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Comparison of the Radial Integrals of Variational Wave Functions for Two-electron systems

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Abstract

In this work, two-electron systems such as H^- ion, He atom and Li^+ ion are investigated by using variational method. Hylleraas-type 3-parameter wave function is used as the trial wave function proposed by Mukoyama. The radial integrals of variational wave functions for the above mentioned systems are calculated to check their accuracy. The radial integrals are used for determining the properties of the two-electron system such as dipole polarizability and electron scattering factor. They are calculated and the obtained results are also compared with the other results. It is found that they are in good agreement with other results.

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Introduction

Two-electron Systems and Variational Method

The ground-state energies of two-electron systems (H^-, He, Li^+) have been a subject of interest for a long time [1-7] and it continues to attract the attention of many investigators [8-12]. The variational technique is considered as a powerful tool for estimating the ground-state energy of a quantum system. Over the years, this method has been applied to a two-electron system in different types of wave functions.

The Hylleraas Coordinate

The suitable coordinate for the treatment of a two-electron system is the Hylleraas coordinate. In this coordinate system, the three distance coordinates s, t, and u are defined as $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$ where r_1 and r_2 are the distances of the first and second electrons from the origin respectively and r_{12} being their mutual separation. The resulting volume element is then found to be $d\tau = 2\,\pi^2\,(s^2 - t^2)\,u\,ds\,du\,dt$ and the limits of integration are $0 \le t \le u \le s \le \infty$.

The Choice of Wave Function

The trial wave function crucially determines the accuracy of the variational calculation. The trial wave function has been of the Hylleraas type,

$$\psi(s,t,u) = e^{-\frac{1}{2}ks} \sum_{l,n,m=0}^{\infty} c_{n,2l,m} \ (ks)^n \ (kt)^{2l} \ (ku)^m \tag{1}$$

The Radial Integrals of Variational Wave Functions

Many different wave functions are proposed for two-electron atoms by many authors. The most common type of wave function is variational. The main aim of the variational method is to obtain a good approximation of the energy. It is assumed that better approximations can be obtained by using wave functions with more parameters. But there is no guarantee that the trial wave function is close to the exact wave function. To check the accuracy of these wave functions, the radial integrals are calculated for the wave functions. The radial integrals are defined as follows:

$$\langle r_{12} \rangle = \langle u \rangle = 2 \ \pi^2 \ N^2 \int_{s=0}^{\infty} \int_{u=0}^{s} \int_{t=0}^{u} \psi^* u^2 \psi (s^2 - t^2) \, dt \ du \ ds \tag{2}$$

$$\langle r_{12}^2 \rangle = \langle u^2 \rangle = 2 \ \pi^2 \ N^2 \int_{s=0}^{\infty} \int_{u=0}^{s} \int_{t=0}^{u} \psi^* u^3 \psi (s^2 - t^2) \, dt \ du \ ds \tag{3}$$

$$\langle r_1 \rangle = \frac{1}{2} \langle s \rangle = \pi^2 \ N^2 \int_{s=0}^{\infty} \int_{u=0}^{s} \int_{t=0}^{u} \psi^* \ s \ u \ \ \psi (s^2 - t^2) \, dt \ du \ ds \tag{4}$$

$$\langle r_1^2 \rangle = \frac{1}{4} \langle s^2 + t^2 \rangle = \frac{\pi^2 N^2}{2} \int_{s=0}^{\infty} \int_{u=0}^{s} \int_{t=0}^{u} \psi^* (s^4 - t^4) \ \psi \, dt \ du \ ds \tag{5}$$

Calculation of Radial Integrals and Their Comparison

Hylleraas-type 3-parameter Trial Wave Function

In Mukoyama's paper[14], the Hylleraas-type 3-parameter trial wave functions were calculated numerically for two-electron systems. Following Hylleraas,a simple 3-parameter function is considered:

$$\phi = \exp(-\frac{1}{2}s)(c_0 + c_1 u + c_2 t^2). \tag{6}$$

The numerical values of the parameters obtained were expressed as a simple function of the atomic number Z. These results were very useful for many fields of applications because of their simple form. For this trial function, the parameters are expressed as

$$N_0 = \frac{Z^3}{\pi}(1 - 1.069372/Z + 0.2096187/Z^2 + 0.01328097/Z^3 + 0.04569446/Z^4),$$

$$k = 2Z(1 - 0.1598726/Z - 0.02149917/Z^2 - 0.05152167/Z^3 - 0.001302860/Z^4),$$

$$c_0 = 1,\ \ c_1 = 0.1221154/Z + 0.06801699/Z^2 + 0.02360940/Z^3 - 0.005988795/Z^4,$$

$$c_2 = 0.009255006/Z + 0.01333793/Z^2 + 0.006919765/Z^3 + 0.01799133/Z^4,$$

Calculation of Radial Integrals of the Trial Wave Function for Helium Atom

For the ground state trial wave function,

$$\Psi(s,t,u) = N_0\phi(ks,kt,ku) \qquad [\phi = e^{-\frac{1}{2}ks}(c_0 + c_1ku + c_2k^2t^2)] \tag{7}$$

the radial integrals are calculated as

$$\langle r\rangle = \frac{1}{2}\langle s\rangle = \pi^2 N_0^2 \int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\, su(s^2 - t^2)\, dt\, du\, ds = 0.9261\, au$$

$$\langle r^2\rangle = \frac{1}{4}\langle s^2 + t^2\rangle = \frac{\pi^2 N_0^2}{2}\int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\ (s^4u - ut^4)\, dt\, du\, ds = 1.1796\, au$$

$$\langle r_{12}\rangle = \langle u\rangle = 2\pi^2 N_0^2 \int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\ (s^2u^2 - u^2t^2)\, dt\, du\, ds = 1.4210\, au$$

$$\langle r_{12}^2\rangle = \langle u^2\rangle = 2\pi^2 N_0^2 \int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\ (s^2u^3 - u^3t^2)\, dt\, du\, ds = 2.5057\, au$$

Radial Integrals of the Trial Wave Function for H^- ion

The values of radial integrals for Mukoyama wave function are

$$\langle r\rangle = \frac{1}{2}\langle s\rangle = \pi^2 N_0^2 \int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\, su(s^2 - t^2)\, dt\, du\, ds = 2.6762\, au$$

$$\langle r^2\rangle = \frac{1}{4}\langle s^2 + t^2\rangle = \frac{\pi^2 N_0^2}{2}\int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\ (s^4u - ut^4)\, dt\, du\, ds = 9.4767\, au$$

$$\langle r_{12}\rangle = \langle u\rangle = 2\pi^2 N_0^2 \int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\ (s^2u^2 - u^2t^2)\, dt\, du\, ds = 4.2691\, au$$

$$\langle r_{12}^2\rangle = \langle u^2\rangle = 2\pi^2 N_0^2 \int_0^\infty\int_0^s\int_0^u e^{-ks}(c_0 + c_1ku + c_2k^2t^2)^2\ (s^2u^3 - u^3t^2)\, dt\, du\, ds = 20.3913\, au$$

Radial Integrals of the Trial Wave Function for Li^+ ion

The values of radial integralsfor Mukoyama wave function are

$$\langle r\rangle = \frac{1}{2}\langle s\rangle = \pi^2 N_0^2 \int_0^\infty \int_0^s \int_0^u e^{-ks}(c_0 + c_1 ku + c_2 k^2 t^2)^2\, su\,(s^2 - t^2)\, dt\, du\, ds = 0.5721 au$$

$$\langle r^2\rangle = \frac{1}{4}\langle s^2 + t^2\rangle = \frac{\pi^2 N_0^2}{2} \int_0^\infty \int_0^s \int_0^u e^{-ks}(c_0 + c_1 ku + c_2 k^2 t^2)^2\ (s^4 u - u t^4)\, dt\, du\, ds = 0.4451 au$$

$$\langle r_{12}\rangle = \langle u\rangle = 2\pi^2 N_0^2 \int_0^\infty \int_0^s \int_0^u e^{-ks}(c_0 + c_1 ku + c_2 k^2 t^2)^2\ (s^2 u^2 - u^2 t^2)\, dt\, du\, ds = 0.8639\, au$$

$$\langle r_{12}^2\rangle = \langle u^2\rangle = 2\pi^2 N_0^2 \int_0^\infty \int_0^s \int_0^u e^{-ks}(c_0 + c_1 ku + c_2 k^2 t^2)^2\ (s^2 u^3 - u^3 t^2)\, dt\, du\, ds = 0.9313 au$$

Table (1) GS energy, Dipole polarizability and electron scattering factor for He atom (in au)

No.	Trial Wave Function	Ground state (GS) energy	$\langle r^2 \rangle$	$\langle r_{12}^2 \rangle$	α_d	$f_e(0)$
1.	$\psi_0 = N_0 e^{-\frac{1}{2}ks}(c_0 + c_1 k u + c_2 k^2 t^2)$	-2.9024	1.1795	2.5057	1.0880	0.7864
2.	Ten-Parameter Wave Function [15]	-2.9037	1.1902	2.5077	1.1281	0.7935
3.	Twenty-parameter Wave Function[15]	-2.9070	1.1933	2.5161	1.1321	0.7955
4.	Exact [16]	-2.9037	1.1935	2.5164	1.1326	0.7957

Table (2) GS energy, Dipole polarizability and electron scattering factor for H^- ion (in au)

No.	Trial Wave Function	Ground state (GS) energy	$\langle r^2 \rangle$	$\langle r_{12}^2 \rangle$	α_d	$f_e(0)$
1.	$\psi_0 = N_0 e^{-\frac{1}{2}ks}(c_0 + c_1 k u + c_2 k^2 t^2)$	-0.5254	9.4767	20.3913	68.1776	6.3178
2.	$\psi_0 = N_0 e^{-\frac{1}{2}ks}(c_0 + c_1 k u + c_2 k^3 s t^2)$	-0.5253	9.6538	20.5440	72.5716	6.4359
3.	Six-parameter Wave Function[15]	-0.5264	9.6050	20.5410	71.0353	9.4033
4.	Pekeris [17]	-0.5278	11.9137	25.2020	112.0285	7.9425

Table (3) GS energy, Dipole polarizability and electron scattering factor for Li^+ ion (in au)

No.	Trial Wave Function	Ground state (GS) energy	$\langle r^2 \rangle$	$\langle r_{12}^2 \rangle$	α_d	$f_e(0)$
1.	$\psi_0 = N_0 e^{-\frac{1}{2}ks}(c_0 + c_1 k u + c_2 k^2 t^2)$	-7.3651	0.4451	0.9313	0.1602	0.2967
2.	Four-Parameter Wave Function [15]	-7.2799	0.4414	0.9419	0.1508	0.2943
3.	Pekeris [17]	-7.2819	0.4463	0.9271	0.1636	0.2975

Discussion

In the evaluation of the value of physical observables using the principles of quantum mechanics, it is found that they depend on the radial integrals $\langle r^n \rangle$. For example, the electric dipole polarizability depends on $\langle r^2 \rangle$ and $\langle r_{12}^2 \rangle$, and the electron scattering factor on $\langle r^2 \rangle$.

Therefore, the radial integrals of trail wave functions for atoms and ions are useful for checking the accuracy of the wave functions and for determining the physical quantities of atoms and ions such as dipole polarizability, and electron scattering factor.

The electric dipole polarizability of a two-electron system can be expressed in radial integrals as $\alpha_d = \frac{2}{9}\left[4\langle r^2\rangle - \langle r_{12}^2\rangle\right]^2$. The theory of electron scattering provides information on electronic density distributions in matter. The atomic scattering factor represents the shielding effect of the atomic electrons upon the nuclear charge. The atomic electron scattering factor for two-electron systems is $f_e(0) = \frac{2}{3}\left\langle r^2\right\rangle$ in atomic units. This relation shows that the electron scattering factor depends on the nucleus-electron radial integral $\left\langle r^2\right\rangle$. In Tables (1), (2) and (3), the values of ground state energy, dipole polarizability and electron scattering factor for *He* atom, H^- ion and Li^+ ion with Mukoyama trial wave function are compared with the other results obtained from different variational wave functions and analytical result. It is found that the present calculated result fairly agrees with these values.

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