PHYSICAL REVIEW A VOLUME 49, NUMBER 5 MAY 1994

Principles of the first and second kind of balance in a varying-parameters method for eigenvalue problems in quantum mechanics

Guo F. Chen
Department of Physics, Southwest-China Teachers University, Chongqing 630715, Sichuan, People's Republic of China

(Received 1 June 1992; revised manuscript received 26 August 1993)

In this paper a method for eigenvalue problems in quantum mechanics is developed. Principles of the first and second kinds of balance in a varying-parameters method take advantage of the standard perturbation theory and the standard variational principle. According to this method, we not only obtain the best approach for obtaining eigenvalues and wave functions, but we also determine structures of a quantum system. The extended Hamiltonian in a varying-parameters method is different from a standard Hamiltonian. The parameters are inserted into a Hamiltonian by adding and subtracting appropriate terms which contain the essential parameters. Thus it becomes possible to study the inner structure of a quantum system by applying principles of balance. In order to interpret the physical meanings of balance parameters, several examples are described. Applications are also made to the helium atom, heliumlike ions, and the lithium atom. We theoretically predict energies and structure parameters and obtain good agreement with experimental data, especially for high-orbit electrons (clearly this is a character of perturbation theory). It is quite interesting that the theoretical predictions of energy levels of parahelium in the S state are lower than the energy levels of orthohelium and that theoretical predictions of singlet (triplet) states are close to the experimental data of triplet (singlet) states. It would seem that the experimental data of triplet and singlet are reversed. Is that possible?

PACS number(s): 03.65.−w

I. THEORY

We investigate a quantum system H_0 which acts under a perturbing potential H'. We are interested in a certain effect in the unperturbed system which is caused by the perturbing potential H', and this effect can be described by a number of n parameters $\boldsymbol{\lambda}=(\lambda_1,\ldots,\lambda_i\ldots,\lambda_n)$. For example, the electron screening effect [17] in an atomic system is caused by the perturbing potential of interactions between electrons and we can describe this electron screening effect by a number of parameters. As is well known, in this case these parameters are effective nuclear charges for each orbit electron. In general we can investigate certain effects which are similar to electron screening in an interesting quantum system.

One of the main tasks of this work is developing a method to determine these unknown parameters $\boldsymbol{\lambda}$ (values of the parameters $\boldsymbol{\lambda}$ are certain: we will give a proof later) and study this effect physically. Then it becomes possible to understand the inner structure of this quantum system.

Suppose the Schrödinger equation for a system under investigation is

$$H\Psi(\mathbf{x})=E\Psi(\mathbf{x}) \tag{1a}$$

and the traditionally original Hamiltonian consist of two parts:

$$H=H_0+H' , \tag{1b}$$

where H_0 is the traditional unperturbed Hamiltonian and H' the traditional perturbing Hamiltonian. We assume that the original Hamiltonian H, H_0, H', and wave function $\Psi(\mathbf{x})$ are defined in X space. The dimensions of X space will depend on the system investigated.

By convention we assume that there is no interaction between an unperturbed Hamiltonian H_0 and a perturbing potential H', when they form the total Hamiltonian, so that we may write Eq. (1b). But this is not true in general because an interaction between H_0 and H' exists and the subsystems H_0 and H' will act upon each other and may balance at a certain point.

Remark 1. As isolated Hamiltonians H_0 and H' form the total Hamiltonian H, because of the interaction between H_0 and H', both H_0 and H' are changed. Suppose that the isolated, unperturbed Hamiltonian H_0 contains a set of constants $\mathbf{C}$, acting under the perturbing potential H'. These shift to another a set of constants $\mathbf{C}'$, so that the unperturbed Hamiltonian H_0 is changed:

$$\Delta H_0=H_0(\mathbf{C}')-H_0(\mathbf{C}) .$$

On the other hand, the unperturbed Hamiltonian H_0 gives a reaction to the perturbing potential H' so that the perturbing potential H' is changed as well:

$$\Delta H'=H'-\Delta H_0 .$$

As the total Hamiltonian has been formed, the final unperturbed Hamiltonian $H_0(\mathbf{C}')$ and perturbing potential $H'(\mathbf{C}')$ are as follows:

$$\begin{aligned}H_0(\mathbf{C}')&=H_0(C)+\Delta H_0\\&=H_0(\mathbf{C}')\end{aligned}$$

and

$$\begin{aligned}H'(\mathbf{C}')&=H'-\Delta H_0\\&=H'+H_0(\mathbf{C})-H_0(\mathbf{C}')\ .\end{aligned}$$

Now the subsystems H_0 and H' will balance each other at the point $\mathbf{C}'$. We thus call $\mathbf{C}'$ the balance point of H_0 and H' and note that the total system formed is stable at the point $\mathbf{C}'$.

Unfortunately, the values of the balance point $\mathbf{C}'$ are unknown for the quantum system investigated. In order to determine the value of the unknown constant $\mathbf{C}'$, we split the original Hamiltonian H into two parts and technically insert parameters $\boldsymbol{\lambda}$ into the unperturbed Hamiltonian H_0 and the perturbation term of the Hamiltonian H'. We obtain an extension of the original Hamiltonian H, namely,

$$\mathcal{H}=H_0(\boldsymbol{\lambda})+H_1(\boldsymbol{\lambda})\ , \tag{2}$$

where $H_0(\boldsymbol{\lambda})$ is a new unperturbed Hamiltonian with n parameters and $H_1(\boldsymbol{\lambda})=H_0-H_0(\boldsymbol{\lambda})+H'$ is a new perturbing Hamiltonian with n parameters.

Remark 2. We add and subtract appropriate terms of $H_0(\boldsymbol{\lambda})$ in the original Hamiltonian H. Then applying the varying-parameter $\boldsymbol{\lambda}$ method, we create an n-dimensional Π space. Thus the original X space is extended into $X\oplus\Pi$ space. The extension of the Hamiltonian

$$\mathcal{H}=H_0(\boldsymbol{\lambda})+H_1(\boldsymbol{\lambda})\subset X\oplus\Pi \text{ space}$$

and the extension of the original Schrödinger equation (1a) is

$$\mathcal{H}\Psi(\mathbf{x};\boldsymbol{\lambda})=E(\boldsymbol{\lambda})\Psi(\mathbf{x};\boldsymbol{\lambda})\ , \tag{3}$$

where $\mathcal{H}$ and $\Psi(\mathbf{x};\boldsymbol{\lambda})$ belong to $X\oplus\Pi$ space and $E(\boldsymbol{\lambda})$ belongs to Π parameter space. Thus we are making three basic assumptions.

(i) We suppose that the eigenvalue $E^{(0)}(\boldsymbol{\lambda})$ of the extended unperturbation $H_0(\boldsymbol{\lambda})$ exists and depends on parameters $\boldsymbol{\lambda}$ in $X\oplus\Pi$ space:

$$H_0(\mathbf{x};\boldsymbol{\lambda})\Psi_{(\alpha\beta\ldots)}(\mathbf{x};\boldsymbol{\lambda})=E_{(\alpha\beta\ldots)}{}^{(0)}(\boldsymbol{\lambda})\Psi_{(\alpha\beta\ldots)}(\mathbf{x};\boldsymbol{\lambda})\ ,$$

where $(\alpha\beta\ldots)$ are the quantum numbers of the eigenstates. The unperturbed Hamiltonian $H_0(\boldsymbol{\lambda})$ contains the parameter $\boldsymbol{\lambda}=(\lambda_1,\ldots,\lambda_i,\ldots,\lambda_n)$, which depends on a $(\alpha\beta\ldots)$ state, and so they give certain physical meanings to these n parameters which are associated with the perturbing effect.

Remark 3: The extended unperturbed Hamiltonian $H_0(\boldsymbol{\lambda})$, perturbing potential $H_1(\boldsymbol{\lambda})$ and eigenfunctions $\{\Psi_{(\alpha\beta\ldots)}(\mathbf{x};\boldsymbol{\lambda})\}$ are defined in $X\oplus\Pi$ space, the corresponding eigenvalues $\{E_{(\alpha\beta\ldots)}(\boldsymbol{\lambda})\}$ is defined on Π parameter space.

(ii) We suppose that the extended perturbation $H_1(\boldsymbol{\lambda})$, which depends on parameters $\boldsymbol{\lambda}$, is an analytic function of $\boldsymbol{\lambda}$ in $X\oplus\Pi$ space.

(iii) A certain point $\boldsymbol{\lambda}^*$ exists in Π space. When solutions of the extended Schrödinger equation (3) take that point in $X\oplus\Pi$ space, the eigenvalue set $\{E_k(\boldsymbol{\lambda})\}$ of $\mathcal{H}$ and the corresponding eigenfunction set $\{\Psi_k(\mathbf{x};\boldsymbol{\lambda})\}$ of the kth state will identify with the eigenvalue set $\{E_k\}$ of the original H and the eigenfunction $\{\Psi_k(\mathbf{x})\}$ of kth state in Eq. (1a), namely,

$$E_k=E_k(\boldsymbol{\lambda})|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}^*}\ , \tag{4a}$$

$$\Psi_k(\mathbf{x})=\Psi_k(\mathbf{x};\boldsymbol{\lambda})|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}^*}\ , \tag{4b}$$

and

$$S_H=S_{\mathcal{H}}(\boldsymbol{\lambda})|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}^*}\ , \tag{4c}$$

where S_H is the original system and $S_{\mathcal{H}}$ is an extension of the original system.

We call this point $\boldsymbol{\lambda}^*$ in Π space "the identical point" (or the balance point of S_{H_0} and S_{H_1}). These parameters $\boldsymbol{\lambda}^*$ have certain physical meanings and are associated with some of the effects in the quantum system investigated. For example, in electron screening they are effective nuclear charges for each orbital electron.

In order to solve the extended Schrödinger equation (3), we have to extend standard perturbation theory from X space into $X\oplus\Pi$ space. We choose $\{\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})\}$, which is a complete set of orthonormal eigenfunctions of $H_0(\boldsymbol{\lambda})$, as the function basis in $X\oplus\Pi$ space. The corresponding set of eigenvalues is designated by $\{E_k^{(0)}(\boldsymbol{\lambda})\}$,

We take the same steps as in standard perturbation theory [18–20] for each parameter $\boldsymbol{\lambda}$ in Π space. Thus we can write for the kth state of the perturbed system in $X\oplus\Pi$ space

$$\Psi_k(\mathbf{x};\boldsymbol{\lambda})=\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})+\Psi_k^{(1)}(\mathbf{x};\boldsymbol{\lambda})+\Psi_k^{(2)}(\mathbf{x};\boldsymbol{\lambda})+\cdots\ ,$$

$$E_k(\boldsymbol{\lambda})=E_k^{(0)}(\boldsymbol{\lambda})+E_k^{(1)}(\boldsymbol{\lambda})+E_k^{(2)}(\boldsymbol{\lambda})+\cdots\ ,$$

and the sth-order perturbation function is expanded in the complete set of eigenfunctions of the unperturbed state, namely,

$$\Psi_k^{(s)}(\mathbf{x};\boldsymbol{\lambda})=\sum_{i=o}^{\infty}C_{ik}^{(s)}\Psi_i^{(0)}(\mathbf{x};\boldsymbol{\lambda})\ .$$

We choose the wave function of the perturbed state such that

$$\langle\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|\Psi_k(\mathbf{x};\boldsymbol{\lambda})\rangle=1\ ,$$

which means that all the perturbation wave functions $\Psi_k^{(s)}(\mathbf{x};\boldsymbol{\lambda})$ are orthogonal to $\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})$ for any parameter $\boldsymbol{\lambda}$ in $X\oplus\Pi$ space, namely,

$$\langle\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|\Psi_k^{(s)}(\mathbf{x};\boldsymbol{\lambda})\rangle=\delta_{0s}\ ,\quad s=0,1,2,\ldots\ .$$

Then we obtain the total energy for the kth state of the perturbed system:

$$\begin{aligned}E_k(\boldsymbol{\lambda})&=E_k^{(0)}(\boldsymbol{\lambda})+E_k^{(1)}(\boldsymbol{\lambda})+E_k^{(2)}(\boldsymbol{\lambda})+\cdots\\&=E_k^{(0)}(\boldsymbol{\lambda})+\sum_{s=1}^{\infty}E_k^{(s)}(\boldsymbol{\lambda})\\&=E_k^{(0)}(\boldsymbol{\lambda})+\Delta_k(\boldsymbol{\lambda})\ ,\end{aligned} \tag{5}$$

where

$$E_k^{(0)}(\boldsymbol{\lambda})=\langle\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|H_0(\boldsymbol{\lambda})|\Psi_k(\mathbf{x};\boldsymbol{\lambda})\rangle\ , \tag{6}$$

$$E_k^{(s)}(\boldsymbol{\lambda})=\langle\Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|H_1(\boldsymbol{\lambda})|\Psi_k^{(s-1)}(\mathbf{x};\boldsymbol{\lambda})\rangle\ ,$$

and

$$\Delta_k(\boldsymbol{\lambda})=\langle \Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|H_1(\boldsymbol{\lambda})|\Psi_k(\mathbf{x};\boldsymbol{\lambda})\rangle \ . \tag{7}$$

Remark 4. According to extended perturbation theory, we obtain the energy for the perturbed kth state in the extended Schrödinger equation (3),

$$\begin{aligned} E_k(\boldsymbol{\lambda})&=\langle \Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|H_0(\boldsymbol{\lambda})+H_1(\boldsymbol{\lambda})|\Psi_k(\mathbf{x};\boldsymbol{\lambda})\rangle \\ &=\langle \Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|\mathcal{H}|\Psi_k(\mathbf{x};\boldsymbol{\lambda})\rangle \ , \end{aligned} \tag{8}$$

where the extended Hamiltonian $\mathcal{H}$ is a constant in Π space, the integral is over all X space, and the potential energy $E_k(\boldsymbol{\lambda})$ is a function of parameters $\boldsymbol{\lambda}$ in Π parameter space.

Remark 5. Corresponding to assumption (iii) the integral equation (8) at the identical point $\boldsymbol{\lambda}^*$ converges to the energy of the original Schrödinger equation (1a). In general we assume that there corresponds an n-dimensional sphere around point $\boldsymbol{\lambda}^*$ such that the integral converges. The radius of convergence is $R\in[0,\infty]$.

Remark 6. The extended Hamiltonian $\mathcal{H}$ consists of two parts $H_0(\boldsymbol{\lambda})$ and $H_1(\boldsymbol{\lambda})$ in Π parameter space. This means that the extended system $S_{\mathcal{H}}(\boldsymbol{\lambda})$ is divided into two subsystem $S_{H_0}(\boldsymbol{\lambda})$ and $S_{H_1}(\boldsymbol{\lambda})$. Thus it is clear in Eqs. (6) and Eq. (7) that $H_0(\boldsymbol{\lambda})$ is the unique contributor of the potential $E_k^{(0)}(\boldsymbol{\lambda})$ and $H_1(\boldsymbol{\lambda})$ is the unique contributor of the potential $\Delta_k(\boldsymbol{\lambda})$. Thus we can define potential fields for the kth state in Π parameter space as follows:

$$E_S(\boldsymbol{\lambda})=\langle \Psi_k^{(0)}(\mathbf{x};\boldsymbol{\lambda})|H_S(\boldsymbol{\lambda})|\Psi_k(\mathbf{x};\boldsymbol{\lambda})\rangle \ , \tag{9}$$

where S represents $S_{\mathcal{H}}$, S_{H_0} or S_{H_1}, respectively, and $H_S(\boldsymbol{\lambda})$ is the responding Hamiltonian of S system.

If one is only interested in the Nth-order approximation to the eigenvalue $E_k^N(\boldsymbol{\lambda})$ for kth state, the energy eigenvalue is obtained from Eq. (8),

$$\begin{aligned} E_k^N(\boldsymbol{\lambda})&=E_k^{(0)}(\boldsymbol{\lambda})+\sum_{i=1}^{N} E^{(i)}(\boldsymbol{\lambda}) \\ &=E_k^{(0)}(\boldsymbol{\lambda})+\Delta_k^N(\boldsymbol{\lambda}) \ . \end{aligned} \tag{10}$$

In order to determine these unknown values of identical parameters (or the balance point) $\boldsymbol{\lambda}$, two means are developed in this work. One of them is called the principle of the first kind of balance: It is suitable for cases in which $H_0(\lambda)$ only has one parameter and the perturbation H' is very small.

(i) The principle of the first kind of balance. If a system is in the first kind of balance, the sum of ith-order perturbation energy will vanish at the balance points λ^*, namely

$$\sum_{i=1}^{N} E_k^{(i)}(\lambda^*)=0 \ . \tag{11}$$

Explanation: Because $H_1(\lambda)=H-H_0(\lambda)$ and $H_1(\lambda)$ is the unique contributor of the potential term $\sum_{i=1}^{N} E_k^{(i)}(\lambda)$, the potential of $S_{H_1}(\lambda)$ vanishes at point λ^*. That means the contributions of H and $H_0(\lambda)$ will balance each other at the point λ^* in Π parameter space. In general cases we have n parameters $\boldsymbol{\lambda}$ and the principle of the second kind of balance will be sufficient.

(ii) The principle of the second kind of balance. If a system is in the second kind of balance, the total extensive forces will vanish at the balance point $\boldsymbol{\lambda}'$, namely

$$\mathbf{g}_k(\boldsymbol{\lambda}')+\mathbf{h}_k(\boldsymbol{\lambda}')=\mathbf{0} \ . \tag{12}$$

The extensive forces $\mathbf{g}_k(\boldsymbol{\lambda})$ and $\mathbf{h}_k(\boldsymbol{\lambda})$ are defined in an n-dimensional Π space as follows:

$$\mathbf{h}_k(\boldsymbol{\lambda})=\left[-\frac{\partial E_k^{(0)}(\boldsymbol{\lambda})}{\partial \lambda_1},\ldots,-\frac{\partial E_k^{(0)}(\boldsymbol{\lambda})}{\partial \lambda_i},\ldots,-\frac{\partial E_k^{(0)}(\boldsymbol{\lambda})}{\partial \lambda_n}\right]$$

and

$$\mathbf{g}_k(\boldsymbol{\lambda})=\left[-\frac{\partial \Delta_k(\boldsymbol{\lambda})}{\partial \lambda_1},\ldots,-\frac{\partial \Delta_k(\boldsymbol{\lambda})}{\partial \lambda_i},\ldots,-\frac{\partial \Delta_k(\boldsymbol{\lambda})}{\partial \lambda_n}\right] .$$

The explanation is as follows. The standard Hamiltonian H can be decomposed into two parts $H_0(\boldsymbol{\lambda})$ and $H_1(\boldsymbol{\lambda})$. Responding to the original system, S_H is extended into two subsystem $S_{H_0}(\boldsymbol{\lambda})$ and $S_{H_1}(\boldsymbol{\lambda})$. The nth-order approximation total energy potential Eq. (10) consists of two parts. But $H_0(\boldsymbol{\lambda})$ is the unique contributor of the potential $E_k^{(0)}(\boldsymbol{\lambda})$ and $H_1(\boldsymbol{\lambda})$ is the unique contributor of the potential $\sum_{i=1}^{N} E_k^{(i)}(\boldsymbol{\lambda})$. Thus, physically the $E_k^{(0)}(\boldsymbol{\lambda})$ represents the potential of the subsystem $S_{H_0}(\boldsymbol{\lambda})$ and the term $\sum_{i=1}^{N} E_k^{(i)}(\boldsymbol{\lambda})$ represents the Nth-order approximation potential of the subsystem $S_{H_1}(\boldsymbol{\lambda})$ at a point $\boldsymbol{\lambda}$ in the n parameter Π space. The extensive force of the subsystem $S_{H_0}(\boldsymbol{\lambda})$ on point $\boldsymbol{\lambda}$ is $\mathbf{h}_k(\boldsymbol{\lambda})$ and the force of the subsystem $S_{H_1}(\boldsymbol{\lambda})$ on point $\boldsymbol{\lambda}$ is $\mathbf{g}_k(\boldsymbol{\lambda})$. The potential acts to keep the total system stable. Thus the condition (12) means that the two subsystems $S_{H_0}(\boldsymbol{\lambda})$ and $S_{H_1}(\boldsymbol{\lambda})$ will balance each other at point $\boldsymbol{\lambda}'$ in the n parameter Π space.

Physically this balance point $\boldsymbol{\lambda}'$ is identical to the point in assumption (iii). It is easy to rewrite Eq. (12) as

$$\frac{\partial E_k^{(0)}(\boldsymbol{\lambda})}{\partial \lambda_i}+\frac{\partial \Delta_k^N(\boldsymbol{\lambda})}{\partial \lambda_i}=0 \ , \quad i=1,2,\ldots,i,\ldots,n$$

or

$$E_k^N(\boldsymbol{\lambda}')=\min_{\{\lambda_i\}}\{E_k^{(0)}(\boldsymbol{\lambda})+\Delta_k^N(\boldsymbol{\lambda})\}|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}'}$$

if the balance is stable (we always assume that the balance is stable in the cases investigated here).

Suppose the initial value of $\boldsymbol{\lambda}$ is not equal to $\boldsymbol{\lambda}'$, because the total force $\mathbf{g}_k(\boldsymbol{\lambda})+\mathbf{h}_k(\boldsymbol{\lambda})$ does not vanish, under the interaction between H_0 and H'. The total system will then tend to the balance position. Therefore parameters $\boldsymbol{\lambda}$ automatically tend to $\boldsymbol{\lambda}'$. Once the parameters $\boldsymbol{\lambda}$ take the values of parameter $\boldsymbol{\lambda}'$, the total force vanishes at point $\boldsymbol{\lambda}'$. The extended system will then remain in the bottom of the potential well in Π parameter space. This means that the extended Hamiltonian is only identical to the original Hamiltonian H if parameters $\boldsymbol{\lambda}$ satisfy conditions (12). In other words, physically, the balance parameter $\boldsymbol{\lambda}^*$ determined so is the identical point in Π space.

Remark 7. We define a conventional point $\boldsymbol{\lambda}^T$ in Π space that is the point at which the extended unperturbed Hamiltonian $H_0(\boldsymbol{\lambda}^T)$ is equal to the initial unperturbed Hamiltonian H_0 and the extended perturbing $H_1(\boldsymbol{\lambda}^T)$ is equal to the initial perturbing Hamiltonian H'. We have to point out that the conventional point $\boldsymbol{\lambda}^T$ is not the balance point of subsystems of $H_0(\boldsymbol{\lambda})$ and $H_1(\boldsymbol{\lambda})$.

Remark 8. The energy eigenvalues $E_k(\boldsymbol{\lambda})$ for the kth state are different between the identical point $\boldsymbol{\lambda}^*$ and the conventional point $\boldsymbol{\lambda}^T$ in Eq. (8), namely,

$$E_k(\boldsymbol{\lambda}^T)\neq E_k(\boldsymbol{\lambda}^*) \ .$$

This means that the standard perturbation theory does not give the exact solutions of the original Schrödinger equation (1a). Why is this? The reason is that the initial H' is not the real perturbing potential for an investigated system. One can see this conclusion explicitly in the examples given in Sec. II.

If one considers the energy in first-order approximation and the ground state only, Eq. (12) is identical to

$$\min_{\{\lambda_i\}}\left\{\frac{\langle \psi(\mathbf{x},\boldsymbol{\lambda},|\mathcal{H}|\psi(\mathbf{x},\boldsymbol{\lambda})\rangle}{\langle\psi|\psi\rangle}\right\} .$$

As is well known, the above equation is the standard variational principle if one chooses the eigenfunction $\Psi^{(0)}_{(\alpha\beta\ldots)}(\boldsymbol{\lambda})$ as a trial function for a ground state.

We substitute the balance point $\boldsymbol{\lambda}'$ (i.e., the identical point) into Eq. (10). Finally the Nth-order approximation energy of the original Schrödinger equation is obtained:

$$E_{(\alpha\beta\ldots)}(\boldsymbol{\lambda}')=E^{(0)}_{(\alpha\beta\ldots)}(\boldsymbol{\lambda}')+\sum_{i=1}^{N}E^{(i)}(\boldsymbol{\lambda}') \ ,$$

where $(\alpha\beta\ldots)$ are the quantum numbers of the eigenstates.

Remark 9. The extended Schrödinger equation (3) plus the balance principles give us more knowledge about an interesting quantum system than does the original Schrödinger equation (1a).

II. EXAMPLES OF APPLYING PRINCIPLES OF THE FIRST AND THE SECOND KIND OF BALANCE TO ONE-PARAMETER PROBLEMS

A. Hydrogenlike atoms

In order to further interpret the physical meaning of parameter λ and to illustrate principles of the first and second kind of balance, we have investigated hydrogenlike atoms and three examples will be described.

The total Hamiltonian of hydrogenlike atoms is routinely divided into two parts and a parameter is inserted into each part, respectively,

$$H=H_0(\lambda)+H_1(\lambda) \ , \tag{13}$$

where the extended unperturbed Hamiltonian is

$$H_0(\lambda)=-\tfrac{1}{2}\nabla^2-\lambda/r \tag{14}$$

and the extended perturbing potential is

$$H_1(\lambda)=-(Z-\lambda)/r+H' \ . \tag{15}$$

We choose the nuclear charge as the varying parameter, based on the idea that any perturbing potential will cause nuclear charge screening, and change parameter λ until a new balance position is reached.

Example 1. The initial perturbing potential, the extended unperturbed Hamiltonian, and the extended perturbing potential

$$\begin{aligned}&H'=-\delta/r^2 \quad (0<\delta<1) \ ,\\ &H_0(\lambda)=-\tfrac{1}{2}\nabla^2-\frac{\lambda}{r} \ ,\\ &H_1(\lambda)=-\frac{Z-\lambda}{r}-\frac{\delta}{r^2} \ .\end{aligned} \tag{16}$$

The zeroth-order approximation and the first-order correction to the energy are

$$E_0(\lambda)=-\frac{\lambda^2}{2n^2} \ , \quad E^{(1)}(\lambda)=-\frac{(Z-\lambda)\lambda}{n^2}-\frac{\delta\lambda^2}{n^3(l+\frac{1}{2})} \ . \tag{17}$$

Using the principle of the first kind of balance, we obtain the root

$$E^{(1)}(\lambda)=0 \ , \quad \lambda^*=\frac{Z(l+\frac{1}{2})}{l+\frac{1}{2}-\delta/n} \tag{18}$$

and the first-order approximation to the energy can be obtained:

$$E_0(\lambda^*)=-\frac{Z^2}{2n'^2} \ , \quad n'=n-\frac{\delta}{l+\frac{1}{2}} \ . \tag{19}$$

With the principle of the second kind of balance, the root obtained is

$$\begin{aligned}&\frac{dE_1(\lambda)}{d\lambda}=\frac{d}{d\lambda}\left[-\frac{\lambda^2}{2n^2}-\frac{(Z-\lambda)\lambda}{n^2}-\frac{\delta\lambda^2}{n^3(l+\frac{1}{2})}\right]=0 \ ,\\ &\lambda^*=\frac{Z(l+\frac{1}{2})}{l+\frac{1}{2}-2\delta/n}\end{aligned} \tag{20}$$

and the energy is

$$\begin{aligned}&E_1(\lambda^*)=-\frac{Z^2}{2n'^2} \ ,\\ &n'=n\left[1-\frac{2\delta}{(l+\frac{1}{2})n}\right]^{1/2}\approx n-\frac{\delta}{l+\frac{1}{2}} \ .\end{aligned} \tag{21}$$

The exact solution [it is easy to obtain a radial equation $(R=u/r)$] is

$$-\tfrac{1}{2}u''+\left[\frac{l(l+1)}{2r^2}-\frac{1}{r}-\frac{\delta}{r^2}\right]u=Eu\ .$$

Setting

$$l(l+1)-2\delta=l'(l'+1)\ ,$$

we have a standard hydrogen radial equation

$$-\tfrac{1}{2}u''+\left[\frac{l'(l'+1)}{2r^2}-\frac{1}{r}\right]u=Eu\ .$$

Therefore

$$E_{nl}=-\frac{1}{2n'^2}\ ,\quad n'=n_r+l'+1\ . \tag{22}$$

Setting

$$l'=l+\Delta l\ , \tag{23}$$

$$\begin{aligned} n'&=n_r+l+\Delta l+1\\ &=n+\Delta l\ , \end{aligned} \tag{24}$$

from Eq. (23) we deduce without difficulty

$$l(l+1)-2\delta=l(l+1)+(2l+1)\Delta l+(\Delta l)^2\ . \tag{25}$$

Omitting $(\Delta l)^2$, we therefore obtain

$$\Delta l\approx-\delta/(l+\tfrac{1}{2}) \tag{26}$$

and

$$E_n=-\frac{1}{2n'^2}\ ,\quad n'=n-\delta/(l+\tfrac{1}{2})\ .$$

We obtain results as in Eqs. (19) and (21).

Example 2. The initial perturbing potential is

$$H'=-2/r\ . \tag{27}$$

For the principle of the first kind of balance, the root is

$$E^{(1)}(\lambda)=-\frac{(Z+2-\lambda)\lambda}{n^2}=0\ ,\quad \lambda^*=Z+2 \tag{28}$$

and the energy is

$$E_0(\lambda^*)=-\frac{(Z+2)^2}{2n^2}\ . \tag{29}$$

For the principle of the second kind of balance, the root is

$$\frac{d}{d\lambda}E_1(\lambda)=\frac{\lambda}{n^2}-\frac{Z+2}{n^2}=0\ ,\quad \lambda^*=Z+2 \tag{30}$$

and the energy is

$$E_1(\lambda^*)=-\frac{(Z+2)^2}{2n^2}\ . \tag{31}$$

In the exact solution, we obtain

$$E_n=-(Z+2)^2/2n^2\ . \tag{32}$$

We note that this is the same as Eqs. (29) and (31), while the solution of a standard Rayleigh-Schrödinger perturbation is

$$E_n^*=-Z^2/2n^2-2Z/n^2\ . \tag{33}$$

Example 3. For a uniformly charged sphere of a radius R, the initial perturbing potential is

$$H'=\begin{cases} Z\left[\dfrac{1}{r}+\dfrac{r^2}{2R^3}-\dfrac{3}{2R}\right]\ , & r\le R\\ 0,\quad r>R\ . \end{cases} \tag{34}$$

The condition of the first kind of balance for the (1*s*) orbit is

$$E^{(1)}(\lambda)=\tfrac{2}{5}Z^4R^2-(Z-\lambda)\lambda=0\ . \tag{35}$$

The root of Eq. (35) is

$$\lambda^*=\frac{Z}{2}+\left[\frac{Z^2}{4}-\frac{2}{5}Z^4R^2\right]^{1/2}\approx Z-\tfrac{2}{5}Z^3R^2 \tag{36}$$

and the corresponding energy eigenvalue is

$$\begin{aligned} E_0(\lambda^*)&=-\frac{Z^2}{8}[1+(1-\tfrac{8}{5}Z^2R^2)^{1/2}]^2\\ &\approx-\frac{Z^2}{2}+\frac{2}{5}Z^4R^2\ . \end{aligned} \tag{37}$$

The condition of the second kind of balance for the (1*s*) orbit is

$$\frac{d}{d\lambda}E_1(\lambda)=\frac{d}{d\lambda}\left\{-\frac{\lambda^2}{2}+\frac{2}{5}Z^4R^2-(Z-\lambda)\lambda\right\}=0\ . \tag{38}$$

We obtain the root $\lambda^*=Z$ and the corresponding energy eigenvalue

$$E_1(\lambda^*)=-\frac{Z^2}{2}+\frac{2}{5}Z^4R^2\ . \tag{39}$$

B. The harmonic oscillators

In this part we will follow the ideas above to study the behavior of the harmonic oscillators when acted upon by the perturbing potential H' and illustrate the interesting changes of the essential properties of the harmonic oscillator. The extended Hamiltonians are

$$H_0(\Omega)=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\tfrac{1}{2}m\Omega^2x^2 \tag{40}$$

and

$$H_1(\Omega)=\tfrac{1}{2}mw^2x^2-\tfrac{1}{2}m\Omega^2x^2+H'\ , \tag{41}$$

where the frequency Ω is a varying parameter which is proportional to k which is a force constant. This implies that the harmonic oscillator changes the essential force constant to balance the perturbing potential. We will discuss two examples.

Example 1. The initial perturbing potential is

$$H'=\frac{\lambda}{2}mw^2x^2 \tag{42}$$

and the extended unperturbed Hamiltonian and the energy eigenvalues are

$$H_0(\Omega)=-\frac{\hbar^2}{2m}\frac{d^2}{dX^2}+\frac{1}{2}m\Omega^2X^2\ ,$$
$$E_0(\Omega)=(n+\tfrac{1}{2})\hbar\Omega\ . \tag{43}$$

The perturbation term of the extended Hamiltonian with a parameter is

$$H_1(\Omega)=H'+\tfrac{1}{2}m\left[\frac{w^2}{\Omega^2}-1\right]\Omega^2X^2\ . \tag{44}$$

We start from extended perturbation theory and obtain the energy corrections up to the third-order approximation. Because the matrix elements

$$x_{n+1,n}=x_{n,n+1}=\left[\frac{n+1}{2}\frac{\hbar}{m\Omega}\right]^{1/2}\ , \tag{45}$$

therefore

$$H'_{nn}=[(1+\lambda)w^2/\Omega^2-1](n+\tfrac{1}{2})\hbar\Omega/2 \tag{46}$$

and

$$H'_{n,n+2}=H'_{n+2,n}$$
$$=\sqrt{(n+1)(n+2)}[(1+\lambda)w^2/\Omega^2-1]\hbar\Omega/4\ . \tag{47}$$

From Eqs. (46) and (47), it is easy to obtain the perturbation energies to third order:

$$E^{(1)}(\Omega)=H'_{nn}$$
$$=\tfrac{1}{2}\left[(1+\lambda)\frac{w^2}{\Omega^2}-1\right](n+\tfrac{1}{2})\hbar\Omega\ , \tag{48}$$

$$E^{(2)}(\Omega)=\frac{1}{2\hbar\Omega}[|H'_{n-2,n}|^2-|H'_{n+2,n}|^2]$$
$$=-\tfrac{1}{8}\left[(1+\lambda)\frac{w^2}{\Omega^2}-1\right]^2(n+\tfrac{1}{2})\hbar\Omega\ ,$$

$$E^{(3)}(\Omega)=\sum_l{}'\sum_k{}''\frac{H'_{nl}H'_{lk}H'_{kn}}{(E_n^{(0)}-E_l^{(0)})(E_n^{(0)}-E_k^{(0)})}$$
$$-H'_{nn}\sum_k{}'\frac{|H'_{kn}|^2}{(E_n^{(0)}-E_k^{(0)})^2} \tag{49}$$
$$=\tfrac{1}{16}\left[(1+\lambda)\frac{w^2}{\Omega^2}-1\right]^3(n+\tfrac{1}{2})\hbar\Omega\ , \tag{50}$$

where from Eqs. (46)–(50) the notation H' represents the extended perturbing potential $H_1(\Omega)$.

For the condition of the first kind of balance the first-order approximation to the energy eigenvalue is

$$E^{(1)}(\Omega)=0\ ,$$
$$\Omega^*=w(1+\lambda)^{1/2}\ , \tag{51}$$
$$E_0(\Omega^*)=(n+\tfrac{1}{2})\hbar w(1+\lambda)^{1/2}\ .$$

The second-order approximation to the energy eigenvalue is

$$E^{(1)}(\Omega)+E^{(2)}(\Omega)=0\ ,$$
$$\Omega^*=w(1+\lambda)^{1/2}\ , \tag{52}$$
$$E_0(\Omega^*)=(n+\tfrac{1}{2})\hbar w(1+\lambda)^{1/2}\ .$$

The third-order approximation to the energy eigenvalue is

$$E^{(1)}(\Omega)+E^{(2)}(\Omega)+E^{(3)}(\Omega)=0\ ,$$
$$\Omega^*=w(1+\lambda)^{1/2}\ , \tag{53}$$
$$E_0(\Omega^*)=(n+\tfrac{1}{2})\hbar w(1+\lambda)^{1/2}\ .$$

For the condition of the second kind of balance the first-order approximation to the energy eigenvalue is

$$\frac{d}{d\Omega}E_1(\Omega)=0\ ,$$
$$\Omega^*=w(1+\lambda)^{1/2}\ , \tag{54}$$
$$E_1(\Omega^*)=(n+\tfrac{1}{2})\hbar w(1+\lambda)^{1/2}\ .$$

The second-order approximation to the energy eigenvalue is

$$\frac{d}{d\Omega}E_2(\Omega)=0\ ,$$
$$\Omega^*=w(1+\lambda)^{1/2}\ , \tag{55}$$
$$E_2(\Omega^*)=(n+\tfrac{1}{2})\hbar w(1+\lambda)^{1/2}\ .$$

The third-order approximation to the energy eigenvalue is

$$\frac{d}{d\Omega}E_3(\Omega)=0\ ,$$
$$\Omega^*=w(1+\lambda)^{1/2}\ , \tag{56}$$
$$E_3(\Omega^*)=(n+\tfrac{1}{2})\hbar w(1+\lambda)^{1/2}\ .$$

The exact energy is

$$E_n=(n+\tfrac{1}{2})(1+\lambda)^{1/2}\hbar w$$
$$=(n+\tfrac{1}{2})(1+\lambda/2-\lambda^2/8+\lambda^3/16+\cdots)\hbar w\ . \tag{57}$$

We thus obtain results similar to Eqs. (51)–(56), but the standard Rayleigh-Schrödinger perturbation solution [18–24] up to third-order approximation is

$$E_n=E_0+E^{(1)}+E^{(2)}+E^{(3)}$$
$$=(n+\tfrac{1}{2})(1+\lambda/2-\lambda^2/8+\lambda^3/16)\hbar w\ . \tag{58}$$

Example 2. If the initial perturbing potential for the anharmonic oscillator [25–28,30] is

$$H'=\beta x^3\ , \tag{59}$$

we calculate the perturbation energies up to second order in the energy

$$E^{(1)}(\Omega)=\frac{1}{2}\left[\frac{w^2}{\Omega^2}-1\right](n+\tfrac{1}{2})\hbar\Omega\ , \tag{60}$$

$$E^{(2)}(\Omega)=-\frac{1}{8}\left[\frac{w^2}{\Omega^2}-1\right]^2(n+\tfrac{1}{2})\hbar\Omega$$
$$-\frac{15}{4}\frac{\beta\hbar^2}{m^3w^4}(n^2+n-\tfrac{11}{30})\ , \tag{61}$$

where w^4 appears instead of Ω^4 in last term as an approximation.

The condition of the first kind of balance is

$$x^2-6x+5-A=0\ , \tag{62}$$

where $x=w^2/\Omega^2$ and $A=-30(\beta\hbar/m^3w^5)\ (n^2+n-\tfrac{11}{30})/n+\tfrac{1}{2}$.

One of roots of Eq. (62) is

$$x=3-2\left[1+\frac{A}{4}\right]^{1/2}\approx 1-\frac{A}{4} \tag{63}$$

and

$$\Omega=w\left[1-\frac{A}{4}\right]^{-1/2}\approx w+\frac{wA}{8}\ . \tag{64}$$

So the energy is

$$E_0(\Omega^*)=(n+\tfrac{1}{2})\hbar w-\frac{15}{4}\frac{\beta\hbar^2}{m^3w^4}(n^2+n-\tfrac{11}{30})\ . \tag{65}$$

The condition of the second kind of balance is

$$\frac{d}{d\Omega}E_2(\Omega)=\frac{d}{d\Omega}\{E_0(\Omega)+E^{(1)}(\Omega)+E^{(2)}(\Omega)\}=0\ . \tag{66}$$

We deduce the Eq. (66)

$$\frac{3}{8}-\frac{3}{4}\frac{w^2}{\Omega^2}+\frac{3}{8}\frac{w^4}{\Omega^4}=0\ .$$

The reasonable root is $\Omega^*=w$, so the energy is

$$E_2(\Omega^*)=(n+\tfrac{1}{2})\hbar w-\frac{15}{4}\frac{\beta\hbar^2}{m^3w^4}(n^2+n-\tfrac{11}{30})\ . \tag{67}$$

C. The helium atom and heliumlike ions in one-parameter cases

Example 1. The $(1S)^a$ state of heliumlike ions has the Hamiltonian

$$H_0=-\frac{1}{2}\nabla_1^2-\frac{\lambda}{r_1}-\frac{1}{2}\nabla_2^2-\frac{\lambda}{r_2} \tag{68}$$

and

$$H_1=1/r_{12}-(z-\lambda)/r_1-(z-\lambda)/r_2\ . \tag{69}$$

The first-order approximation to the energy eigenvalue in $(1s)^2$ state is

$$E_{1s}(\lambda)=E_0(\lambda)+E^{(1)}(\lambda)$$
$$=-\lambda^2-2(z-\lambda)\lambda+5\lambda/8\ . \tag{70}$$

Using the principle of the first kind of balance, the balance condition is

$$5\lambda/8-2(z-\lambda)\lambda=0\ . \tag{71}$$

The root is found

$$\lambda^*=(z-\tfrac{5}{16})\ . \tag{72}$$

The energy in first-order approximation for the ground state is

$$E=-(z-\tfrac{5}{16})^2\ . \tag{73}$$

Using the principle of the second kind of balance, the balance condition is

$$\frac{d}{d\lambda}[-\lambda^2-2(z-\lambda)\lambda+5\lambda/8]=0\ . \tag{74}$$

The root of Eq. (74) is

$$\lambda^*=(z-\tfrac{5}{16}) \tag{75}$$

and the energy of the ground state is

$$E=-(z-\tfrac{5}{16})^2\ . \tag{76}$$

Example 2. For the $(2S)^2$ state of heliumlike ions the first-order approximation to the energy eigenvalue in the $(2s)^2$ state is

$$E_{2s}(\lambda)=E_0(\lambda)+E^{(1)}(\lambda)$$
$$=-\lambda^2/4-2(z-\lambda)\lambda/4+77\lambda/512\ , \tag{77}$$

where Coulombic integral $J=77\lambda/512$. On the one hand, the condition of the first kind of balance is

$$(z-\lambda)\lambda/2-77\lambda/512=0 \tag{78}$$

and the parameter of the first kind of balance is

$$\lambda^*=z-\tfrac{77}{256}\ . \tag{79}$$

On the other hand, the condition of the second kind of balance is

$$\frac{d}{d\lambda}E_{2s}(\lambda)=(\lambda-z)/2+\tfrac{77}{512}=0\ . \tag{80}$$

We can also obtain the parameter of the second kind of balance

$$\lambda^*=(z-\tfrac{77}{256})\ . \tag{81}$$

The principles of the first and the second kind of balance give the same value of

$$E=-(z-\tfrac{77}{256})^2/4\ . \tag{82}$$

For $z=2$, $E=-0.721\,836$ a.u., compared to the experimental value of $-0.778\,164+0.0014$ a.u. [31–33].

Example 3. For the helium atom in single excited non-S state suppose the helium atom is in a single excited state, an inner-shell electron has effective nuclear charges $Z=2$, and an outer-shell electron has effective nuclear charge λ. Applying the varying-parameter technique to the helium atom, we insert a parameter λ into H_0 and H_1:

$$H=H_0(\lambda)+H_1(\lambda)\ , \tag{83}$$

where the extended unperturbed Hamiltonian is

$$H_0(\lambda)=-\tfrac{1}{2}\nabla_1^2-\frac{2}{\hat{r}_{1s}}-\tfrac{1}{2}\nabla_2^2-\frac{\lambda}{\hat{r}_{nl}} \tag{84}$$

and the extended perturbation is

$$H_1(\lambda)=1/r_{12}-(2-\lambda)/\hat{r}_{nl}\ . \tag{85}$$

In Eqs. (84) and (85) the state operators $\hat{r}_{1s}$ and $\hat{r}_{n1}$ are defined by

$$(1/\hat{r}_{1s})|\cdots\Psi_{1s}(r_i)\cdots\rangle$$
$$=(1/r_i)|\cdots\Psi_{1s}(r_i)\cdots\rangle \tag{86}$$

and

$$(1/\hat{r}_{nl})|\cdots\Psi_{nl}(r_i)\cdots\rangle$$
$$=(1/r_j)|\cdots\Psi_{nl}(r_j)\cdots\rangle\ . \tag{87}$$

Since one electron is fixed in the ground state and the other is in an excited state, the eigenfunction for the unperturbed Hamiltonian $H_0(\lambda)$ is

$$|\Psi\rangle=[|(1s)_{z=2}(nl)_{z=\lambda}\rangle+\varepsilon|(nl)_{z=\lambda}(1s)_{z=2}\rangle]/\sqrt{2} \tag{88}$$

where $\varepsilon=+$ for singlet states, $\varepsilon=-$ for triplet states, and the wave function

$$|(1s)_{z=2}(nl)_{z=\lambda}\rangle=\Psi_{1s}^{Z=2}(\mathbf{r}_{ls})\Psi_{nl}^{z=\lambda}(\mathbf{r}_{nl})\ , \tag{89}$$

where Ψ is the hydrogenlike wave function. Obviously, under the new concept of state operator, the symmetric or antisymmetric wave function $|\Psi\rangle$ is the zeroth order eigenvector

$$H_0(\lambda)|\Psi\rangle=E_0(\lambda)|\Psi\rangle \tag{90}$$

and the eigenvalue of $H_0(\lambda)$ is

$$E_0(\lambda)=-(2+\lambda^2/2n^2)\ . \tag{91}$$

We calculate the first-order energy shift for $H_1(\lambda)$

$$\Delta^{(1)}(\lambda)=\langle\Psi|H_1(\lambda)|\Psi\rangle$$
$$=J(\lambda)-(2-\lambda)\lambda/n^2+\varepsilon K(\lambda)\ . \tag{92}$$

We define notations for Coulombic and exchange in-

TABLE I. Ionization potential of the helium atom in $1s2p$ terms followed by the numerical calculations of Eq. (92) for $3p$ triplet ($\varepsilon=-$) and $3p$ singlet ($\varepsilon=+$). Numbers in square brackets denote powers of ten.

ε	This work	Perturbation[a]	Experimental values[b]
	(eV)	(eV)	(eV)
+	3.328	3.325	3.368
−	3.543	3.533	3.623

λ	$\Delta(\lambda)$ (a.u.)	$E_0(\lambda)$ (a.u.)	$J(\lambda)$ (a.u.)	$K(\lambda)$ (a.u.)
		$1s3p$ triplet		
0.995 000[0]	−0.211 426[−2]	−0.205 500[1]	0.110 208[0]	0.121 350[−2]
0.100 000[1]	−0.158 972[−2]	−0.205 556[1]	0.110 756[0]	0.123 468[−2]
0.100 500[1]	−0.105 992[−2]	−0.205 611[1]	0.111 304[0]	0.125 608[−2]
0.101 000[1]	−0.524 918[−3]	−0.205 667[1]	0.111 853[0]	0.127 770[−2]
0.101 500[1]	0.153 421[−4]	−0.205 723[1]	0.112 401[0]	0.129 953[−2]
0.102 000[1]	0.560 828[−3]	−0.205 780[1]	0.112 949[0]	0.132 159[−2]
0.102 500[1]	0.111 152[−2]	−0.205 837[1]	0.113 497[0]	0.134 386[−2]
0.103 000[1]	0.166 747[−2]	−0.205 894[1]	0.114 045[0]	0.136 635[−2]
0.103 500[1]	0.222 862[−2]	−0.205 951[1]	0.114 593[0]	0.138 906[−2]
0.104 000[1]	0.279 505[−2]	−0.206 009[1]	0.115 140[0]	0.141 199[−2]
		$1s3p$ singlet		
0.965 000[0]	−0.296 949[−2]	−0.205 173[1]	0.106 915[0]	0.109 099[−2]
0.970 000[0]	−0.243 663[−2]	−0.205 227[1]	0.107 464[0]	0.111 086[−2]
0.975 000[0]	−0.189 811[−2]	−0.205 281[1]	0.108 013[0]	0.113 096[−2]
0.980 000[0]	−0.135 391[−2]	−0.205 336[1]	0.108 561[0]	0.115 127[−2]
0.985 000[0]	−0.804 020[−3]	−0.205 390[1]	0.109 110[0]	0.117 179[−2]
0.990 000[0]	−0.248 489[−3]	−0.205 445[1]	0.109 659[0]	0.119 254[−2]
0.995 000[0]	0.312 749[−3]	−0.205 500[1]	0.110 208[0]	0.121 350[−2]
0.100 000[1]	0.879 649[−3]	−0.205 556[1]	0.110 756[0]	0.123 468[−2]
0.100 500[1]	0.145 224[−2]	−0.205 611[1]	0.111 304[0]	0.125 608[−2]
0.101 000[1]	0.203 048[−2]	−0.205 667[1]	0.111 853[0]	0.127 770[−2]

[a] Reference [34].

[b] Reference [9].

tegrals as follows:

$$J=\langle (1s)_{z=2}(nl)_{z=\lambda}|(r_{12})^{-1}|(1s)_{z=2}(nl)_{z=\lambda}\rangle \ , \qquad (93)$$

$$K=\langle (1s)_{z=2}(nl)_{z=\lambda}|(r_{12})^{-1}|(nl)_{z=\lambda}(1s)_{z=2}\rangle \ . \qquad (94)$$

Thus we obtain the first-order approximation to the energy eigenvalue

$$E_{nl}(\lambda)=-(2+\lambda^2/2n^2)+J(\lambda)-(2-\lambda)\lambda/n^2+\varepsilon K(\lambda) \ . \qquad (95)$$

We wish now to apply the principle of the first kind of balance to the helium atom and a root λ^* will be found from

$$J(\lambda)-(2-\lambda)\lambda/n^2+\varepsilon K(\lambda)=0 \ . \qquad (96)$$

Then the energy level is obtained

$$E_{nl}(\lambda^*)=-(2+\lambda^{*2}/2n^2) \ . \qquad (97)$$

The comparisons with standard Rayleigh-Schrodinger perturbation theory for $1s2p$ terms are shown in Table I.

We now apply the principle of the second kind of balance to the helium atom. The condition of the second kind of balance is

$$\begin{aligned}\frac{d}{d\lambda}E_{n1}(\lambda)&=(\lambda-2)/n^2+\frac{d}{d\lambda}[J(\lambda)+\varepsilon K(\lambda)]\\&=0 \ . \qquad (98)\end{aligned}$$

Explicitly, we assume the helium atom is in the $(1s2p)$ state. The analytical forms of Coulombic integral and exchange integral are

$$J(\lambda)=\lambda/4-2\lambda^5/(4+\lambda)^5-\lambda^5/4(4+\lambda)^4 \qquad (99)$$

and

$$K(\lambda)=7\lambda^5/3(2+\lambda/2)^7 \ . \qquad (100)$$

So substituting J and K into Eq. (98), we obtain

$$\frac{\lambda-1}{4}-\frac{24\lambda^5+240\lambda^4+\lambda^6}{4(4+\lambda)^6}+\epsilon\frac{7}{3}\frac{10\lambda^4-\lambda^5}{\left[2+\frac{\lambda}{2}\right]^8}=0 \ . \qquad (101)$$

The numerical solutions of Eq. (101) are

$$\lambda=0.964\,622 \text{ a.u.}, \quad E=-2.122\,39 \text{ a.u.} \qquad (102)$$

for $\varepsilon=+$ and

$$\lambda=1.088\,03 \text{ a.u.}, \quad E=-2.130\,65 \text{ a.u.} \qquad (103)$$

for $\varepsilon=-$. In the $(1s)(3d)$ case, the explicit forms of Coulombic integral and exchange integral are

$$J(\lambda)=\frac{8^2}{81^2 2^6}\left[3^6\lambda+\frac{\lambda^7}{\left[2+\frac{\lambda}{3}\right]^6}-\frac{6\lambda^7}{\left[2+\frac{\lambda}{3}\right]^7}\right] \qquad (104)$$

and

$$K(\lambda)=\frac{8^2}{81^2}\frac{27}{16}\frac{1}{5}\frac{8\lambda^7}{\left[2+\frac{\lambda}{3}\right]^9} \ . \qquad (105)$$

Hence the equation of the second kind of balance is

$$\begin{aligned}\frac{d}{d\lambda}E_{3d}(\lambda)=\frac{\lambda-2}{9}+\varepsilon\frac{8^2}{81^2}\frac{27}{16}\frac{1}{5}&\left[\frac{56\lambda^6}{\left[2+\frac{\lambda}{3}\right]^9}-\frac{24\lambda^7}{\left[2+\frac{\lambda}{3}\right]^{10}}\right]\\&+\frac{8^2}{81^2 2^6}\left[3^6-\frac{7\lambda^6}{\left[2+\frac{\lambda}{3}\right]^6}+\frac{2\lambda^7}{\left[2+\frac{\lambda}{3}\right]^7}-\frac{42\lambda^6}{\left[2+\frac{\lambda}{3}\right]^7}+\frac{14\lambda^7}{\left[2+\frac{\lambda}{3}\right]^8}\right]=0 \ . \qquad (106)\end{aligned}$$

The numerical solutions of Eq. (106) are

$$\lambda=0.999\,524 \text{ a.u.}, \quad E=-2.055\,55 \text{ a.u.} \qquad (107)$$

for $\varepsilon=+$ and

$$\lambda=1.000\,85 \text{ a.u.}, \quad E=-2.055\,57 \text{ a.u.} \qquad (108)$$

for $\varepsilon=-$. It is convenient to solve Eqs. (96) and (98) numerically. We have calculated energy levels and balance parameter λ for P, D, F, and G terms. The results are shown in Table II.

Remark 1. Let ΔE be the difference between the energies of the first and second kind of balance. Then

$$\Delta E=E_N^{(0)}(\lambda^*)-E_N(\lambda')=0 \ , \quad \text{if } \lambda^*=\lambda' \qquad (109)$$

and

$$\Delta E=E_N^{(0)}(\lambda^*)-E_N(\lambda')=O[(\lambda^*-\lambda')^2] \quad \text{if } \lambda^*\neq\lambda', \qquad (110)$$

where $E_N^{(0)}(\lambda^*)$ and $E_N(\lambda')$ are Nth-order approximation energies of the first and the second kind of balance, λ^* is the point of the first kind of balance, and λ' is the point of the second of kind of balance.

For Taylor's expansion series of $E_N(\lambda^*)$ we find

$$\begin{aligned}E_N(\lambda^*)&=E_N(\lambda')+\frac{2}{\partial\lambda}E_N(\lambda')(\lambda^*-\lambda')\\&\quad+\frac{1}{2}\frac{z^2}{\partial\lambda^2}E_N(\lambda')(\lambda^*-\lambda')^2+\cdots \ , \qquad (111)\end{aligned}$$

and according to the conditions of the first and the second kind of balance equations (11) and (12), we obtain

$$E_N^{(0)}(\lambda^*)=E_N(\lambda')+\frac{1}{2}\frac{z^2}{\partial\lambda^2}E_N(\lambda')(\lambda^*-\lambda')^2+\cdots \ . \tag{112}$$

From this we conclude that the difference ΔE is of the order of $(\lambda^*-\lambda')^2$, namely,

$$\Delta E=O[(\lambda^*-\lambda')^2] \quad \text{if } \lambda^*\neq\lambda' \tag{113}$$

and the proof of Eq. (109) is obvious.

Remark 2. We now discuss the convergence of a perturbation expansion series. It is a familiar problem [29] to judge whether a perturbation expansion series is divergent or convergent. We have seen that solutions of the

TABLE II. Energy eigenvalues (in a.u.) of *P*, *D*, *F*, and *G* states for infinite-mass helium nuclei. (Negative signs are omitted for energies and the accuracy is estimated to be ±1 in the last digit.)

State	E^{a}	$E_{\min}{}^{b}$	Expt.[c]	λ^{a}	λ^{b}	Pekeris and co-workers[b]	Park *et al.*[e]	Cordes and Altick[f]
				Triplet $\varepsilon=-$				
2*p*	2.13019	2.13065	2.13318	1.020547	1.088	2.133164		2.132931
3*p*	2.05721	2.05731	2.05810	1.014817	1.056	2.058081		2.057954
4*p*	2.03197	2.03200	2.03235	1.011516	1.041	2.032324		2.032259
5*p*	2.02037	2.02038	2.02057	1.009101	1.031			
6*p*	2.01411	2.01411		1.008774	1.025			
7*p*	2.01034	2.01035		1.006402	1.022			
8*p*	2.00790	2.00791		1.005858	1.020			
9*p*	2.00624	2.00624		1.005344	1.017			
3*d*	2.05558	2.05557	2.055655	1.000181	0.999			
4*d*	2.03127	2.03127	2.03131	1.000240	0.999			
5*d*	2.02000	2.02001	2.02005	1.000000	0.999			
6*d*	2.01389	2.01389		1.000187	1.000			
7*d*	2.01021	2.01021		1.000245	1.000			
8*d*	2.00782	2.00782		1.000185	1.000			
9*d*	2.00618	2.00618		1.000312	1.000			
4*f*	2.03125	2.03125		1.000001	1.000			
5*f*	2.02000	2.02000		0.999992	1.000			
6*f*	2.01389	2.01389		1.000025	1.000			
5*g*	2.02000	2.02000		0.999987	0.996			
6*g*	2.01389	2.01389		0.999997	0.999			
				Singlet $\varepsilon=+$				
2*p*	2.12230	2.12239	2.12385	0.989153	0.965	2.123843	2.121460	2.123656
3*p*	2.05469	2.05470	2.05516	0.992211	0.975	2.055146	2.054055	2.055056
4*p*	2.03089	2.03090	2.03109	0.994257	0.980	2.031069	2.030575	2.03084
5*p*	2.01981	2.01981	2.01993	0.995168	0.983			
6*p*	2.01375	2.01378	2.01386	0.995085	0.985			
7*p*	2.01013	2.01014	2.01020	0.996565	0.987			
8*p*	2.00777	2.00777		0.997064	0.990			
9*p*	2.00614	2.00614		0.997588	0.991			
3*d*	2.05520	2.05555	2.055642	0.996803	1.000			
4*d*	2.03125	2.03125	2.03130	1.00000	1.000			
5*d*	2.02000	2.02000	2.02004	0.999249	1.000			
6*d*	2.01389	2.01389	2.01392	1.000040	1.000			
7*d*	2.01020	2.01021	2.01024	0.999878	1.000			
8*d*	2.00781	2.00781		1.000032	1.000			
9*d*	2.00618	2.00618		1.000175	1.000			
4*f*	2.03125	2.03125		1.000011	1.000			
5*f*	2.02000	2.02000		0.999987	1.000			
6*f*	2.01389	2.01389		1.000025	1.000			
5*g*	2.02000	2.02000		0.999987	1.000			
6*g*	2.01389	2.01389		0.999997	1.000			

[a] The first kind of balance.

[b] The second kind of balance.

[c] Reference [9].

[d] References [11–13].

[e] Reference [10].

[f] Reference [14].

TABLE III. The numerical values of energies (in a.u.) obtained from Eqs. (117), (19), (21), and (116).

δ	E^a	E^b	E^c	E^d	n^a	n^b	n^c	n^d
$Z=1,\ n=1,\ l=0$								
0.01	−0.520 00	−0.520 62	−0.520 83	−0.521 06	0.980 58	0.980 00	0.979 80	0.979 58
0.02	−0.540 00	−0.542 53	−0.543 48	−0.544 51	0.962 25	0.960 00	0.959 17	0.958 26
0.03	−0.560 00	−0.565 87	−0.568 18	−0.570 85	0.944 91	0.940 00	0.938 08	0.935 89
0.04	−0.580 00	−0.590 74	−0.595 24	−0.600 74	0.928 48	0.920 00	0.916 52	0.912 31
0.05	−0.600 00	−0.617 28	−0.625 00	−0.625 08	0.912 87	0.900 00	0.894 43	0.887 30
0.06	−0.620 00	−0.645 66	−0.657 89	−0.675 17	0.898 03	0.880 00	0.871 78	0.860 56
0.07	−0.640 00	−0.676 04	−0.694 44	−0.722 90	0.883 88	0.860 00	0.848 53	0.831 66
0.08	−0.660 00	−0.708 62	−0.735 29	−0.781 25	0.870 39	0.840 00	0.824 62	0.800 00
0.09	−0.680 00	−0.743 61	−0.781 25	−0.855 32	0.857 49	0.820 00	0.800 00	0.764 58
0.10	−0.700 00	−0.781 25	−0.833 33	−0.954 91	0.845 15	0.800 00	0.774 60	0.723 61
$Z=1,\ n=2,\ l=0$								
0.01	−0.127 50	−0.127 54	−0.127 55	−0.127 59	1.980 30	1.980 00	1.979 90	1.979 58
0.02	−0.130 00	−0.130 15	−0.130 21	−0.130 39	1.961 16	1.960 00	1.959 59	1.958 26
0.03	−0.132 50	−0.132 85	−0.132 98	−0.133 42	1.942 57	1.940 00	1.939 07	1.935 89
0.04	−0.135 00	−0.135 63	−0.135 87	−0.136 73	1.924 50	1.920 00	1.918 33	1.912 31
0.05	−0.137 50	−0.138 50	−0.138 89	−0.140 37	1.906 93	1.900 00	1.897 37	1.887 30
0.06	−0.140 00	−0.141 47	−0.142 05	−0.144 44	1.889 82	1.880 00	1.876 17	1.860 56
0.07	−0.142 50	−0.144 53	−0.145 35	−0.149 03	1.873 17	1.860 00	1.854 72	1.831 66
0.08	−0.145 00	−0.147 68	−0.148 81	−0.154 32	1.856 95	1.840 00	1.833 03	1.800 00
0.09	−0.147 50	−0.150 95	−0.152 44	−0.160 58	1.841 15	1.820 00	1.811 08	1.764 58
0.10	−0.150 00	−0.154 32	−0.156 25	−0.168 30	1.825 74	1.800 00	1.788 85	1.723 61
$Z=1,\ n=2,\ l=1$								
0.01	−0.125 83	−0.125 84	−0.125 84	−0.125 84	1.993 37	1.993 33	1.993 32	1.993 32
0.02	−0.126 67	−0.126 68	−0.126 69	−0.126 69	1.986 80	1.986 67	1.969 62	1.986 61
0.03	−0.127 50	−0.127 54	−0.127 55	−0.127 56	1.980 30	1.980 00	1.979 90	1.979 86
0.04	−0.128 33	−0.128 40	−0.128 42	−0.128 43	1.973 86	1.973 33	1.973 15	1.973 09
0.05	−0.129 17	−0.129 27	−0.129 31	−0.129 32	1.967 48	1.966 67	1.966 38	1.966 29
0.06	−0.130 00	−0.130 15	−0.130 21	−0.130 23	1.961 16	1.960 00	1.959 59	1.959 45
0.07	−0.130 83	−0.131 04	−0.131 12	−0.131 14	1.954 91	1.953 33	1.952 78	1.952 58
0.08	−0.131 67	−0.131 94	−0.132 04	−0.132 08	1.948 71	1.946 67	1.945 94	1.945 68
0.09	−0.132 50	−0.132 85	−0.132 98	−0.133 02	1.942 57	1.940 00	1.939 07	1.938 75
0.10	−0.133 33	−0.133 77	−0.133 93	−0.133 98	1.936 49	1.933 33	1.932 18	1.931 78
$Z=1,\ n=3,\ l=0$								
0.01	−0.056 30	−0.056 30	−0.056 31	−0.056 32	2.980 20	2.980 00	2.979 93	2.979 58
0.02	−0.057 04	−0.057 07	−0.057 08	−0.057 13	2.960 78	2.960 00	2.959 73	2.958 26
0.03	−0.057 78	−0.057 85	−0.057 87	−0.058 01	2.941 74	2.940 00	2.939 39	2.935 89
0.04	−0.058 52	−0.058 64	−0.058 69	−0.058 95	2.923 06	2.920 00	2.918 90	2.912 31
0.05	−0.059 26	−0.059 45	−0.059 52	−0.059 98	2.904 74	2.900 00	2.898 28	2.887 30
0.06	−0.060 00	−0.060 28	−0.060 39	−0.061 10	2.886 75	2.880 00	2.877 50	2.860 56
0.07	−0.060 74	−0.061 13	−0.061 27	−0.062 36	2.869 10	2.860 00	2.856 57	2.831 66
0.08	−0.061 48	−0.061 99	−0.062 19	−0.063 78	2.851 76	2.840 00	2.835 49	2.800 00
0.09	−0.062 22	−0.062 87	−0.063 13	−0.065 42	2.834 73	2.820 00	2.814 25	2.764 58
0.10	−0.062 96	−0.063 78	−0.064 10	−0.067 40	2.818 01	2.800 00	2.792 85	2.723 61
$Z=1,\ n=3,\ l=1$								
0.01	−0.055 80	−0.055 80	−0.055 80	−0.055 80	2.993 36	2.993 33	2.993 33	2.993 32
0.02	−0.056 05	−0.056 05	−0.056 05	−0.056 05	2.986 75	2.986 67	2.986 64	2.986 61
0.03	−0.056 30	−0.056 30	−0.056 31	−0.056 31	2.980 20	2.980 00	2.979 93	2.979 86
0.04	−0.056 54	−0.056 56	−0.056 56	−0.056 57	2.973 68	2.973 33	2.973 21	2.973 09
0.05	−0.056 79	−0.056 81	−0.056 82	−0.056 83	2.967 21	2.966 67	2.966 48	2.966 29
0.06	−0.057 04	−0.057 07	−0.057 08	−0.057 09	2.960 78	2.960 00	2.959 73	2.959 45
0.07	−0.057 28	−0.057 33	−0.057 34	−0.057 35	2.954 39	2.953 33	2.952 96	2.952 58
0.08	−0.057 53	−0.057 58	−0.057 60	−0.057 62	2.948 05	2.946 67	2.946 18	2.945 68
0.09	−0.057 78	−0.057 85	−0.057 87	−0.057 90	2.941 74	2.940 00	2.939 39	2.938 75
0.10	−0.058 02	−0.058 11	−0.058 14	−0.058 17	2.935 48	2.933 33	2.932 58	2.931 78

TABLE III. (*Continued.*)

δ	E^{a}	E^{b}	E^{c}	E^{d}	n^{a}	n^{b}	n^{c}	n^{d}
				$Z=1,\ n=3,\ l=2$				
0.01	−0.055 70	−0.055 70	−0.055 70	−0.055 70	2.996 01	2.996 00	2.996 00	2.996 00
0.02	−0.055 85	−0.055 85	−0.055 85	−0.055 85	2.992 03	2.992 00	2.991 99	2.991 99
0.03	−0.056 00	−0.056 00	−0.056 00	−0.056 00	2.988 07	2.988 00	2.987 98	2.987 97
0.04	−0.056 15	−0.056 15	−0.056 15	−0.056 15	2.984 13	2.984 00	2.983 96	2.983 95
0.05	−0.056 30	−0.056 30	−0.056 31	−0.056 31	2.980 20	2.980 00	2.979 93	2.979 92
0.06	−0.056 44	−0.056 46	−0.056 46	−0.056 46	2.976 28	2.976 00	2.975 90	2.975 88
0.07	−0.056 59	−0.056 61	−0.056 61	−0.056 61	2.972 39	2.972 00	2.971 87	2.971 84
0.08	−0.056 74	−0.056 76	−0.056 77	−0.056 77	2.968 50	2.968 00	2.967 83	2.967 79
0.09	−0.056 89	−0.056 91	−0.056 92	−0.056 92	2.964 64	2.964 00	2.963 78	2.963 74
0.10	−0.057 04	−0.057 07	−0.057 08	−0.057 08	2.960 78	2.960 00	2.959 73	2.959 67

[a] The standard Rayleigh-Schrödinger perturbation expansion.
[b] The first kind of balance perturbation expansion.
[c] The second kind of balance perturbation expansion.
[d] The exact solutions.

first and the second kind of balance are immediately convergent to the exact solutions in many of the examples shown above. In some of the examples, although they are not immediately convergent to the exact solutions, they converge faster than the standard Rayleigh-Schrodinger perturbation expansion. Such an example is a hydrogen-like atom with the initial perturbation potential Eq. (16)

$$H'=-\delta/r^2 \ .$$

To omit repeating steps shown previously, we start from Eq. (25)

$$l(l+1)-2\delta=l(l+1)+(2l+1)\Delta l+(\Delta l)^2 \ .$$

This will lead to a quadratic equation

$$x^2+(2l+1)x+2\delta=0 \ . \tag{114}$$

Therefore the root is

$$\Delta l=\frac{-(2l+1)+[(2l+1)^2-8\delta]^{1/2}}{2} \ . \tag{115}$$

The value thus obtained can be put into Eq. (26) and the exact energy is

$$E_N=-Z^2/2n'^2, \quad n'=n+\Delta l \ . \tag{116}$$

Also it is easy to obtain solutions for standard Rayleigh-Schrodinger perturbation

$$\begin{aligned} E_{n1}&=\langle nl|H|nl\rangle \\ &=-\frac{Z^2}{2n^2}+\langle nl|H'|nl\rangle \\ &=-\frac{Z^2}{2n^2}-\frac{\delta Z^2}{n^3(l+\frac{1}{2})} \\ &=-\frac{Z^2}{2n'^2} \ , \end{aligned} \tag{117}$$

where

$$n'=n\left[\frac{l+\frac{1}{2}}{l+\frac{1}{2}+2\delta/n}\right]^{1/2} \tag{118}$$

and

$$\left\langle nl\left|\frac{1}{r^2}\right|nl\right\rangle=\frac{Z^2}{n^3(l+\frac{1}{2})} \ . \tag{119}$$

To compare the convergence of the first and the second kind of balance perturbation expansion series and the standard Rayleigh-Schröndinger perturbation expansion series, we compute the numerical values of energies Eqs. (117), (19), (21), and (116). Comparisons are made in Table III by obtaining numerical values of the parameters Z, δ, n, and l. From Table III it is easy to conclude that

$$V_a<V_b<V_c \ , \tag{120}$$

where the V_a, V_b, and V_c are the speeds of convergence of three kinds of perturbation expansions.

We also can see that energies of the first and the second kind of balance both have the character of perturbation theory: As a particle goes to a high orbit, energies will be closer to exact energies.

Remark 3. It is obvious that the energies of the first and the second kind of balance will tend toward exact energies as a particle goes to high orbits. Clearly this is a character of perturbation theory. Thus the difference of balance parameters λ^* and λ' will tend toward zero for high orbits. For example, $\Delta\lambda$, the difference of balance parameter λ^* and λ' in Eq. (19) and (21), is

$$\Delta\lambda=-\frac{Z\delta}{[n(l+\frac{1}{2})-2\delta]\left[1-\dfrac{\delta}{n(l+\frac{1}{2})}\right]} \ , \tag{121}$$

where $\Delta\lambda=\lambda^*-\lambda'$,

$$\lambda^*=\frac{Z(l+\frac{1}{2})}{l+\frac{1}{2}-\delta/n} \ , \tag{122}$$

$$\lambda'=\frac{Z(l+\frac{1}{2})}{l+\frac{1}{2}-\dfrac{2\delta}{n}} \ , \tag{123}$$

and if n approaches infinity, then

$$\lim_{n\to\infty} \Delta\lambda = 0 \ . \tag{124}$$

III. THE STRUCTURE OF THE HELIUM ATOM AND HELIUMLIKE IONS: APPLICATIONS OF THE PRINCIPLE OF THE SECOND KIND OF BALANCE

A. The potential well of the helium atom and heliumlike ions

To apply the principle of the second kind of balance, let us assume that the extended Schrödinger equation for the helium atom and heliumlike ions is

$$\{-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2-\lambda_1/r_1-\lambda_2/r_2 + 1/r_{12}-(Z-\lambda_1)/r_1-(Z-\lambda_2)/r_2\} \times\Psi(\mathbf{r},\lambda_1,\lambda_2)=E(\lambda_1,\lambda_2)\Psi(\mathbf{r},\lambda_1,\lambda_2) \ , \tag{125}$$

where λ_1 and λ_2 are structure parameters of the helium atom and heliumlike ions, λ_1 is the effective nuclear charge for an inner-shell electron, and λ_2 is the effective nuclear charge for an outer-shell electron.

The energy with two parameters in first-order perturbation approximation is for non-s terms:

$$E(\lambda_1,\lambda_2)=-\left[\frac{\lambda_1^2}{2n_1^2}+\frac{\lambda_2^2}{2n_2^2}\right]-\frac{(Z-\lambda_1)\lambda_1}{n_1^2}-\frac{(Z-\lambda_2)\lambda_2}{n_2^2} +J(\lambda_1,\lambda_2)+\varepsilon k(\lambda_1,\lambda_2) \tag{126}$$

and for s terms

$$E(\lambda_1,\lambda_2)=-\left[\frac{\lambda_1^2}{2n_1^2}+\frac{\lambda_2^2}{2n_2^2}\right]+\frac{-\dfrac{(Z-\lambda_1)\lambda_1}{n_i^2}-\dfrac{(Z-\lambda_2)\lambda_2}{n_2^2}+J+\varepsilon[K-(2Z-\lambda_1-\lambda_2)\mathcal{J}_{SS}\mathcal{J}_{ZR}]}{1+\varepsilon\mathcal{J}_{SS}^2} \ , \tag{127}$$

where we assumed that one electron is fixed in the S state. Integrals $\mathcal{J}_{SS}(\lambda_1,\lambda_2)$ and $\mathcal{J}_{ZR}(\lambda_1,\lambda_2)$ are defined as follows:

$$\mathcal{J}_{SS}(\lambda_1,\lambda_2)=\int\Psi^*_{\lambda_1,n_1,s}(\mathbf{r},\lambda_1,\lambda_2)\Psi_{\lambda_2n_2s}(\mathbf{r},\lambda_1,\lambda_2)r^2dr\,d\Omega \ , \tag{128}$$

$$\mathcal{J}_{ZR}(\lambda_1,\lambda_2)=\int\Psi^*_{\lambda_1,n_1,s}(\mathbf{r},\lambda_1,\lambda_2)\Psi_{\lambda_2n_2s}(\mathbf{r},\lambda_1,\lambda_2)rdr\,d\Omega \ , \tag{129}$$

and the Coulomb integral

$$J(\lambda_1,\lambda_2)=\langle(nl)_{z=\lambda_1}(n'l')_{z=\lambda_2}|(1/r_{12})|(nl)_{z=\lambda_1}(n'l')_{z=\lambda_2}\rangle \tag{130}$$

and the exchange integral

$$K(\lambda_1,\lambda_2)=\langle(nl)_{z=\lambda_1}(n'l')_{z=\lambda_2}|(1/r_{12})|(n'l')z_{\lambda_2}(nl)_{z=\lambda_1}\rangle \ . \tag{131}$$

We can minimized the energy $E(\lambda_1,\lambda_2)$ on parameter λ_2 analytically. That is, we solve the equations

$$\frac{\partial}{\partial\lambda_2}E(\lambda_1,\lambda_2)=0 \tag{132}$$

and

$$\frac{\partial^2}{\partial\lambda_2^2}E(\lambda_1,\lambda_2)>0 \ . \tag{133}$$

Then

$$E_{\min}(\lambda_1)=E(\lambda_1,\lambda_2)|_{\lambda_2=\lambda_2'} \ , \tag{134}$$

where λ_2' is a root of Eq. (132).

We can minimize the energy $E(\lambda_1,\lambda_2)$ on parameter λ_2 numerically by a computer procedure also,

$$E_{\min}(\lambda_1)=\min[E(\lambda_1,\lambda_2)] \ . \tag{135}$$

Potential wells are defined by

$$\mathcal{W}_{\text{well}}(\lambda_1)=E_{\min}(\lambda_1) \tag{136}$$

and so they can be obtained by either an analytical or a numerical procedure.

We have calculated these potential wells Eq. (136) numerically for $1s2p$, $1s3d$, $1s2s$, $1s3s$, and $2s2p$. Results are tabulated in Table IV.

Remark. Two balance positions exist for the $1s2s$ triplet state. One is $E=-2.037\,43$, $\lambda_1=0.660\,00$, and $\lambda_2=2.095\,94$, and the other is $E=-2.166\,64$, $\lambda_1=2.000$, and $\lambda_2=1.5553$. More detailed calculations show that jump points exist for S terms. We list them below.

Term	λ_1 (a.u.)	$E_{\min}$ (a.u.)
	$\varepsilon=+$	
$1s2s$	0.118 14, 0.118 15	−0.640 877, −0.260 184
$1s3s$	0.023 933, 0.023 934	−0.247 906, −0.583 064
	$\varepsilon=-$	
$1s2s$	0.022 56, 0.022 57	−0.521 727, −0.185 257
$1s3s$	0.052 137 4, 0.052 137 5	−0.269 71, −0.252 048

Except for the above jump points, the potential curves are continuous.

B. The structure of the helium atom and heliumlike ions

As is well known, the effective nuclear charges plays an important role in the structure of atoms. Applying the

TABLE IV. $E_{\min}(\lambda_1)$ (in a.u.) calculated from Eq. (135). Numbers in square brackets denote powers of ten.

λ_1	$E_{\min}(\lambda_1)$	$E_{\min}(\lambda_1+0.2)$	$E_{\min}(\lambda_1+0.4)$	$E_{\min}(\lambda_1+0.6)$	$E_{\min}(\lambda_1+0.8)$
			1*s*2*p* $\varepsilon=+$		
0.2	−0.680 765[0]	−0.877 322[0]	−0.113 516[1]	−0.139 396[1]	−0.161 598[1]
1.2	−0.179 796[1]	−0.193 955[1]	−0.204 076[1]	−0.210 169[1]	−0.212 239[1]
2.2	−0.210 292[1]	−0.204 333[1]	−0.194 364[1]	−0.180 389[1]	−0.162 408[1]
3.2	−0.140 424[1]	−0.114 436[1]	−0.844 463[0]	−0.504 545[0]	−0.124 612[0]
			1*s*2*p* $\varepsilon=-$		
0.2	−0.723 621[0]	−0.988 563[0]	−0.124 213[1]	−0.146 855[1]	−0.166 526[1]
1.2	−0.183 041[1]	−0.196 147[1]	−0.205 611[1]	−0.211 279[1]	−0.213 065[1]
2.2	−0.210 922[1]	−0.204 822[1]	−0.194 750[1]	−0.180 698[1]	−0.162 659[1]
3.2	−0.140 629[1]	−0.114 606[1]	−0.845 878[0]	−0.505 734[0]	−0.125 619[0]
			1*s*3*d* $\varepsilon=+$		
0.2	−0.451 865[0]	−0.774 705[0]	−0.107 492[1]	−0.133 524[1]	−0.155 540[1]
1.2	−0.173 547[1]	−0.187 551[1]	−0.197 553[1]	−0.203 554[1]	−0.205 555[1]
2.2	−0.203 555[1]	−0.197 555[1]	−0.187 555[1]	−0.173 555[1]	−0.155 555[1]
3.2	−0.133 555[1]	−0.107 555[1]	−0.775 555[0]	−0.435 555[0]	−0.555 553[−1]
			1*s*3*d* $\varepsilon=-$		
0.2	−0.475 097[0]	−0.784 372[0]	−0.107 793[1]	−0.133 639[1]	−0.155 590[1]
1.2	−0.173 572[1]	−0.187 564[1]	−0.197 560[1]	−0.203 558[1]	−0.205 557[1]
2.2	−0.203 557[1]	−0.197 556[1]	−0.187 558[1]	−0.173 556[1]	−0.155 556[1]
3.2	−0.133 556[1]	−0.107 556[1]	−0.775 557[0]	−0.435 556[0]	−0.555 561[−1]
			1*s*2*s* $\varepsilon=+$		
0.2	−0.430 297[0]	−0.811 158[0]	−0.114 281[1]	−0.142 562[1]	−0.166 020[1]
1.2	−0.184 760[1]	−0.198 965[1]	−0.208 912[1]	−0.214 889[1]	−0.217 039[1]
2.2	−0.215 365[1]	−0.209 824[1]	−0.200 380[1]	−0.187 005[1]	−0.169 683[1]
3.2	−0.148 399[1]	−0.123 147[1]	−0.939 194[0]	−0.607 126[0]	−0.235 235[0]
			1*s*2*s* $\varepsilon=-$		
0.2	−0.128 074[1]	−0.187 431[1]	−0.203 384[1]	−0.201 458[1]	−0.197 604[1]
1.2	−0.197 962[1]	−0.203 120[1]	−0.209 932[1]	−0.214 941[1]	−0.216 662[1]
2.2	−0.214 611[1]	−0.208 610[1]	−0.198 579[1]	−0.184 481[1]	−0.166 294[1]
3.2	−0.133 787[1]	−0.107 700[1]	−0.776 525[0]	−0.436 272[0]	−0.561 612[−1]
			1*s*3*s* $\varepsilon=+$		
0.2	−0.441 608[0]	−0.794 342[0]	−0.107 025[1]	−0.133 889[1]	−0.156 431[1]
1.2	−0.174 712[1]	−0.188 808[1]	−0.198 814[1]	−0.204 815[1]	−0.206 858[1]
2.2	−0.204 950[1]	−0.199 081[1]	−0.189 242[−1]	−0.175 424[1]	−0.157 621[1]
3.2	−0.135 828[1]	−0.110 043[1]	−0.802 642[0]	−0.464 889[0]	−0.871 125[−1]
			1*s*3*s* $\varepsilon=-$		
0.2	−0.620 117[0]	−0.885 052[0]	−0.111 817[1]	−0.137 804[1]	−0.159 001[1]
1.2	−0.175 937[1]	−0.189 105[1]	−0.198 668[1]	−0.204 475[1]	−0.206 377[1]
2.2	−0.204 298[1]	−0.198 203[1]	−0.188 076[1]	−0.173 905[1]	−0.155 684[1]
3.2	−0.133 422[1]	−0.107 104[1]	−0.767 349[0]	−0.423 132[0]	−0.310 131[−1]
			2*s*2*p* $\varepsilon=+$		
0.2	−0.545 344[0]	−0.587 874[0]	−0.626 866[0]	−0.656 059[0]	−0.673 084[0]
1.2	−0.678 606[0]	−0.674 381[0]	−0.662 528[0]	−0.645 474[0]	−0.626 441[0]
2.2	−0.610 250[0]	−0.592 900[0]	−0.567 578[0]	−0.532 907[0]	−0.488 497[0]
3.2	−0.434 190[0]	−0.369 913[0]	−0.295 628[0]	−0.211 314[0]	−0.116 963[0]
			2*s*2*p* $\varepsilon=-$		
0.2	−0.549 882[0]	−0.596 129[0]	−0.633 782[0]	−0.665 337[0]	−0.693 332[0]
1.2	−0.717 844[0]	−0.737 066[0]	−0.748 963[0]	−0.752 204[0]	−0.746 121[0]
2.2	−0.730 439[0]	−0.705 089[0]	−0.670 096[0]	−0.625 528[0]	−0.571 469[0]
3.2	−0.508 000[0]	−0.435 191[0]	−0.353 094[0]	−0.261 738[0]	−0.161 126[0]

principle of the second kind of balance to the first-order perturbation energy Eqs. (126) and (127), we can determine these balance parameters λ_1 and λ_2 numerically. We can predict the structure parameters and energy levels for nuclear charges Z and configurations n,l,m and obtain good agreement with experiment. However, $\lambda_1=2$ and $\lambda_2=1$ are no longer obvious.

Explicitly we first investigate the simplest cases of the helium atom in the configurations of $(1s)(2p)$ and $(1s)(3d)$. From Eq. (126) we obtain the first-order approximation to the energy eigenvalue from the extended perturbation theory:

$$\begin{aligned} E_{nl}(\lambda_{1s},\lambda_{nl}) = & -\left[\frac{\lambda_{1s}^2}{2}+\frac{\lambda_{nl}^2}{2n^2}\right]+J(\lambda_{1s},\lambda_{nl}) \\ & -(2-\lambda_{1s})\lambda_{1s}-\frac{(2-\lambda_{nl})\lambda_{nl}}{n^2} \\ & +\varepsilon k(\lambda_{1s},\lambda_{nl}) . \end{aligned} \tag{137}$$

According to the principle of the second kind of balance, the associated equations are

$$\frac{\partial}{\partial\lambda_{1s}} E_{nl}(\lambda_{1s},\lambda_{nl})=0 , \tag{138}$$

$$\frac{\partial}{\partial\lambda_{nl}} E_{nl}(\lambda_{1s},\lambda_{nl})=0 . \tag{139}$$

In the $(1s)(2p)$ case, the analytical forms of $J(\lambda_{1s},\lambda_{2p})$ and $K(\lambda_{1s},\lambda_{2p})$ are as follows:

$$J(\lambda_{1s},\lambda_{2p})=\frac{\lambda_{2p}}{4}-\frac{\lambda_{1s}\lambda_{2p}^5}{(2\lambda_{1s}+\lambda_{2p})^5}-\frac{\lambda_{2p}^5}{4(2\lambda_{1s}+\lambda_{2p})^4} \tag{140}$$

and

$$K(\lambda_{1s},\lambda_{2p})=\frac{7}{24}\frac{\lambda_{1s}^3\lambda_{2p}^5}{\left[\lambda_{1s}+\frac{\lambda_{2p}}{2}\right]^7} . \tag{141}$$

So we obtain the explicit form of Eqs. (138) and (139)

$$\lambda_{1s}-2+\frac{\lambda_{2p}^5}{(2\lambda_{1s}+\lambda_{2p})^5}+\frac{10\lambda_{1s}\lambda_{2p}^5}{(2\lambda_{15}+\lambda_{2p})^6}+\varepsilon\frac{7}{24}\left[\frac{3\lambda_{1s}^2\lambda_{2p}^5}{(\lambda_{1s}+\lambda_{2p/2})^7}-\frac{7\lambda_{1s}^3\lambda_{2p}^5}{(\lambda_{1s}+\lambda_{2p/2})^8}\right]=0 , \tag{142}$$

$$\begin{aligned} & \frac{\lambda_{2p}-1}{4}-\frac{5\lambda_{1s}\lambda_{2p}^4}{(2\lambda_{1s}+\lambda_{2p})^5}+\frac{5\lambda_{1s}\lambda_{2p}^5}{(2\lambda_{1s}+\lambda_{2p})^6}-\frac{5\lambda_{2p}^4}{4(2\lambda_{1s}+\lambda_{2p})^4}+\frac{\lambda_{2p}^5}{(2\lambda_{1s}+\lambda_{2p})^5}+\varepsilon\frac{7}{24} \\ & \qquad \left[\frac{5\lambda_{15}^3\lambda_{2p}^4}{\left[\lambda_{1s}+\frac{\lambda 2p}{2}\right]^7}-\frac{7\lambda_{1s}^3\lambda_{2p}^5}{2\left[\lambda_{1s}+\frac{\lambda_{2p}}{2}\right]^8}\right]=0 . \end{aligned} \tag{143}$$

The numerical solutions of Eqs. (142) and (143) are

$\lambda_{1s}=2.003\,024\,3$ a.u.,

$\lambda_{2p}=0.964\,730$ a.u.,

$E=-2.122\,39$ a.u.

for $\varepsilon=+$ and

$\lambda_{1s}=1.991\,186$ a.u.,

$\lambda_{2p}=1.089\,15$ a.u.,

$E=-2.130\,69$ a.u

for $\varepsilon=-$.

In the other simple case $(1s)(3d)$, the analytical forms for J and K are as follows:

$$\begin{aligned} J(\lambda_{1s},\lambda_{3d})=\frac{8^2}{81^2 2^6} & \left[3^6\lambda_{3d}-\frac{\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^6}\right. \\ & \left. -\frac{3\lambda_{1s}\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^7}\right] \end{aligned} \tag{144}$$

and

TABLE V. Non-S term single excited states (in a.u.).

	λ_1 [a]	λ_2 [a]	$E_{\min}$ [a]	Expt. [b]
		Singlet $\varepsilon=+$		
$1s2p$	2.0032	0.9650	2.122 39	2.123 86
$1s3p$	2.0000	0.9750	2.054 70	2.055 16
$1s4p$	2.0000	0.9875	2.030 90	2.031 09
$1s5p$	2.0000	0.9900	2.019 81	2.019 93
$1s6p$	2.0000	0.9900	2.013 78	2.013 86
$1s7p$	2.0000	0.9900	2.010 14	2.010 20
$1s3d$	1.9988	1.0000	2.055 55	2.055 64
$1s4d$	2.0000	1.0000	2.031 25	2.031 30
$1s5d$	2.0000	1.0000	2.020 00	2.020 04
$1s6d$	2.0000	1.0000	2.013 89	2.013 92
$1s7d$	2.0000	1.0000	2.010 21	2.010 24
		Triplet $\varepsilon=-$		
$1s2p$	1.9915	1.0875	2.130 69	2.133 18
$1s3p$	2.0000	1.0560	2.057 31	2.058 10
$1s4p$	2.0000	1.0410	2.032 00	2.032 35
$1s5p$	2.0000	1.0312	2.020 38	2.020 57
$1s6p$	2.0000	1.0250	2.014 11	
$1s7p$	2.0000	1.0220	2.010 35	
$1s3d$	2.0000	1.0000	2.055 57	2.055 655
$1s4d$	2.0000	1.0000	2.031 27	2.031 31
$1s5d$	2.0000	1.0000	2.020 01	2.020 05

[a] This work

[b] Reference [9].

TABLE VI. S-term single excited states (in a.u.). A comparison with these theroetical predictions suggests that the experimental data of the triplet and singlet in the S terms are reversed. Can it be possible?

	λ_1[a]	λ_2[a]	$E_{\min}$[a]	Expt.[b]
		Singlet $\varepsilon=+$		
$1s2s$	2.0128	0.9256	2.170 47	2.145 980
$1s3s$	2.0031	0.9243	2.068 59	2.061 291
$1s4s$	2.0025	0.9406	2.036 66	2.033 607
$1s5s$	2.0013	0.9406	2.022 73	2.021 200
$1s6s$	2.0000	0.9500	2.015 46	2.014 589
$1s7s$	2.0000	0.9547	2.011 19	2.010 653
		Triplet $\varepsilon=-$		
$1s2s$	1.9925	1.5500	2.166 64	2.175 241
$1s3s$	1.9956	1.3925	2.063 78	2.068 709
$1s4s$	1.9963	1.2938	2.033 90	2.036 537
$1s5s$	1.9975	1.2359	2.021 08	2.022 64
$1s6s$	2.0000	1.1938	2.014 42	
$1s7s$	2.0000	1.1750	2.010 49	

[a] This work.
[b] Reference [9].

$$K(\lambda_{1s},\lambda_{3d})=\frac{8^2}{81^2}\frac{27}{16}\frac{1}{5}\frac{\lambda_{1s}^3\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^9}\ . \tag{145}$$

TABLE VII. Non-S-terms double excited states (in a.u.). λ_1 and λ_2 are the effective nuclear charges for inner-shell and outer-shell electrons, respectively.

	λ_1	λ_2	$E_{\min}$
	Singlet $\varepsilon=+$		
$2s2p$	1.2066	1.9931	0.678 611
$2s3p$	1.9200	1.3500	0.562 284
$2s4p$	1.9725	1.2250	0.533 740
$2s5p$	1.9900	1.1750	0.521 176
$2s6p$	1.9950	1.1375	0.514 540
$2s7p$	1.9937	1.1094	0.510 605
$2s3d$	2.0025	0.9750	0.554 746
$2s4d$	2.0000	0.9875	0.530 894
$2s5d$	2.0000	1.0000	0.519 816
$2s6d$	2.0000	1.0000	0.513 785
$2s7d$	2.0000	1.0000	0.510 141
	Triplet $\varepsilon=-$		
$2s2p$	1.7704	1.6969	0.752 302
$2s3p$	1.9800	1.2250	0.573 943
$2s4p$	1.9925	1.1500	0.538 087
$2s5p$	1.9950	1.1000	0.523 301
$2s6p$	1.9975	1.1000	0.515 746
$2s7p$	2.0025	1.1000	0.511 360
$2s3d$	1.9750	1.1000	0.558 649
$2s4d$	1.9900	1.1015	0.532 695
$2s5d$	1.9950	1.0781	0.520 748
$2s6d$	1.9950	1.0000	0.514 324
$2s7d$	1.9975	1.0000	0.510 478

TABLE VIII. S-terms double excited states (in a.u.). λ_1 and λ_2 are the effective nuclear charges for inner-shell and outer-shell electrons, respectively.

	λ_1	λ_2	$E_{\min}$
	Singlet $\varepsilon=+$		
$2s3s$	1.9800	1.1156	0.584 998
$2s4s$	1.9925	1.0781	0.543 306
$2s5s$	1.9950	1.0594	0.526 058
$2s6s$	2.0041	1.0563	0.517 357
$2s7s$	2.0000	1.0500	0.512 379
	Triplet $\varepsilon=-$		
$2s3s$	1.9900	1.6484	0.582 870
$2s4s$	1.9900	1.4813	0.539 921
$2s5s$	1.9950	1.3859	0.523 691
$2s6s$	1.9950	1.3121	0.515 773
$2s7s$	2.0000	1.2500	0.511 278

Similarly, the associated equation is

$$\begin{aligned}\lambda_{1s}-2+\frac{8^2}{81^2 2^6}&\left[\frac{3\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^7}+\frac{21\lambda_{1s}\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^8}\right]\\ +\varepsilon\frac{8^2}{81^2}\frac{27}{16}\frac{1}{5}&\left[\frac{3\lambda_{1s}^2\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^9}-\frac{9\lambda_{1s}^3\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^{10}}\right]=0\ ,\end{aligned} \tag{146}$$

$$\begin{aligned}\frac{\lambda_{3d}-2}{9}+\frac{8^2}{81^2 2^6}&\left[3^6-\frac{7\lambda_{3d}^6}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^6}+\frac{2\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^7}\right.\\ &\left.-\frac{21\lambda_{1s}\lambda_{3d}^6}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^7}+\frac{7\lambda_{1s}\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^8}\right]\\ +\varepsilon\frac{8^2}{81^2}\frac{27}{16}\frac{1}{5}&\left[\frac{7\lambda_{1s}^3\lambda_{3d}^6}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^9}-\frac{3\lambda_{1s}^3\lambda_{3d}^7}{\left[\lambda_{1s}+\frac{\lambda_{3d}}{3}\right]^{10}}\right]=0\ .\end{aligned} \tag{147}$$

We determine the roots and the corresponding energy E numerically from the above equations:

$\lambda_{1s}=2.000\,021\,81$ a.u.,

$\lambda_{3d}=0.999\,524$ a.u.,

$E=-2.055\,55$ a.u.

for $\varepsilon=+$ and

$$\lambda_{1s}=1.999\,96 \text{ a.u.},$$

$$\lambda_{3d}=1.000\,85 \text{ a.u.},$$

$$E=-2.055\,57 \text{ a.u.}$$

for $\varepsilon=-$.

The structures of the helium atom and heliumlike ions has been investigated numerically for some interesting cases. The results are shown in Table V for non-S terms, in Table VI for S terms in single excited states in Table VII for non-S terms, and in Table VIII for S terms in double excited states. We also have tabulated the results of calculations for heliumlike ions in $2s2p$ and $1s2s$ states in Tables IX and X. Negative signs are omitted for energies and the accuracy is estimated to be ±1 in last digit. The results are for an infinite mass heliumlike nucleus.

IV. THE STRUCTURE OF THE LITHIUM ATOM: APPLICATIONS OF THE PRINCIPLE OF THE SECOND KIND OF BALANCE

A. The potential well of the lithium atom

Let us assume that the extended Schrödinger equation for the lithium atom is

TABLE IX. Energy levels (in a.u.) of heliumlike ions for $2s2p$.

Z	λ_1[a]	λ_2[a]	$E_{\min}$[a]	Projected[b]	Expt.
			Singlet $\varepsilon=+$		
2	1.2066	1.9931	0.678 61	0.692 54	0.693 71±0.000 55[c] 0.692 94±0.000 37[d]
3	2.2575	2.9562	1.730 35	1.757 01	1.756 5±0.00 2[e] 1.756±0.001[f]
4	3.3110	3.9125	3.285 64	3.318 89	
5	4.3838	4.8681	5.342 45	5.379 58	
6	5.5000	5.8250	7.900 1	7.939 62	
7	6.3800	6.8575	10.958 2	10.999 27	
8	7.3900	7.8475	14.516 4	14.558 67	
9	8.4000	8.8450	18.574 7	18.618 64	
10	9.4000	9.8375	23.133 1	23.176 97	
11	10.4100	10.8375	28.191 5		
12	11.4100	11.8325	33.749 9		
13	12.4100	12.8250	39.808 4		
14	13.4100	13.8250	46.366 9		
15	14.4200	14.825	53.425 4		
			Triplet $\varepsilon=-$		
2	1.7704	1.6969	0.752 30	0.761 471	0.7605±0.0011[g]. 0.7609±0.0011[h]
3	2.7686	2.6999	1.869 47	1.879 384	1.877±0.001[i] 1.881±0.02[j]
4	3.900	3.6900	3.485 15	3.496 955	
5	4.7800	4.7000	5.603 83	5.614 376	
6	5.7800	5.7025	8.221 01	8.231 723	
7	6.7800	6.7025	11.338 2	11.349 027	
8	7.7800	7.7025	14.955 4	14.966 302	
9	8.7800	8.7025	19.072 6	19.083 526	
10	9.7800	9.7050	23.689 8	23.700 775	
11	10.7800	10.7025	28.806 9		
12	11.7800	11.7050	34.424 1		
13	12.7800	12.7050	40.543 1		
14	13.7800	13.7025	47.158 5		
15	14.7800	14.7050	54.275 7		

[a] This work.
[b] Reference [1].
[c] Reference [2].
[d] Reference [3].
[e] Reference [4].
[f] Reference [5].
[g] Reference [6].
[h] Reference [7].
[i] Reference [5].
[j] Reference [8].

TABLE X. Energy levels (in a.u.) of heliumlike ions for 1*s*2*s*.

Z	λ_1	λ_2	$E_{\min}$
	Singlet $\varepsilon=+$		
2	2.013	0.925	2.17047
3	3.030	1.679	5.09061
4	4.030	2.463	9.25707
5	5.040	3.264	14.6707
6	6.040	4.088	21.3323
7	7.040	4.928	29.2421
8	8.040	5.778	38.4005
9	9.050	6.625	48.8078
10	10.050	7.498	60.4641
	Triplet $\varepsilon=-$		
2	1.993	1.555	2.16664
3	3.000	2.570	5.10258
4	4.010	3.580	9.28913
5	5.010	4.584	14.7259
6	6.010	5.587	21.4128
7	7.020	6.589	29.3497
8	8.020	7.588	38.5368
9	9.020	8.593	48.9738
10	10.020	9.593	60.6608

$$\left\{-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\tfrac{1}{2}\nabla_3^2-\frac{\lambda_1}{r_1}-\frac{\lambda_1}{r_2}-\frac{\lambda_2}{r_3}+\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right.$$
$$\left.-\frac{3-\lambda_1}{r_1}-\frac{3-\lambda_1}{r_2}-\frac{3-\lambda_2}{r_3}\right\}\Psi(\mathbf{r},\lambda_1,\lambda_2)$$
$$=E(\lambda_1,\lambda_2)\Psi(\mathbf{r},\lambda_1,\lambda_2)\ , \qquad (148)$$

where λ_1 is effective nuclear charge for the inner-shell electrons and λ_2 is the effective nuclear charge for an outer-shell electron. We apply the principle of the second kind of balance to the above equation and the antisymmetrical wave function is

$$\Psi=\frac{1}{\sqrt{6}}\begin{vmatrix} u(1)\alpha(1) & u(2)\alpha(2) & u(3)\alpha(3)\\ u(1)\beta(1) & u(2)\beta(2) & u(3)\beta(3)\\ v(1)\alpha(1) & v(2)\alpha(2) & v(3)\alpha(3)\end{vmatrix}\ , \qquad (149)$$

where $u(1)$ is a wave function for the ground state, $v(1)$ is a wave function for an excited state, and $\alpha(1)$ and $\beta(1)$ are spin wave functions corresponding to $\pm\hbar/2$, respectively.

The first-order perturbation approximation to the expectation value of the energy is

$$\langle\Psi|E|\Psi\rangle=\langle\Psi|H|\Psi\rangle\ . \qquad (150)$$

After the summation of spins, we obtain [15]

$$\int\int\int d\tau_1 d\tau_2 d\tau_3\{u(1)u(2)v(3)-v(1)u(2)u(3)\}$$
$$\times(H-E)u(1)u(2)v(3)=0\ . \qquad (151)$$

We have defined the notation

$$\tilde{E}=\int\int\int d\tau_1 d\tau_2 d\tau_3 u(1)u(2)v(3)Hu(1)u(2)v(3)\ , \qquad (152)$$

$$\mathcal{E}=\int\int\int d\tau_1 d\tau_2 d\tau_3 v(1)u(2)u(3)Hu(1)u(2)v(3)\ , \qquad (153)$$

$$\mathcal{J}_{SS}=\int d\tau_1 v(1)u(1)\ . \qquad (154)$$

Finally, the first-order perturbation approximation to the energy of the lithium atom is

$$E=\frac{\tilde{E}-\mathcal{E}}{1-\mathcal{J}_{SS}^2}\ . \qquad (155)$$

For non-*s* terms

$$E(\lambda_1,\lambda_2)=-\left[\frac{\lambda_1^2}{n_1^2}+\frac{\lambda_2^2}{2n_2^2}\right]+J(\lambda_1,\lambda_1)-\frac{2(3-\lambda_1)\lambda_1}{n_1^2}$$
$$-\frac{(3-\lambda_2)\lambda_2}{n_2^2}+2J(\lambda_1,\lambda_2)-k(\lambda_1,\lambda_2) \qquad (156)$$

and for *s* terms

$$E(\lambda_1,\lambda_2)=-\left[\frac{\lambda_1^2}{n_1^2}+\frac{\lambda_2^2}{2n_2^2}\right]+\left\{J(\lambda_1,\lambda_1)-\frac{2(3-\lambda_1)\lambda_1}{n_1^2}-\frac{(3-\lambda_2)\lambda_2}{n_2^2}+2J(\lambda_1,\lambda_2)\right.$$
$$\left.+(6-\lambda_1-\lambda_2)\mathcal{J}_{SS}\mathcal{J}_{ZR}+\frac{(3-\lambda_1)\lambda_1\mathcal{J}_{SS}^2}{n_1^2}-2\mathcal{J}_{SS}Y(\lambda_1,\lambda_2)-K(\lambda_1,\lambda_2)\right\}\Big/(1-\mathcal{J}_{SS}^2)\ ,$$
$$(157)$$

where we assumed that two electrons are fixed in the S state and $Y(\lambda_1\lambda_2)$ is an integral which is defined by

$$Y(\lambda_1,\lambda_2)=\int\int d\tau d\tau'\frac{u^2(\mathbf{r})u(\mathbf{r}')v(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ . \qquad (158)$$

We minimize the energy $E(\lambda_1,\lambda_2)$ and the potential well which depends on λ_1 is obtained by numerical procedures

$$E_{\min}(\lambda_1)=\min[E(\lambda_1,\lambda_2)]\ . \qquad (159)$$

We have calculated these potential wells Eq. (159) numerically for $(1s)^2 2p$, $(1s)^2 3d$, and $(2s)^2 2p$. Results are shown in Table XI.

TABLE XI. $E_{\mathrm{min}}(\lambda_1)$ (in a.u.) calculated from Eq. (159). Numbers in square brackets denote powers of ten.

λ_1	E_{min} (λ_1)	E_{min} $(\lambda_1+0.1)$	E_{min} $(\lambda_1+0.2)$	E_{min} $(\lambda_1+0.3)$	E_{min} $(\lambda_1+0.4)$
			$(1s)^2 2p$		
1.6	−0.618 019[1]	−0.638 486[1]	−0.657 020[1]	−0.673 602[1]	−0.688 219[1]
2.1	−0.700 863[1]	−0.711 526[1]	−0.720 205[1]	−0.726 896[1]	−0.731 597[1]
2.6	−0.734 305[1]	−0.735 020[1]	−0.733 739[1]	−0.730 463[1]	−0.725 191[1]
3.1	−0.717 921[1]	−0.708 654[1]	−0.697 389[1]	−0.684 126[1]	−0.668 864[1]
			$(1s)^2 3d$		
1.6	−0.609 561[1]	−0.630 310[1]	−0.649 059[1]	−0.665 808[1]	−0.680 557[1]
2.1	−0.693 307[1]	−0.704 057[1]	−0.712 807[1]	−0.719 556[1]	−0.724 306[1]
2.6	−0.727 056[1]	−0.727 806[1]	−0.726 556[1]	−0.723 306[1]	−0.718 056[1]
3.1	−0.710 806[1]	−0.701 556[1]	−0.690 306[1]	−0.677 056[1]	−0.661 806[1]
			$(2s)^2 2p$		
1.6	−0.205 776[1]	−0.208 503[1]	−0.210 875[1]	−0.212 884[1]	−0.214 522[1]
2.1	−0.215 780[1]	−0.216 648[1]	−0.217 117[1]	−0.217 179[1]	−0.216 827[1]
2.6	−0.216 055[1]	−0.214 858[1]	−0.213 230[1]	−0.211 170[1]	−0.208 672[1]
3.1	−0.205 736[1]	−0.202 359[1]	−0.198 541[1]	−0.194 279[1]	−0.189 573[1]

TABLE XII. Non-S-term single excited states (in a.u.) Numbers in square brackets denote powers of ten.

Term	λ_1[a]	λ_2[a]	E_{min}[a]	Theoretical ionization potential	Expt.[b]
$(1s)^2 2p$	2.6863	1.0500	7.350 39	0.127 73[0]	0.130 25[0]
$(1s)^2 3p$	2.6863	1.0500	7.279 11	0.564 54[−1]	0.572 40[−1]
$(1s)^2 4p$	2.6875	1.0500	7.254 32	0.316 64[−1]	0.319 81[−1]
$(1s)^2 5p$	2.6875	1.0500	7.242 86	0.202 04[−1]	0.203 88[−1]
$(1s)^2 6p$	2.6850	1.0188	7.236 66	0.140 04[−1]	0.141 27[−1]
$(1s)^2 7p$	2.6888	1.0344	7.232 95	0.102 94[−1]	
$(1s)^2 3d$	2.6850	1.0031	7.278 21	0.555 55[−1]	0.556 13[−1]
$(1s)^2 4d$	2.6850	1.0031	7.253 91	0.312 54[−1]	0.312 79[−1]
$(1s)^2 5d$	2.6850	1.0031	7.242 65	0.199 94[−1]	0.200 05[−1]
$(1s)^2 6d$	2.6850	0.9953	7.236 54	0.138 84[−1]	0.138 85[−1]
$(1s)^2 7d$	2.6875	1.0031	7.232 87	0.102 14[−1]	
$(1s)^2 4f$	2.6850	1.0031	7.253 90	0.312 44[−1]	0.312 47[−1]

[a]Present paper.
[b]Reference [9].

TABLE XIII. S-term single excited states (in a.u.).

Term	λ_1[a]	λ_2[a]	E_{min}[a]	Theoretical ionization potential	Expt.[b]
$(1s)^2 2s$	2.6800	1.8688	7.393 60	0.170 94[0]	0.198 17[0]
$(1s)^2 3s$	2.6900	1.5650	7.283 02	0.603 64[−1]	0.741 92[−1]
$(1s)^2 4s$	2.6850	1.3969	7.254 37	0.317 14[−1]	0.386 25[−1]
$(1s)^2 5s$	2.6850	1.2875	7.242 44	0.197 84[−1]	0.236 42[−1]
$(1s)^2 6s$	2.6863	1.2500	7.236 29	0.136 34[−1]	0.159 49[−1]

[a]Present paper.
[b]Reference [9].

TABLE XIV. Non-S-term triple excited states (in a.u.).

Term	$\lambda_1{}^{a}$	$\lambda_2{}^{a}$	$E_{\min}{}^{a}$	Theoretical ionization potential
$(2s)^2 2p$	2.3800	2.4763	2.172 04	0.350 59[0]
$(2s)^2 3p$	2.6725	1.5000	1.903 68	0.822 35[−1]
$(2s)^2 4p$	2.6900	1.3078	1.862 16	0.407 15[−1]
$(2s)^2 5p$	2.6950	1.2250	1.845 89	0.244 45[−1]
$(2s)^2 3d$	2.6950	1.0500	1.878 17	0.567 24[−1]
$(2s)^2 4d$	2.6950	1.0485	1.853 34	0.318 95[−1]
$(2s)^2 5d$	2.6975	1.0406	1.841 79	0.203 45[−1]
$(2s)^2 6d$	2.6975	1.0250	1.835 55	0.141 05[−1]
$(2s)^2 4f$	2.7000	0.9937	1.852 70	0.312 54[−1]
$(2s)^2 5f$	2.7000	0.9937	1.841 45	0.200 05[−1]
$(2s)^2 6f$	2.7000	1.0094	1.835 34	0.138 95[−1]
$(2s)^2 5h$	2.7000	0.9937	1.841 44	0.199 95[−1]
$(2s)^2 6h$	2.7000	0.9937	1.835 33	0.138 85[−1]

[a]Present paper.
[b]Reference [19].

B. The structure of the lithium atom

Applying the principle of the second kind of balance to the first-order perturbation energy Eqs. (156) and (157), we can determine these balance parameters λ_1 and λ_2 numerically. The structure of the lithium atoms has been investigated for a few cases. The theoretical predictions of balance parameters and energies are tabulated in Table XII for non-S terms, in Table XIII for S terms in single excited states, in Table XIV for non-S terms, and in Table XV for S terms in triple excited states. Negative signs are omitted for energies and the accuracy is estimated to be ±1 in the last digit. These results are for an infinite-mass lithium nucleus and where the theoretical values of the ionization potential $\mathcal{V}_{\text{IP}}$, which are defined for $(1s)^2(nl)$

$$\mathcal{V}_{\text{IP}}=-(3-\tfrac{5}{16})^2-E_{\min} \tag{160}$$

and for $(2s)^2(nl)$

$$\mathcal{V}_{\text{IP}}=-(3-\tfrac{77}{256})^2/4-E_{\min}\ , \tag{161}$$

are also listed.

TABLE XV. S-term triple excited states (in a.u.).

Term	$\lambda_1{}^{a}$	$\lambda_2{}^{a}$	$E_{\min}{}^{a}$	Theoretical ionization potential
$(2s)^2 3s$	2.6825	2.1000	1.917 17	0.957 25[−1]
$(2s)^2 4s$	2.6887	1.8000	1.863 49	0.420 45[−1]
$(2s)^2 5s$	2.6975	1.3000	1.845 88	0.244 35[−1]

[a]Present paper.
[b]Reference [9].

V. DISCUSSION AND CONCLUSIONS

In the present paper extended Hamiltonians which contained structure parameters are provided in a varying-parameters method for simple atomic systems. Although we merely add and subtract appropriate parameters terms in a standard Hamiltonian, we show that this can lead to interesting physical results.

We apply principles of the first and the second kind of balance to these extended Hamiltonians, which permit structure parameters to be determined as balance parameters. Balance principles indicate that a quantum system will tend to a new balance position under the influence of a perturbation Hamiltonian through varying-balance parameters. Thus balance parameters can imply the essential properties of a quantum system. Physically, if a quantum system is acted upon by a perturbing potential, this quantum system is essentially changing its structure parameters until new balance positions are reached.

In this work, most of calculations have been performed numerically. The programs which have been developed by the author are universal for a^k, F^k, b^k, G^k, and associated integrals [16], such as J, K, $\mathcal{J}_{SS}$, $\mathcal{J}_{ZR}$, etc., and are available for n or $n' \leq 12$, and reasonable values of z and z'. These programs also have been verified by comparing with individual analytical calculations. The numerical relative error is less than 10^{-5} for a configuration of z,n,l,m and z',n',l',m'.

All numerical calculations have been performed on a personal computer with software written by the author.

ACKNOWLEDGMENT

The author is extremely thankful to Professor R. E. Welsh for considerable editorial assistance in the composition of this manuscript and his kindness when the author was at The College of William and Mary.

---

[1] Jorge M. Seminario and Frank C. Sanders, Phys. Rev. A **42**, 2562 (1990).
[2] R. P. Madden and K. Codling, Astrophys. J. **141**, 364 (1965).
[3] H. D. Morgan and D. L. Ederer, Phys. Rev. A **29**, 1901 (1984).
[4] P. K. Carroll and E. T. Kennedy, Phys. Rev. Lett. **38**, 1068 (1977).
[5] P. Zeim, R. Bruch, and N. Stolterfoht, J. Phys. B **8**, L480 (1975).
[6] P. J. Hicks and J. Comer, J. Phys. B **8**, 1866 (1975).
[7] F. Gelebart, R. J. Tweed, and J. Peresse, J. Phys. B **9**, 1739 (1976).
[8] R. Bruch, G. Paul, J. Andra, and L. Lipsky, Phys. Rev. A **12**, 1808 (1975).
[9] I. I. Sobelman, *Introduction to the Theory of Atomic Spectra* (Pergamon, New York, 1972).
[10] C. H. Park, A. F. Starace, J. Tan, and C. D. Lin, Phys. Rev. A **33**, 1000 (1986).
[11] B. Schiff, H. Lifson, C. L. Pekeris, and P. Rabinowitz,

Phys. Rev. **140**, 1104 (1965).
[12] C. L. Pekeris, Phys. Rev. **126**, 1470 (1962); **127**, 509 (1962); **115**, 1216 (1959); **112**, 1649 (1958).
[13] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).
[14] D. Cordes and P. L. Altick, Phys. Rev. **40**, 20 (1989).
[15] S. Flugge, *Practical Quantum Mechanics* (Springer-Verlag, Berlin, 1974).
[16] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).
[17] M. Karplus and R. N. Porter, Atoms and Molecules (Benjamin, New York, 1970).
[18] Donald A. McQuarrie, *Quantum Chemistry* (Oxford University Press, Oxford, England, 1983).
[19] Mitchel Weissbluth, *Atoms and Molecules* (Academic, New York, 1978).
[20] F. L. Pilar, *Elementary Quantum Chemistry* (McGraw-Hill, New York, 1968).
[21] I. G. Halliday and P. Suranyi, Phys. Rev. D **21**, 1529 (1980).
[22] P. K. Patnaik, Phys. Rev. D **35**, 1234 (1987).
[23] P. K. Patnaik, Phys. Rev. Lett. A **150**, 269 (1990).
[24] P. K. Patnaik, Phys. Rev. D **33**, 3145 (1986).
[25] C. M. Bender and T. T. Wu, Phys. Rev. **184**, 1231 (1969).
[26] Shau-Jin. Chang, Phys. Rev. D **12**, 1071 (1975).
[27] S. Coleman, Phys. Rev. D **11**, 2088 (1975).
[28] K. Banerjee and S. P. Bhatnagar, Phys. Rev. D **18**, 4767 (1978).
[29] F. J. Dyson, Phys. Rev. **85**, 631 (1952).
[30] C. Bender and T. T. Wu, Phys, Rev. D **7**, 1620 (1973).
[31] P. Froelich and S. A. Alexander, Phys. Rev. A **42**, 2250 (1990).
[32] P. J. Hicks and J. Comer, J. Phys. B **8**, 1866 (1975).
[33] F. Gelbart, R. J. Tweed, and J. Peresse, J. Phys. B **9**, 1739 (1976).
[34] J. Ceng, *Quantum Mechanics (II)* (Science Press, Beijing, 1981).