns,js}=\frac{h^{(m-1)}(Z)}{Z^i}\,\Delta C^{(m-1)}_{1ns,js}, \quad m\geqslant 3 \tag{78}$$

and

$$C^{\langle 1\rangle}_{Zns,js}=\frac{h^{(1)}(Z)}{Z^i}\,C^{\langle 1\rangle}_{1ns,js}, \quad m=2, \tag{79}$$

where $h^{(m-1)}(Z)$ are the correct coefficients of a 1/Z expansion and $h^{(m-1)}(1)=1$ for $m\geqslant 2$ and if $j<n$, $i=j$; $j>n$, $i=j-1$ is chosen as a convention.

We here apply the equal-factors assumption to an H^- ion. First, the coefficient of the $(m-1)$th-order approximate wave function in expanding of equal factors is

$$C^{\langle m-1\rangle}_{1ns,js}=f^{(1)}_nE^{\langle 2\rangle}_{(2is)^2}+f^{(2)}_n\Delta E^{(3)}_{(2is)^2}+\cdots+f^{(m-1)}_n\Delta E^{(m)}_{(2is)^2}$$
$$\text{if } j<n,\quad i=j;\quad j>n,\quad i=j-1, \tag{80}$$

where $E^{\langle 2\rangle}_{(2is)^2}$ and $\Delta E^{(m)}_{(2is)^2}$ correspond to energy levels and the energy-level difference of a neutral helium atom ($Z=2$). The $f^{(1)}_n, f^{(2)}_n,\ldots,f^{(m-1)}_n$ are equal factors for an H^- ion. In this case they are independent of the principle quantum number n. We have determined these equal factors up to the fourth-order approximation by the trial

$$f^{(1)}=1, \quad f^{(2)}=5.75, \quad f^{(3)}=-3.6. \tag{81}$$

Finally we obtain the coefficients for charge Z systems:

$$\begin{aligned}C^{\langle m-1\rangle}_{Zns,js}&=\frac{1}{Z^i}\{h^{(1)}(Z)f^{(1)}E^{\langle 2\rangle}_{(2is)^2}+h^{(2)}(Z)f^{(2)}\Delta E^{(3)}_{(2is)^2}+\cdots\\&\quad+h^{(m-1)}(Z)f^{(m-1)}\Delta E^{(m)}_{(2is)^2}\}\\&=\frac{1}{Z^i}\{U^{(1)}(Z)E^{\langle 2\rangle}_{(2is)^2}+U^{(2)}(Z)\Delta E^{(3)}_{(2is)^2}+\cdots\\&\quad+U^{(m-1)}(Z)\Delta E^{(m)}_{(2is)^2}\},\end{aligned} \tag{82}$$

where

$$U^{(m-1)}(Z)=h^{(m-1)}(Z)f^{(m-1)}, \quad m\geqslant 2, \tag{83}$$

and if $j<n$, $i=j$; $j>n$, $i=j-1$ is chosen as a convention.

We have determined these correct coefficients $U^{(m-1)}$(Z) of 1/Z expansion up to the fourth-order approximation and tabulate them in Table II.

We are also interested in the second-order approximate coefficient

$$C^{\langle 1\rangle}_{Zns,js}=\frac{h^{(1)}(Z)f^{(1)}}{Z^i}\,E^{\langle 2\rangle}_{(2is)^2}. \tag{84}$$

We suppose in the second-order approximation of the coefficient an exact $1/Z$ expansion, namely,

$$h^{(1)}(Z)f^{(1)}=1, \tag{85}$$

where $f^{(1)}$ is the first-order equal-factor constant and $h^{(1)}(1)=1$. Thus, we obtain the first-order equal-factor constant

$$f^{(1)}=1. \tag{86}$$

Substituting coefficients $C^{\langle m-1\rangle}_{Zns,js}$ in Eq. (82) into Eqs. (69), (70), and (76), we obtain

$$\alpha^{(m)}_{(Zns)^2}=Z-\frac{n^2}{2}\,[j_{(ns)^2}+A_1+A_2+\cdots+A_{m-1}],$$
$$n=1,2,\ldots,M, \tag{87}$$

$$E^{\langle m\rangle}_{(Zns)^2}=-\left\{Z-\frac{n^2}{2}\,[j_{(ns)^2}+A_1+A_2+\cdots+A_{m-1}]\right\}^2\Big/\,n^2,\quad n=1,2,\ldots,M, \tag{88}$$

and

$$\Delta E^{(m)}_{(Zns)^2}=\left\{Z-\frac{n^2}{2}\,[j_{(ns)^2}+A_1+A_2+\cdots+A_{m-3}]-\frac{n^2}{4}\,[A_{m-2}+A_{m-1}]\right\}(A_{m-2}+A_{m-1}). \tag{89}$$

Notations in Eqs. (87)–(89) are defined as

$$A_1=\sum_{j<n}^{M+1}\frac{E^{\langle 2\rangle}_{(2js)^2}}{Z^j}\,k_{(ns)(js)}+\sum_{j>n}^{M+1}\frac{E^{\langle 2\rangle}_{[2(j-1)s]^2}}{Z^{j-1}}\,k_{(ns)(js)}\,, \tag{90}$$

$$A_2=\sum_{j<n}^{M+1}\frac{U^{(2)}(Z)\Delta E^{(3)}_{(2js)^2}}{Z^j}\,k_{(ns)(js)}+\sum_{j>n}^{M+1}\frac{U^{(2)}(Z)\Delta E^{(3)}_{[2(j-1)s]^2}}{Z^{j-1}}\,k_{(ns)(js)}\,, \tag{91}$$

$$\vdots$$

$$A_{m-1}=\sum_{j<n}^{M+1}\frac{U^{(m-1)}(Z)\Delta E^{(m)}_{(2js)^2}}{Z^j}\,k_{(ns)(js)}+\sum_{j>n}^{M+1}\frac{U^{(m-1)}(Z)\Delta E^{(m)}_{[2(j-1)s]^2}}{Z^{j-1}}\,k_{(ns)(js)}\,. \tag{92}$$

We can obtain the first-order approximate energy levels for $(Zns)^2$ states of heliumlike ions with charge Z [1]:

$$E^{\langle 1\rangle}_{(Zns)^2}=-\left[Z-\frac{n^2}{2}\,j_{(ns)^2}\right]^2\Big/\,n^2,\quad n=1,2,\ldots,M. \tag{93}$$

Clearly, as mentioned in Eq. (44), the nondegenerate condition is suitable for $(Zns)^2$ cases.

First we perform calculations in the second-order approximation in Eq. (88)

$$E^{\langle 2\rangle}_{(Zns)^2}=-\left\{Z-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j<n}^{M+1}\frac{E^{\langle 2\rangle}_{(2js)^2}}{Z^j}\,k_{(ns)(js)}+\sum_{j>n}^{M+1}\frac{E^{\langle 2\rangle}_{[2(j-1)s]^2}}{Z^{j-1}}\,k_{(ns)(js)}\right]\right\}^2\Big/\,n^2,$$
$$n=1,2,\ldots,M. \tag{94a}$$

We notice that if charge Z takes the value 2 on the left side of Eq. (94a), the energy sets $\{E^{\langle 2\rangle}_{(2ns)^2}\}$ and $\{E^{\langle 2\rangle}_{(2js)^2}\}$ become the same, i.e., the Eq. (94a) becomes a self-consistent equation:

$$E^{\langle 2\rangle}_{(2ns)^2}=-\left\{2-\frac{n^2}{2}\left[j_{(ns)^2}+\sum_{j<n}^{M+1}\frac{E^{\langle 2\rangle}_{(2js)^2}}{2^j}\,k_{(ns)(js)}+\sum_{j>n}^{M+1}\frac{E^{\langle 2\rangle}_{[2(j-1)s]^2}}{2^{j-1}}\,k_{(ns)(js)}\right]\right\}^2\Big/\,n^2,$$
$$n=1,2,\ldots,M. \tag{94b}$$

Thus, this equation can be solved in an exact manner with Hartree-Fock self-consistent field calculations [2]. Here we show how these sets $\{E^{\langle 2\rangle}_{(2ns)^2}\}$ can be obtained by an iterative technique using the method of successive approximation. We notice that the first-order approximation of the energy levels in Eq. (93) is just the initial solution. So we repeat iteratively substituting expression (93) into the right-hand side of Eq. (94b) until the difference between energy-level sets in the right- and left-hand sides in Eq. (94b) is less than a given small ε, i.e., the energy-level sets for the right- and left-hand sides lead to the same value, such that

$$\Delta E=|E^{(k+1)}_{(2ns)^2}-E^{(k)}_{(2ns)^2}|<\varepsilon \tag{95a}$$

and

$$E^{(k)}_{(2ns)^2}=E^{(k+1)}_{(2ns)^2}=E^{\langle 2\rangle}_{(2ns)^2}\,, \tag{95b}$$

where the integer k is the index of the repeated process. Thus the second-order approximate energy levels of an He atom are obtained for $(2ns)^2$ states.

Second we obtain the third-order approximation to the energy level

$$\Delta E^{(3)}_{(Zns)^2}=\left\{Z-\frac{n^2}{2}\,j_{(ns)^2}-\frac{n^2}{4}\,(A_1+A_2)\right\}(A_1+A_2),$$
$$n=1,2,\ldots,M, \tag{96}$$

and

$$E^{\langle 3\rangle}_{(Zns)^2}=\Delta E^{(3)}_{(Zns)^2}+E^{\langle 1\rangle}_{(Zns)^2}\,. \tag{97}$$

Similarly, we notice that if charge Z takes the value of 2 on the left-hand side of Eq. (96), the sets $\{\Delta E^{(3)}_{(2ns)^2}\}$ and

TABLE III. Comparison of other theoretical results of Refs. [7, 8, 12–17] for $(Z1s)^2$ ground states. (Negative signs are omitted for energies and the accuracy is estimated to be ±1 in the last digit in a.u.)

	Frankowski and Pekeris [14–17]		Freund and co-workers [8,13]	This work			Knight and Scherr [7]
Z	264 terms	Extrapolated	230 terms	$E^{\langle 2\rangle}_{(Z1s)^2}$	$E^{\langle 3\rangle}_{(Z1s)^2}$	$E^{\langle 4\rangle}_{(Z1s)^2}$	Third-order RSPT
1	0.527 751 036 35	0.527 751 016 38	0.527 751 015 3	0.521 569 7	0.527 745 4	0.527 751 0	0.523 97
2	2.903 724 377 032 6	2.903 724 377 033 3	2.903 724 377 034 0	2.903 797 6	2.903 714 9	2.903 724 4	2.903 32
3	7.279 913 412 666 0	7.279 913 412 667 8	7.279 913 412 669 2	7.281 298 6	7.279 912 9	7.279 913 4	7.279 77
4	13.655 566 238 428	13.655 566 238 421	13.655 566 238 423 5	13.657 561 3	13.655 128 5	13.655 566 2	13.655 49
5	22.030 971 580 235	22.030 971 580 239	22.030 971 580 242 7	22.033 321 4	22.030 883 8	22.030 971 5	22.030 93
6	32.406 246 601 889	32.406 246 601 894	32.406 246 601 898 4	32.408 828 7	32.406 387 3	32.406 246 2	32.406 22
7	44.781 445 148 763	44.781 445 148 768	44.781 445 148 772 6	44.784 194 9	44.781 749 7	44.781 444 5	44.781 42
8	59.156 595 122 749	59.156 595 122 755	59.156 595 122 757 8	59.159 465 8	59.157 020 6	59.156 597 1	59.156 58
9	75.531 712 363 950	75.531 712 363 957	75.531 712 363 959 4	75.534 683 2	75.532 234 2	75.531 707 8	75.531 70
10	93.906 806 515 025	93.906 806 515 031	93.906 806 515 037 4	93.909 851 1	93.907 402 0	93.906 806 9	93.906 80

$\{\Delta E^{(3)}_{(2js)^2}\}$ on both sides of Eq. (96) are the same; i.e., Eq. (96) now is self-consistent. As a first step, we set $\{\Delta E^{(3)}_{(2js)}=0\}$ on the right-hand side of Eq. (96). Then we obtain a nonzero set $\{\Delta E^{(3)}_{(2ns)^2}\}$ from the left-hand side of Eq. (96). Routinely we iterate this process until the set $\{\Delta E^{(3)}_{(2ns)^2}\}$ converges. By repeating this process, final results for the mth-order approximate energy levels of a helium atom can be obtained and the isoelectronic sequence as well.

If we limit the work to the computational ability of a personal computer, we can perform calculations of the fourth-order approximation to energy levels of heliumlike ions with $Z=1$ to 10. An infinite series of energy levels is truncated at $M=11$ terms and the iterative processes for all results show stable convergence. Energies for the ground states $(Z1s)^2$ with $Z=1$ to 10 are shown in Table III, in which comparisons are made with the works of Prankowski and Pekeris (264 terms), Freund (230 terms), and Knight and Scherr [third-order Rayleigh-Schrödinger perturbation theory (RSPT)]. As is well known, these latter works require a huge amount of computer time on very powerful computers. The fourth-order approximate energy levels of heliumlike ions

TABLE IV. The fourth-order approximate energy levels of heliumlike ions with $Z=1$ to 10 and $n=1$ to 11. The accuracy is estimated to be ±1 in the last digit (in a.u.).

Z	$E^{\langle 4\rangle}_{(Z1s)^2}$	$E^{\langle 4\rangle}_{(Z2s)^2}$	$E^{\langle 4\rangle}_{(Z3s)^2}$	$E^{\langle 4\rangle}_{(Z4s)^2}$	$E^{\langle 4\rangle}_{(Z5s)^2}$	$E^{\langle 4\rangle}_{(Z6s)^2}$	$E^{\langle 4\rangle}_{(Z7s)^2}$	$E^{\langle 4\rangle}_{(Z8s)^2}$	$E^{\langle 4\rangle}_{(Z9s)^2}$	$E^{\langle 4\rangle}_{(Z10s)^2}$	$E^{\langle 4\rangle}_{(Z11s)^2}$
1	−0.527 751 0	−0.184 364 3	−0.076 565 2	−0.040 138 8	−0.024 424 6	−0.016 383 5	−0.011 735 0	−0.008 809 4	−0.006 858 7	−0.005 483 8	−0.004 487 1
2	−2.903 724 4	−0.779 698 6	−0.338 791 1	−0.188 028 6	−0.119 336 1	−0.082 459 4	−0.060 374 4	−0.046 099 2	−0.036 359 7	−0.029 397 0	−0.024 267 0
3	−7.279 913 4	−1.879 663 1	−0.827 283 9	−0.462 994 5	−0.295 375 1	−0.204 751 7	−0.150 241 9	−0.114 908 9	−0.090 736 6	−0.073 440 0	−0.060 669 3
4	−13.655 566 2	−3.479 606 4	−1.538 408 2	−0.863 157 2	−0.551 505 5	−0.382 645 5	−0.280 951 1	−0.214 983 9	−0.169 814 8	−0.137 489 7	−0.113 605 3
5	−22.030 971 5	−5.579 456 3	−2.471 874 2	−1.388 372 3	−0.887 658 1	−0.616 105 4	−0.452 482 3	−0.346 312 3	−0.273 586 5	−0.221 540 9	−0.183 071 3
6	−32.406 246 2	−8.179 243 1	−3.627 615 9	−2.038 609 0	−1.303 819 4	−0.905 125 0	−0.664 832 0	−0.508 891 9	−0.402 050 4	−0.325 592 7	−0.269 066 7
7	−44.781 444 5	−11.278 985 0	−5.005 606 7	−2.813 855 6	−1.799 984 5	−1.249 701 7	−0.917 998 9	−0.702 722 2	−0.555 206 0	−0.449 644 7	−0.371 591 1
8	−59.156 597 1	−14.878 700 3	−6.605 835 9	−3.714 108 2	−2.376 151 8	−1.649 835 2	−1.211 982 7	−0.927 802 7	−0.733 053 2	−0.593 696 9	−0.490 644 6
9	−75.531 707 8	−18.978 387 8	−8.428 295 1	−4.739 363 7	−3.032 319 8	−2.105 524 5	−1.546 783 1	−1.184 133 3	−0.935 591 8	−0.757 749 1	−0.626 227 1
10	−93.906 806 9	−23.578 067 8	−10.472 985 3	−5.889 621 7	−3.768 489 1	−2.616 769 8	−1.922 400 0	−1.471 714 1	−1.162 821 9	−0.941 801 4	−0.778 338 5

TABLE V. Energy levels up to the fourth-order approximation of a helium atom for $(1s)^2$ to $(11s)^2$ states and the corresponding energy differences. The accuracy is estimated to be ±1 in the last digit.

ns	$\Delta E^{(3)}_{(2ns)^2}$	$\Delta E^{(4)}_{(2ns)^2}$	$E^{\langle 1\rangle}_{(2ns)^2}$	$E^{\langle 2\rangle}_{(2ns)^2}$	$E^{\langle 3\rangle}_{(2ns)^2}$	$E^{\langle 4\rangle}_{(2ns)^2}$
$(1s)$	−0.056 058 7	0.000 073 2	−2.847 656 2	−2.903 797 6	−2.903 714 9	−2.903 724 4
$(2s)$	−0.057 852 4	0.000 078 6	−0.721 836 0	−0.779 777 2	−0.779 688 4	−0.779 698 6
$(3s)$	−0.017 221 4	0.000 029 6	−0.321 565 8	−0.338 820 7	−0.338 787 2	−0.338 791 1
$(4s)$	−0.006 953 1	0.000 011 5	−0.181 074 0	−0.188 040 2	−0.188 027 1	−0.188 028 6
$(5s)$	−0.003 444 3	0.000 005 6	−0.115 891 1	−0.119 341 7	−0.119 335 4	−0.119 336 1
$(6s)$	−0.001 951 5	0.000 003 1	−0.080 507 5	−0.082 462 5	−0.082 459 0	−0.082 459 4
$(7s)$	−0.001 212 3	0.000 001 9	−0.059 161 8	−0.060 376 3	−0.060 374 1	−0.060 374 4
$(8s)$	−0.000 804 9	0.000 001 3	−0.045 294 1	−0.046 100 4	−0.046 099 0	−0.046 099 2
$(9s)$	−0.000 562 0	0.000 000 9	−0.035 797 6	−0.036 360 6	−0.036 359 6	−0.036 359 7
$(10s)$	−0.000 407 9	0.000 000 6	−0.028 989 1	−0.029 397 7	−0.029 397 0	−0.029 397 0
$(11s)$	−0.000 305 5	0.000 000 5	−0.023 961 5	−0.024 267 5	−0.024 267 0	−0.024 267 0

with $Z=1$ to 10 are shown in Table IV. We note a reasonable trend of the data in Table IV: As n increases, the energy levels decrease approximately as $1/n^2$; and as Z increases, the energies increase approximately as Z^2.

In this work the result for the $(22s)^2$ state of a helium atom in fourth-order approximation $E^{\langle 4\rangle}_{(22s)^2}=-0.779\,698$ a.u. can be compared to the experimental value of $-0.777\,816\,4\pm0.0014$ a.u. [9]. As is well known, such doubly excited autoionizing states are of theoretical and experimental interest and are difficult to calculate. Thus, a lack of comparative data is revealed in the literature. However, for the He $(2s)^2$ state, the result from this work is in good agreement with both theory and experiment.

Energy levels up to fourth-order approximations and the corresponding energy-level differences of a helium atom are shown in Table V. One can easily verify the results in this work using the data listed in Tables I, II, and V. The third-order approximate wave functions of $(1s)^2$ to $(11s)^2$ states

TABLE VI. Coefficients of the third-order approximate wave functions of H^- ion $(1s)^2$ to $(11s)^2$ states and the corresponding fourth-order approximate effective nuclear charges (in a.u.). Numbers in square brackets indicate powers of 10.

ns	$\alpha^{\langle 4\rangle}_{(1ns)^2}$	$\|(\alpha 1s)^2\rangle$	$\|(\alpha 2s)^2\rangle$	$\|(\alpha 3s)^2\rangle$	$\|(\alpha 4s)^2\rangle$	$\|(\alpha 5s)^2\rangle$	$\|(\alpha 6s)^2\rangle$
$(1s)$	0.72646[00]	0.10000[01]	−0.31998[01]	−0.10852[+01]	−0.42977[+00]	−0.22476[+00]	−0.13753[00]
$(2s)$	0.85875[00]	−0.31998[01]	0.10000[01]	−0.10852[+01]	−0.42977[+00]	−0.22476[+00]	−0.13753[00]
$(3s)$	0.83011[00]	−0.31998[01]	−0.10852[01]	0.10000[+01]	−0.42977[+00]	−0.22476[+00]	−0.13753[00]
$(4s)$	0.80139[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	0.10000[+01]	−0.22476[+00]	−0.13753[00]
$(5s)$	0.78142[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	0.10000[+01]	−0.13753[00]
$(6s)$	0.76799[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	−0.13753[+00]	0.10000[01]
$(7s)$	0.75830[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	−0.13753[+00]	−0.92768[−01]
$(8s)$	0.75087[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	−0.13753[+00]	−0.92768[−01]
$(9s)$	0.74536[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	−0.13753[+00]	−0.92768[−01]
$(10s)$	0.74053[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	−0.13753[+00]	−0.92768[−01]
$(11s)$	0.73684[00]	−0.31998[01]	−0.10852[01]	−0.42977[+00]	−0.22476[+00]	−0.13753[+00]	−0.92768[−01]
		$\|(\alpha 7s)^2\rangle$	$\|(\alpha 8s)^2\rangle$	$\|(\alpha 9s)^2\rangle$	$\|(\alpha 10s)^2\rangle$	$\|(\alpha 11s)^2\rangle$	$\|(\alpha 12s)^2\rangle$
		−0.92768[−01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.92768[−01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.92768[−01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.92768[−01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.92768[−01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.92768[−01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		0.10000[01]	−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.66778[−01]	0.10000[01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.66778[−01]	−0.50351[−01]	0.10000[+01]	−0.39328[−01]	−0.31551[−01]	−0.25881[−01]
		−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	0.10000[01]	−0.31551[−01]	−0.25881[−01]
		−0.66778[−01]	−0.50351[−01]	−0.39328[−01]	−0.31551[−01]	0.10000[01]	−0.25881[−01]

TABLE VII. Coefficients of the third-order approximate wave functions of the He atom for $(1s)^2$ to $(11s)^2$ states and the corresponding fourth-order approximate effective nuclear charges (in a.u.).

ns	$\alpha^{(4)}_{(2ns)^2}$	$\|(\alpha 1s)^2\rangle$	$\|(\alpha 2s)^2\rangle$	$\|(\alpha 3s)^2\rangle$	$\|(\alpha 4s)^2\rangle$	$\|(\alpha 5s)^2\rangle$	$\|(\alpha 6s)^2\rangle$	$\|(\alpha 7s)^2\rangle$	$\|(\alpha 8s)^2\rangle$	$\|(\alpha 9s)^2\rangle$	$\|(\alpha 10s)^2\rangle$	$\|(\alpha 11s)^2\rangle$	$\|(\alpha 12s)^2\rangle$
$(1s)$	0.170 40[01]	0.100 00[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(2s)$	0.176 60[01]	−0.145 02[01]	0.100 00[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(3s)$	0.174 62[01]	−0.145 02[01]	−0.194 06[00]	0.100 00[01]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(4s)$	0.173 45[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	0.100 00[01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(5s)$	0.172 73[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.100 00[01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(6s)$	0.172 29[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	0.100 00[01]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(7s)$	0.172 00[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	0.100 00[01]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(8s)$	0.171 77[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	0.100 00[01]	−0.179 89[−03]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(9s)$	0.171 61[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	0.100 00[01]	−0.709 51[−04]	−0.286 85[−04]	−0.118 40[−04]
$(10s)$	0.171 46[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	0.100 00[01]	−0.286 85[−04]	−0.118 40[−04]
$(11s)$	0.171 36[01]	−0.145 02[01]	−0.194 06[00]	−0.422 26[−01]	−0.117 27[−01]	−0.372 30[−02]	−0.128 67[−02]	−0.471 13[−03]	−0.179 89[−03]	−0.709 51[−04]	−0.286 65[−04]	0.100 00[01]	−0.118 40[−04]

and the corresponding fourth-order approximate effective nuclear charges for H$^-$ and He are shown in Tables VI and VII, respectively.

IV. DISCUSSION AND CONCLUSIONS

In this paper and a previous work [1], we have discussed the following: (i) concepts of a metastable period of formation in passing from an unperturbed to a perturbed system and the extended Schrödinger equation;

(ii) step-by-step approaches using equal-factors assumptions and iterative self-consistent equations;

(iii) predictions for excited autoionizing states over a large range of n (to $n=11$) of $(Zns)^2$ states of heliumlike ions.

A metastable period exists in very short time periods and the unperturbed wave functions vary until a balance position is reached. The equal-factors approach is developed in this work and is used to the extended Schrödinger equation in some specific cases. Step by step approaches are made in the equal-factors method. We assume that the coefficients $C^{\langle m-1\rangle}_{nj}$ can be expanded in terms of

$$C^{\langle m-1\rangle}_{nj}=C^{\langle 1\rangle}_{nj}+\Delta C^{(2)}_{nj}+\cdots+\Delta C^{(m-1)}_{nj}, \tag{98}$$

and the corresponding energy levels also can be expanded in terms of

$$E^{\langle m\rangle}_{n}=E^{\langle 1\rangle}_{n}+\Delta E^{(3)}_{n}+\cdots+\Delta E^{(m)}_{n}, \quad \text{if } m \text{ is odd}, \tag{99}$$

and

$$E^{\langle m\rangle}_{n}=E^{\langle 2\rangle}_{n}+\Delta E^{(4)}_{n}+\cdots+\Delta E^{(m)}_{n}, \quad \text{if } m \text{ is even}. \tag{100}$$

In particular, the equal-factors method leads to relations between the $(m-1)$th-order approximate coefficients set $\{\Delta C^{(m-1)}_{nj}(1)\}$ of charge $Z=1$ system and the corresponding mth-order approximate energy-level set $\{\Delta E^{(m)}_{Z*i}\}$ of the neutral system. This yields a series of powerful iterative self-consistent equations.

We see that higher-order calculations are based upon those of one order lower for the initial values in an iterative process. These ideas differ somewhat from traditional quantum theory in that any approximations deal with single-energy levels, and various-order approximations of energy corrections $\{\Delta E^{(m)}_{n}\}$ are independent of each other.

In particular, we note that in perturbation theory the $H'\ll 1$ is required, but in the PFSKB theory the equal-factors approach has no such requirements. As an example, the $(Zns)^2$ states of heliumlike ions are investigated. The equal-factors method is computationally simple and easy to implement, and very accurate numerical results are obtained for doubly excited autoionizing states over a large range of n (up to $n=11$). Such excited states are very troublesome to calculate in traditional theory due to the breakdown of the ordinary bound-state variational principle [18,19].

In this work the results for the $(22s)^2$ state of a helium atom in fourth-order approximation $E^{\langle 4\rangle}_{(22s)^2}=-0.779\,698$ a.u. are compared to the experimental value of $-0.777\,816\,4$ ± 0.0014 a. u. [9]. Although the paucity of comparative data makes it difficult to judge the overall accuracy of the present calculations, this work can provide a wide range of values to stimulate and test theory and experiment. The numerical calculations performed in this work yielded a relative error $\leqslant 10^{-5}$, and have been carried out on a personal computer with software written by the author.

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[1] Guo F. Chen, Phys. Rev. A **49**, 3234 (1994).
[2] D. R. Hartree, Proc. Camb. Philos. Soc. **24**, 89 (1928).
[3] A. Dalgarno and A. L. Stewart, Proc. R. Soc. London Ser. A **257**, 534 (1958).
[4] J. N. Silverman, Phys. Rev. A **28**, 498 (1983).
[5] E. Holien and J. Midtdal, J. Chem. Phys. **45**, 2209 (1966).
[6] P. O. Lowdin, J. Mol. Spectrosc. **3**, 48 (1959).
[7] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 430 (1963).
[8] Jonathan D. Baker, David E. Freund, Robert Nyden Hill, and John D. Morgan III, Phys. Rev. A **41**, 1247 (1990).
[9] Jorge M. Seminario and Frank C. Sanders, Phys. Rev. A **42**, 2562 (1990).
[10] P. Froelich and S. A. Alexander, Phys. Rev. A **42**, 2550 (1990).
[11] A. Dalgarno and A. L. Stewart. Proc. R. Soc. London Ser. A **257**, 534 (1960).
[12] H. Shull and P. O. Lowdin, J. Chem. Phys. **30**, 617 (1959); J. N. Silverman *et al.*, Phys. Rev. A **30**, 1554 (1984).
[13] David E. Freund, Batton D. Huxtable, and John D. Morgan III, Phys. Rev. A **29**, 980 (1984).
[14] K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966); **150**, 366E (1966).
[15] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[16] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
[17] C. L. Perkeris, Phys. Rev. **146**, 46 (1966).
[18] J. Midtdal, Phys. Rev. **138**, 1010 (1965).
[19] J. N. Silverman, Phys. Rev. A **23**, 441 (1981).