最弱受约束电子势模型理论下使用双广义拉盖尔多项式 计算氦原子基态能量

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摘要: 计算了在最弱受约束电子势模型理论下使用双广义拉盖尔多项式的氦原子基态能量. 给出了氦原子基态能量期望值的表达式. 通过搜索它的极小, 找到了氦原子基态能量的极小值. 将我们的结果与双 ζ (zeta)函数的 Hartree-Fock(HF)方法的结果进行比较后发现, 我们的结果略优于双 ζ (zeta)函数的 Hartree-Fock(HF)方法的结果. 如此表明线性组合技术可以应用在最弱受约束电子势模型理论中.

关键词: 最弱受约束电子势模型理论; 氦原子基态能量; 线性组合

中图分类号: O641

Calculation of He Atom Ground-State Energy Using Double Generalized Laguerre Polynomial in the Weakest Bound Electron Potential Model Theory

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Abstract: We calculated the He atom ground-state energy using a double generalized Laguerre polynomial in the weakest bound electron potential model (WBEPM) theory. An expression for the expectation value of the He atom ground-state energy was derived. We obtained minimum values for the He atom ground-state energy ($E_{\min}$). A comparison was made to the results from the Hartree-Fock (HF) method using a double zeta function. Our result was slightly better than the result obtained using a double zeta function in the HF method. We thus show that the linear combination technique can easily be used in WBEPM theory.

Key Words: WBEPM theory; He atom ground-state energy; Linear combination

In quantum chemistry, some of the theoretical models are based on the indistinguishability of interacting identical particles, such as Hartree-Fock self-consistent-field (HF SCF) method, and some originate from the consideration of separability of many-electron systems, such as model potential method, quantum defect theory, valence bound theory. They encounter their respective difficulties in describing physical and chemical behavior of atoms and molecules. At present, one of advances in quantum chemistry is that various methods (or theories) permeate each other and make up for each other's deficiencies^[1–4]. In our mind, it is of great importance to develop a theory of unification of indistinguishability and separability in order to better interpret

wave-particle duality of electron's behavior in atoms and molecules. This consideration accords with developing tendency of quantum chemistry. Zheng *et al.*^[56] has proposed a theory called WBEPM theory. Many properties of atoms have been successfully investigated in the theory^[7–17]. The WBEPM theory has holden one's interest^[18–29].

Many methods, including variational method, perturbation theory, pseudopotential method, HF SCF etc, have been used to investigate the energy of He atom in the ground state and highly accurate results for its ground state and low-excited states have been obtained^[30–38]. In previous work^[17], we also reported the variational treatment on the energy of He atom in ground state with

Received: January 9, 2009; Revised: March 12, 2009; Published on Web: April 6, 2009.

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the WBEPM theory by using single generalized Laguerre polynomial. The current work does not focus on highly precise calculation of the energy of He atom ground state. Instead, we will employ double generalized Laguerre polynomial in the WBEPM theory to study the energy of He atom in its ground state.

1 Theory and calculation

The WBEPM theory is described in detail in Refs. [5,6]. We introduce it only briefly here. Its main points are as follows: (i) In the processes of successive ionization electrons in an N -electron atom or ion are peeled off one by one as the weakest bound electron (WBE). So an N -electron problem can be treated as one-electron problems of N WBEs; (ii) The WBE is the most active electron and the electron is excited or ionized most easily. It differs from other electrons called non-weakest bound electrons (NWBEs) in the present system in behavior. By separating of the WBE with the (NWBEs) in the present system, one can consider the WBE moving in the potential field provided by NWBEs and the nucleus; (iii) The potential field V (in a.u.), in which the WBE moves, takes a following approximate analytical form in central field approximation

$$V(r_i) = \frac{-Z'}{r_i} + \frac{d(d+1)+2dl}{2r_i^2} \quad (1)$$

where r_i is the distance between the WBE i and the nucleus, Z' is the effective nuclear charge, and d is an adjustable parameter that modifies the integral principal quantum numbers n and angular quantum numbers l into nonintegral principal quantum numbers n' and angular quantum numbers l' ; (iv) The one-electron Schrödinger equation of the WBE i is

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{Z'}{r_i} + \frac{d(d+1)+2dl}{2r_i^2} \right] \Psi_i = \varepsilon_i \Psi_i \quad (2)$$

where $-\frac{1}{2} \nabla_i^2$ is the kinetic energy operator, Ψ_i is the eigenfunction and ε_i is the eigenvalue of WBE i . Solving the Eq. (2) one can get a set of expressions, including energy and radial wavefunction with the generalized Laguerre polynomial^[39].

Now we begin our discussion on He atom ground state. Our previous study^[7] shows that the expectation value of energy of He atom ground state is minimum if spatial orbitals of two electrons are same. In present calculation, thus, we write

$$\Psi = (2!)^{-1/2} \sum_p (-1)^p P \{ \Phi(1)\alpha(1)\Phi(2)\beta(2) \}$$

or

$$\Psi = |\Phi(1)\bar{\Phi}(2)| \quad (3)$$

where Ψ is the total wavefunction, P is an exchange operator, $\alpha(1)$ or $\beta(2)$ are the spin part of spinorbitals, and $\Phi(\mu)$ is the spatial part of spinorbital. Here, $\Phi(\mu)$ is taken as a product of a trial radial wavefunction and the spherical harmonics, that is, $\Phi(\mu) = R(\mu)Y_{lm}(\theta_\mu, \varphi_\mu)$ and the trial radial wavefunction of $\Phi(\mu)$ will be written as a linear combination with two generalized Laguerre polynomials, namely, double generalized Laguerre polynomial^[5-7]. We have

$$\Phi(\mu) = c_1\varphi_1(\mu) + c_2\varphi_2(\mu) \quad (4)$$

where

$$\varphi_i(\mu) = \frac{1}{\sqrt{4\pi\Gamma(2l'_i+3)}} \left(\frac{2z'_i}{n'_i} \right)^{l'_i+3/2} r_\mu^{l'_i} e^{-z'_i r_\mu / n'_i} \quad (5)$$

$n'_i = n_i + d_i$, $l'_i = l_i + d_i$, n_i and l_i are principal quantum number and angular quantum number, respectively, z'_i and d_i here are undetermined parameters. $\Gamma(2l'_i+3)$ is a gamma function.

If the wavefunction of He atom ground state is represented by Ψ , its expression of the expectation value of the energy is given by

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (6)$$

where

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \sum_{\mu=1}^2 \left(\hat{h}(\mu) + \sum_{\nu, \mu < \nu} \frac{1}{r_{\mu\nu}} \right) \quad (7)$$

The expressions of $\langle \Psi | \Psi \rangle$ and $\langle \Psi | H | \Psi \rangle$ have been derived

$$\langle \Psi | \Psi \rangle = [(c_1^2 + c_2^2) + 2c_1c_2S]^2 \quad (8)$$

and

$$\langle \Psi | H | \Psi \rangle = c_1^4 A + 4c_1^3 c_2 B + 4c_1^2 c_2^2 C + 2c_1^2 c_2^2 D + 4c_1 c_2^3 E + c_2^4 F \quad (9)$$

where

$$\begin{aligned} A &= \langle \varphi_1(1)\varphi_1(2) | H | \varphi_1(1)\varphi_1(2) \rangle \\ &= \langle \varphi_1(1) | \hat{h}(1) | \varphi_1(1) \rangle + \langle \varphi_1(2) | \hat{h}(2) | \varphi_1(2) \rangle + \\ &\quad \langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_1(2) \rangle \end{aligned} \quad (10)$$

$$\begin{aligned} B &= \langle \varphi_1(1)\varphi_1(2) | H | \varphi_2(1)\varphi_1(2) \rangle \\ &= \langle \varphi_1(1) | \hat{h}(1) | \varphi_2(1) \rangle + \langle \varphi_1(2) | \hat{h}(2) | \varphi_1(2) \rangle S + \\ &\quad \langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_1(2) \rangle \end{aligned} \quad (11)$$

$$\begin{aligned} C &= \langle \varphi_1(1)\varphi_1(2) | H | \varphi_2(1)\varphi_2(2) \rangle \\ &= \langle \varphi_1(1) | \hat{h}(1) | \varphi_2(1) \rangle S + \langle \varphi_1(2) | \hat{h}(2) | \varphi_2(2) \rangle S + \\ &\quad \langle \varphi_1(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_2(2) \rangle \end{aligned} \quad (12)$$

$$\begin{aligned} D &= \langle \varphi_2(1)\varphi_1(2) | H | \varphi_2(1)\varphi_1(2) \rangle \\ &= \langle \varphi_2(1) | \hat{h}(1) | \varphi_2(1) \rangle + \langle \varphi_1(2) | \hat{h}(2) | \varphi_1(2) \rangle + \\ &\quad \langle \varphi_2(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_1(2) \rangle \end{aligned} \quad (13)$$

$$\begin{aligned} E &= \langle \varphi_2(1)\varphi_1(2) | H | \varphi_2(1)\varphi_2(2) \rangle \\ &= \langle \varphi_2(1) | \hat{h}(1) | \varphi_2(1) \rangle S + \langle \varphi_1(2) | \hat{h}(2) | \varphi_2(2) \rangle + \\ &\quad \langle \varphi_2(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_2(2) \rangle \end{aligned} \quad (14)$$

Table 1 Comparison between the present results and references' values

Result	I	II	III	IV
T.E.	-2.861672864	-2.8616726	-2.85421	-2.8476562
K.E.	2.861725029	2.8616855	2.85421	2.8479562
P.E.	-5.723397893	-5.7233581	-5.70842	-5.6953125
V.T.	-1.9999818	-1.9999955	-2.0000000	-2.0000000
T.R.P.E.	1.025871991		1.04186	
T.A.P.E.	-6.749269884		-6.75028	
Normality of $\varphi_i(\mu)$	0.9999999	0.9999956 ^a	1	1

T.E.: total energy of He atom ground state; K.E.: total kinetic energy; P.E.: total potential energy; V.T.=P.E./K.E.; T.R.P.E.: total repulsion potential energy; T.A.P.E.: total attraction potential energy. energy in a.u.; I: present results; II: values of HF method using double zeta function^[40]; III: values from WBE theory using single generalized Laguerre polynomial^[7]; IV: values of HF method using single zeta function^[41]; a) this value is calculated by substituting parameters of double zeta function in Ref.[41] into Eq.(8) (taking $d_1=0$, $d_2=0$).

Table 2 Several minima near the accurate minimum of E in this work

No.	1	2	3	4'	5
T.E.	-2.861672955	-2.861672971	-2.861672860	-2.861672864	-2.861672846
c_1	0.84694	0.846928	0.843	0.843	0.843
c_2	0.18404	0.184127	0.1814	0.1814	0.1814
z_1'	1.45194	1.45196	1.45322	1.45328	1.45316
z_2'	2.89381	2.89272	2.89986	2.9	2.89972
d_1	-0.000081	-0.000058	-0.000081	-0.000081	-0.000081
d_2	-0.00086	-0.001	-0.00086	-0.00086	-0.00086
V.T.	-1.9999978	-1.9999870	-2.0000679	-1.9999818	2.00015408
Normality of $\varphi(\mu)$	1.0127295	1.0128779	1.0000008	0.9999999	1.0000017

energy in a.u.; There are many minima for the expectation value of the energy of He atom ground-state in this work, we list some of these minima in Table 2 for readers,

*the result we reported in Table 1 and the text

$$\begin{aligned}
 F &= \langle \varphi_2(1)\varphi_2(2) | H | \varphi_2(1)\varphi_2(2) \rangle \\
 &= \langle \varphi_2(1) | \hat{h}(1) | \varphi_2(1) \rangle + \langle \varphi_2(2) | \hat{h}(2) | \varphi_2(2) \rangle + \\
 &\quad \langle \varphi_2(1)\varphi_2(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_2(2) \rangle
 \end{aligned} \quad (15)$$

In Eqs.(8, 11, 12, 14)

$$\begin{aligned}
 S &= \langle \varphi_1(1)\varphi_2(1) | [F(2l_1'+3)F(2l_2'+3)]^{-1/2} \left(\frac{2z_1'}{n_1'} \right)^{l_1'+3/2} \cdot \\
 &\quad \left(\frac{2z_2'}{n_2'} \right)^{l_2'+3/2} \left(\frac{z_1'}{n_1'} + \frac{z_2'}{n_2'} \right)^{-l_1'-l_2'-3} F(l_1'+l_2'+3)
 \end{aligned} \quad (16)$$

The expressions of all integrals in Eqs.(10–15) and E in Eq.(6) are shown in supporting information (available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>).

By searching the minimum of E , we obtain $E_{\min} = -2.861672864$ a.u., when $c_1 = 0.843$, $z_1' = 1.45328$, $d_1 = -0.000081$, $c_2 = 0.1814$, $z_2' = 2.9$, and $d_2 = -0.00086$.

2 Results and discussion

The results of present calculation are listed in Table 1.

The experimental value of He atom ground-state energy is -2.90372 a.u.^[41] Table 1 shows that the double generalized Laguerre polynomial leads to a total electronic energy of -2.861672864 a.u.. It is a little superior to the result of Hartree-Fock method using double zeta function (-2.8616726 a.u.)^[40]. If taking $d_i = 0$, namely $n_i' = n_i + d_i = n_i$, $l_i' = l_i + d_i = l_i$, in Eq.(5), one can represent the result of Hartree-Fock method using double zeta function^[40].

From Table 1 one can see that the theoretical calculated total energy of He atom ground state ($E_{\min}$) with the double generalized Laguerre polynomial is much better than the theoretical calculated total energy of He atom ground state ($E_{\min}$) with single-generalized Laguerre polynomial. This means that for the WBEPM theory the Roothaan's procedure^[42,43] expressing the atomic orbital and the molecular orbital as linear combinations of a set of appropriate basis function is still useful, and other functions except the generalized Laguerre polynomial as basis functions^[43–45] is also valuable in the WBEPM theory.

It is difficult to find the accurate minimum of He atom ground-state energy E . Perhaps we can find many minima near the accurate minimum. Some of many minima are listed in Table 2. $E_{\min}$ reported in Table 1 is the one with better normality of $\varphi_i(\mu)$ and better value of ratio between total potential energy and total kinetic energy (P.E./K.E.).

Our results deviate somewhat from the experimental values.

The calculated total energy of He atom in ground state is -2.861672864 a.u., and the experimental value is -2.90372 a.u.^[41]. Deviations between the results reported here and experimental values are due to the following: First of all, the relativistic effect is neglected (about -0.00007 a.u. for He)^[46]; Second, a simplest single determinant wavefunction is used in calculation and this leads to an insufficient evaluation of the correlation energy (about -0.04204 a.u. for He atom)^[30]; Third, a simpler double generalized Laguerre polynomial is used as the trial radial wavefunction. These deviations can be further improved by the linear combination technique, the correction of correlation energy and the relativistic effect.

3 Conclusions

Here we report the analytical results on the energy of He atom ground-state in the WBEPM theory. In calculation the spatial orbitals of two spinorbitals are constructed from the linear combination with two generalized Laguerre polynomials. The good result shows that the form of this function with the generalized Laguerre polynomial could be applied as a kind of basis functions in the linear combination technique, and the linear combination technique can easily be used in the WBEPM theory.

Supporting Information Available: The expressions of all integrals in Eqs.(10–15) and E in Eq.(6) have been included. This information is available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>.

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