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Uncoupled correlated method for helium bound states

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Abstract: An uncoupled correlated variational method for calculating helium bound states is proposed. The projective coordinates $s = r_1 + r_2,\ v = \frac{r_{12}}{r_1+r_2},\ w = \frac{r_1-r_2}{r_{12}}$ are introduced instead of the conventional ones $s = r_1 + r_2,\ t = r_1 - r_2,\ u = r_{12}$. All matrix elements of the total Hamiltonian and the weight function are expressed by simple products of three one-dimensional integrals. The variational basis is formed by a set of Laguerre polynomials with a single nonlinear parameter and two sets of Jacobi polynomials for the projective coordinates s, v, w, correspondingly. It provides a reasonable degree of convergence of the energy, $E = E(N)$, with respect to the number N of expansion terms over the basis of the eigenvectors. In the case of infinite and finite nuclear mass, calculations give the energy of the helium ground state.

Keywords: Variational method; helium bound state; Hamiltonian.

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1 Introduction

In atomic physics, the uncoupling of correlated calculations with a high accuracy has been recently discussed[1]. A variational basis in the new projective coordinates which yields a suitable presentation of the Hamiltonian as a simple product of three one-dimensional integrals was introduced. High accuracy calculations for the ground state of a helium atom with an infinite nuclear mass have been performed. However, such a method leads to a Hamiltonian that contains δ-function terms and exhibits a rather slow convergence of energy, $E = E(N)$, with respect to the number N of basis functions with a single nonlinear parameter. In particular, the value $E = -2.903\,724\,377\,034\,119\,593\,8(50)$ *a.u.* has been achieved for $N = 8066$ without optimization of the nonlinear parameter[1]. In this connection, it is interesting to investigate a simpler set of the projective coordinates which provides an uncoupled presentation of matrix elements of the Hamiltonian and more rapid convergence of energy.

In this paper a set of the projective coordinates is introduced and the corresponding variational basis with a single nonlinear parameter is constructed. A study of energy convergence for the helium ground state and comparison with the known calculations are presented. As a result, new values for the nonrelative energy of the helium isotope ground state are obtained.

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2 Transformation of a conventional nonfactorable variational three-body problem to the factorable one in projective coordinates

For two-electron S states, in terms of the spherical coordinates, the Hamiltonian takes the form

$$H(r_1,r_2,r_{12}) = -\frac{1}{2}\left(1+\frac{1}{M}\right)\left(\frac{\partial^2}{\partial r_1^2}+\frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_2^2}+\frac{2}{r_2}\frac{\partial}{\partial r_2}\right) -$$
$$-\left(\frac{\partial^2}{\partial r_{12}^2}+\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right)-\frac{1}{M}\cos\theta\frac{\partial^2}{\partial r_1\partial r_2}+\frac{r_2\cos\theta-r_1}{r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}+$$
$$+\frac{r_1\cos\theta-r_2}{r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}, \tag{1}$$

where M denotes either infinite or finite nuclear mass, r_i is the distance between the nucleus and the electron, r_{12} is the distance between electrons, and θ is the angle between $\vec{r}_1$ and $\vec{r}_2$. The radial portion of integration can be rewritten in the following way:

$$J=\int_0^\infty r_1dr_1\int_0^\infty r_2dr_2\int_{|r_1-r_2|}^{r_1+r_2} r_{12}dr_{12}g(r_1,r_2,r_{12}) \tag{2}$$

The three dimensional integration becomes uncoupled by the change of variables

$$s=r_1+r_2,\quad v=\frac{r_{12}}{r_1+r_2},\quad w=\frac{r_1-r_2}{r_{12}}. \tag{3}$$

For the new variables Eq (3). the integral Eq (2). is transformed

$$I=\int_0^\infty s^5ds\int_0^1 v^2dv\int_0^1(1-v^2w^2)dwf(s,v,w). \tag{4}$$

If the function f in the integrand has the form

$$f(s,v,w)=U(s)V(v)W(w), \tag{5}$$

then the integral in (4). uncouples into a product of three one-dimensional integrals.

Full advantage of this decoupling is achieved by choosing a radial basis set of the form

$$\psi_{i,j,2k}=U_i(s)V_j(v)W_{2k}(w), \tag{6}$$

where $W_{2k}(w)$ are even functions for $1S$ state of the helium atom. With this basis set, matrix elements of the overlap and of the Hamiltonian can be written as products of one dimensional integrals in the form Eq (4). The simplest basis functions for U_i can be Slater functions and for V_j and W_{2k} simple powers of variables v and w. Notice that unlike the case of perimetric coordinates, there is no limitation on the number of the nonlinear parameters which can be introduced for any of the one-dimensional basis functions.

3 Reduction of the factorable problem to the algebraic finite generalized eigenvalue problem

In this work, the basis sets are based on orthogonal polynomials suited for the domains of integration of each integrals. We use

$$U_i(s)=N_ie^{-\alpha_is}L_i^5(2\alpha_is),\ V_j(v)=\overline{N}_jP_j^{(0,2)}(2v-1),$$

$$W_{2k}(w) = \hat{N}_{2k} P_{2k}^{(1,1)}(w), \tag{7}$$

where N_i, $\overline{N}_j$, $\hat{N}_{2k}$ are normalization constants, L_i^l is a generalized Laguerre polynomial, $P_j^{(q,t)}$ is a Jacobi polynomial and α_i is a variational parameter. The basis set U_i is orthonormal, if one chooses a set with a single parameter α. With these definitions, we have

$$\int_0^\infty s^5 U_n(s) U_m(s) ds = \delta_{n,m}, \quad \int_0^1 v^2 V_n(v) V_m(v) dv = \delta_{n,m},$$

$$\int_0^1 (1-w^2) W_{2n}(w) W_{2m}(w) dw = \delta_{2n,2m}. \tag{8}$$

The overlap matrix is made up of a set of block-diagonal arrays, one for each order of the Laguerre polynomials.

Using the following additional conditions

$$\begin{aligned} t = i + a \cdot j + 2b \cdot k \le Nsvw \\ d = j + 2k \le Nvw, \end{aligned} \tag{9}$$

where $Nsvw$ is the largest value of terms in the sum of the orders U_i, V_j and W_{2k}, Nvw is the largest value of terms in the sum of the orders V_j and W_{2k}, and $a > b > 1$.

Now we can write the trial wave function in the form

$$\Psi(s,v,w) = \sum_{i,j,k=0}^{t \le Nsvw \;\; d \le Nvw} C_{i,j,2k} \psi_{i,j,2k}(s,v,w), \tag{10}$$

where $C_{i,j,2k}$ are unknown constants.

After substitution of expansion Eq (10). into the Rayleigh-Ritz variational functional

$$E(\alpha) = \min_C \frac{< \Psi | H | \Psi >}{< \Psi | \Psi >} \tag{11}$$

and subsequent minimization of the functional, the solution of Eq (1). is reduced to a solution of a generalized eigenvalue problem for an infinite set.

$$A(\alpha,\ Z,\ M)C = E(\alpha)BC, \tag{12}$$

$$A(\alpha,\ Z,\ M) = \alpha^2 A_1(M) + \alpha A_2(Z) \tag{13}$$

here $A(\alpha,\ Z,\ M)$ is a stiffness matrix and B is a mass matrix.

An enormous advantage of using the orthogonal polynomials as basis functions is the very high numerical stability of the calculations, which show no sign of a numerical dependence for the very large basis set. This stability allows one to accelerate the matrix diagonalization when more than 13-digit accuracy is required and quadruple precision calculations are necessary.

We use a method of Inverse Iteration for calculation of eigenvalues. Then we minimized the energy $E \equiv E(\alpha)$ by a nonlinear parameter α.

Table I shows the variational energy E (in a.u.) for the ground state of the helium atom obtained in this work. A comparison with the other available data is presented.

We studied the convergence by using an extrapolation formula in the form

$$E^{as} = E(N) + CN^{-\beta}, \tag{14}$$

to compare the convergence rate of the two methods mentioned above. We looked for the parameters $E^{as},\ C,\ \beta$ minimizing functional

$$\Phi(E^{as},\ C,\ \beta) = \sum_{i=1}^{m} \left(\frac{E^{as} - E(n_i) - C n_i^{-\beta}}{\delta_i} \right)^2 . \tag{15}$$

The asymptotic values of E can be found in Table I and the parameter β, which corresponds to the convergence rate, in Table II.

Table I

Variational energy values E (in a.u.) obtained in this work and

comparison with the data published. $E^{as}$is the extrapolated value.

* Nuclear masses for helium isotopes adopted in present calculations

are $M_{^3He^{2+}} = 5495.8852 m_e$ and $M_{^4He^{2+}} = 7294.2996 m_e$ [4].

N	M=∞	$(^4He^{2+})^*$	$(^3He^{2+})^*$
2204	-2.903 724 377 034 119 549	-2.903 304 557 733 234 348	-2.903 167 210 703 584 071
2937	-2.903 724 377 034 119 593 3	-2.903 304 557 733 234 392 6	-2.903 167 210 703 584 115 5
3424	-2.903 724 377 034 119 596 3	-2.903 304 557 733 234 395 5	-2.903 167 210 703 584 118 5
4077	-2.903 724 377 034 119 597 9	-2.903 304 557 733 234 397 2	-2.903 167 210 703 584 120 1
4683	-2.903 724 377 034 119 598 231	-2.903 304 557 733 234 397 493	-2.903 167 210 703 584 120 433
5272	-2.903 724 377 034 119 598 279	-2.903 304 557 733 234 397 541	-2.903 167 210 703 584 120 481
5669	-2.903 724 377 034 119 598 288	-2.903 304 557 733 234 397 550	-2.903 167 210 703 584 120 489
E^{as}	-2.903 724 377 034 119 598 297	-2.903 304 557 733 234 397 556	-2.903 167 210 703 584 120 495
[2]	-2.903 724 377 034 119 598 296		
[3]	-2.903 724 377 034 119 596		
[1]	-2.903 724 377 034 119 594		
[5]	-2.903 724 377 034 118		
[6]	-2.903 724 377 034 115		
[7]	-2.903 724 377 032 6		

Table II

β is the convergence rate,

and G is the result of [1]

Mass	β
∞	11
$^4He^{2+}$	11
$^3He^{2+}$	11
G	9

From this, we can see the convergence rate, which is calculated the energy by the use Eq (10). with the condition $\partial E(\alpha)/\partial\alpha = 0$, is better than results in [1]. ???

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