Electronic Wave Functions for Helium-Like Atoms

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Expressions for correlated atomic wave functions of various members of the helium isoelectronic sequence are presented. The Hylleraas-type 3-parameter function has been considered. The parameters have been determined variationally and their values are given as a function of the atomic number.

I. INTRODUCTION

In the case of certain atomic processes including K-shell electrons, the use of single-electron wave functions is not adequate and the atomic system should be described by the correlated wave functions. For this purpose, the Rayleigh-Ritz variational method has been most widely employed to calculate the wave functions for the ground states of the helium isoelectronic sequence.[1] Since the first successful application of this method for He by Hylleraas,[2] many calculations have been performed for two-electron atoms with correlation effect and good agreement with experimental results has been achieved for energy eigenvalues and other quantities. However, most calculations are concerned with He and Li+, and there have been reported only a few results for ground states of helium-like ions with large atomic number.

In the present work, the Hylleraas-type 3-parameter wave functions have been calculated numerically for atomic numbers from $Z=2$ to 82. The numerical values of the parameters obtained are expressed as a simple function of the atomic number Z. These results are very useful for many fields of applications because of their simple form.

II. THEORY

Let r_1 and r_2 be the distance of the two electrons from the nucleus of a helium-like atom with the nuclear charge Z. The Hamiltonian of the system can be written in atomic units by

$$H = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{1}$$

where Δ_1 and Δ_2 denote the Laplacian operators with respect to the coordinates of

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electrons 1 and 2, respectively, and r_{12} is the interelectronic separation distance.

Following the method of Hylleraas,[3] we introduce two elliptic coordinates and use the following three variables:

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}. \tag{2}$$

By the use of a parameter k, the eigenfunction of the system $\Psi(s, t, u)$ can be written in the following form

$$\Psi(s, t, u) = N_0 \phi(ks, kt, ku), \tag{3}$$

where N_0 is the normalization constant. The scaling parameter k (the effective nuclear charge) is to be fixed to give a minimum eigenvalue. We assume that the function $\phi(s, t, u)$ is expressed as

$$\phi(s, t, u) = \exp\left(-\frac{1}{2} s\right) \sum_{n, l, m = 0}^{\infty} c(n, 2l, m) s^n t^{2l} u^m. \tag{4}$$

Then the variational principle for $\phi(s, t, u)$ takes the form

$$\frac{k^2 M + k L}{N} = E = \min. \tag{5}$$

The quantity M corresponds to the kinetic energy part of the Hamiltonian in Eq. (2) and is written by

$$M = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt \left\{ u(s^2 - t^2) \left[\left(\frac{\partial \phi}{\partial s}\right)^2 + \left(\frac{\partial \phi}{\partial u}\right)^2 + \left(\frac{\partial \phi}{\partial t}\right)^2 \right] \right. $$
$$\left. + 2s(u^2 - t^2) \frac{\partial \phi}{\partial s} \frac{\partial \phi}{\partial u} + 2t(s^2 - u^2) \frac{\partial \phi}{\partial t} \frac{\partial \phi}{\partial u} \right\}. \tag{6}$$

On the other hand, the potential energy part L is expressed as

$$L = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt \{-4Zsu + s^2 - t^2\} \phi^2, \tag{7}$$

and the normalization condition N is given by

$$N = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt\, u(s^2 - t^2) \phi^2. \tag{8}$$

Using Eqs. (3)–(8), the coefficients $c(n, 2l, m)$, the effective nuclear charge k, and the minimum eigenvalue $E_{\min}$ can be determined by the conditions

$$\frac{\partial E}{\partial c(n, 2l, m)} = 0, \tag{9}$$

and

$$\frac{\partial E}{\partial k} = 0. \tag{10}$$

From Eqs. (5) and (10), k is given by

$$k = -\frac{L}{2M}. \tag{11}$$

Substituting Eq. (11) into Eq. (5), the equation can be written as

$$E = -\frac{L^2}{4MN}. \tag{12}$$

The problem reduces to minimize E in Eq. (12) with respect to $c(n, 2l, m)$.

III. CALCULATED RESULTS

The numerical calculations of the wave functions have been made for the 3-parameter function proposed by Hylleraas.[3] The minimum value of E in Eq. (12) and the corresponding values of the coefficients $c(n, 2l, m)$ were estimated by the non-linear function minimization method of Powell,[4] and the value of k was evaluated from Eq. (11). All the calculations in the present work have been performed with the FACOM M–200 computer in the Data Processing Center of Kyoto University.

Following Hylleraas,[3] a simple 3-parameter function is considered:

$$\phi = \exp\left(-\frac{1}{2}s\right)(c_0 + c_1 u + c_2 t^2). \tag{13}$$

For this trial function, analytical expressions of M, L, and N for He $(Z=2)$ are given in the paper of Hylleraas.[3] Of these three quantities, only L depends on the atomic number, and the analytical expression for arbitrary Z can be written by

$$\begin{aligned}
L = 2\pi^2\{ & c_0{}^2(10-32Z) + c_0 c_1(64-240Z) \\
& + c_0 c_2(72-384Z) + c_1 c_2(384-2240Z) \\
& + c_1{}^2(140-576Z) + c_2{}^2(624-4608Z)\}.
\end{aligned} \tag{14}$$

The parameters to minimize E have been numerically estimated for the region from $Z=2$ to 82 and then their values have been fitted to a polynomial of the reciprocal of Z. The results obtained are expressed as

$$\left.\begin{aligned}
N_0 = {}& \frac{Z^3}{\pi}(1-1.069372/Z+0.2096187/Z^2+0.01328097/Z^3 \\
& +0.04569446/Z^4), \\
k = {}& 2Z(1-0.1598726/Z-0.02149917/Z^2-0.05152167/Z^3 \\
& -0.001302860/Z^4), \\
c_0 = {}& 1, \\
c_1 = {}& 0.1221154/Z+ 0.06801699/Z^2+0.02360940/Z^3 \\
& -0.005988795/Z^4, \\
c_2 = {}& 0.009255006/Z+0.01333793/Z^2+0.006919765/Z^3 \\
& +0.01799133/Z^4.
\end{aligned}\right\} \tag{15}$$

For all Z values, the difference between the parameters calculated directly from Eq. (12) and estimated from Eq. (15) is less than 0.1%.

The energy eigenvalues obtained from Eq. (12) by the use of the parameters estimated from Eq. (15) are compared in Table I with other calculated values for $Z=2$, 3, and 7. These previous calculations except for the Hylleraas' original value have been made for various types of trial functions with many terms; for examples, 39 terms by Kinoshita,[7] configuration interaction of 35 configurations by Weiss,[8] and 125 terms by Thakkar.[10] The most accurate values up to the present are the values obtained by Frankowski and Pekeris.[11] They have made variational calculations for wave functions including logarithmic term and for determinants up to order

246, and then extrapolated the energy eigenvalues with respect to the order of the determinant to ∞.

Table I. Comparison of the Calculated Energy Eigenvalues for $Z=2$, 3, and 7

	$Z=2$	$Z=3$	$Z=7$
Present work	-2.902431	-7.278029	-44.77844
Hylleraas[3]	-2.90244		
Pekeris[6]	-2.90372	-7.27991	-44.78145
Kinoshita[7]	-2.9037225		
Weiss[8]	-2.90320	-7.27924	-44.77979
Radi[9]	-2.903472672	-7.279603108	-44.780947864
Thakkar[10]	-2.90372434287		
Frankowski and Pekeris[11]	-2.90372437703	-7.2799134126678	-44.781445148768

It can be seen from the table that the present results [Eq. (15)] are in fairly good agreement with the values of Frankowski and Pekeris.[11] Considering the small number of terms used in the present wave function, Eq. (15) yields the good estimate of the energy eigenvalues of the ground states of helium-like atoms.

IV. CONCLUSIONS

Atomic wave functions for the ground states of helium isoelectronic sequence have been calculated by the variational method, taking fully into account the electronic correlation. The trial function of 3 parameters has been used and the parameters are presented as a function of the atomic number Z. The energy eigenvalues obtained from these parameters are in satisfactory agreement with more accurate values calculated with many parameters.

The advantage of the present wave function consists in its simplicity of use and the present results are very useful to chemical and astrophysical problems as well as physical ones.

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