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Research paper

An explicitly correlated helium wave function in hyperspherical coordinates

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ABSTRACT

Wave functions of a new functional kind has been proposed in this work for helium-like atoms. These functions depend explicitly on interelectronic and hyperspherical coordinates. The best ground state energy for the helium atom $-2.903724376677 a.u.$ has been calculated using the variational method with a basis including a single exponential parameter. To our knowledge, this is the best result so far using of hyperspherical coordinates. Comparable result has been obtained for the hydrogen anion. For helium atom, our best wave functions matched the Kato cusp conditions within an accuracy below 6.10^{-4}. An important feature of proposed wave functions is the inclusion of negative powers of $R = \sqrt{(r_1^2 + r_2^2)}$ in combination with positive powers of r_{12} into the wave function. We showed that this is necessary condition for proposed wave function to be a formal solution of Schrödinger equation.

1. Introduction

Since Hylleraas' work, it is well known [1,2], that one of the necessary conditions of a rapid convergence towards the exact nonrelativistic ground state helium energy is the inclusion of r_{12} terms into the wave function. Until now many different methods, in which the r_{12} term is used to construct the wave function, have been suggested. These methods could be divided to variational [1–12], correlated-function hyperspherical-harmonic (hh) methods [13–15] (a nice overview of hh methods can be found in the paper of Krivec [15]) and ICI method (iterative complement interaction method)[16–18]. In general, we can state that variational methods converge to globally optimized solutions while hyperspherical-harmonic methods converge pointwise. However it is known (Bartlett et. all [19]), that wave function created from only the Slater functions and powers of r_1, r_2 and r_{12} is not the exact one. Bartlett [20] and Fock [21] were the first, who pointed out that exact wave function must depend on coordinate $R = \sqrt{r_1^2 + r_2^2}$. Fock's wave function depends on the powers of R^2 multiplied by powers of the logarithmic term $\ln R^2$. Due to the mathematical difficulty of direct implementation of Fock's approach it was probably firstly implemented in the work of Sochilin and Ermolaev [22]. The next important work was done by Frankowski and Pekeris [5] in 1966. Their results were improved by Freund, Huxtable and Morgan [6], each group used wave functions based on Hylleraas coordinates and powers of the logarithmic term of the coordinate $s = r_1 + r_2$.

Our effort is concentrated on finding a competitive approach with use of simple functions as coordinate system that could be generalized to more than two electron atoms. We proposed the approach where the wave function depends besides the powers of r_{12} on the hyperradial coordinate $R = \sqrt{r_1^2 + r_2^2}$ and on the coordinate $t = (r_2^2 - r_1^2)/(r_2^2 + r_1^2)$. The function t has only one shortage, it is not well defined at the region where $r_1 \to 0$ and $r_2 \to 0$ (it does not have double limit in the point $r_1 = 0$ and $r_2 = 0$, it depends on path that goes to this point), so it has not derivative in this point. But in the rest area it is well defined, so it is not a significant defect. This function is more simple and easier to handle than that Fock's one. Probably the first attempt to use these coordinates directly in variational approaches was done in [24], but the authors did not used interelectronic coordinates r_{ij}.

As a first test of quality of the basis set all calculations were done with the same exponential scale factor ζ in $\exp(-\zeta R)$. An important feature of this approach is the inclusion of negative powers of R in combination of positive powers of r_{12}. The incorporation of these terms is – similar to the approach of Kinoshita [3] – necessary for the wave function to be a formal solution of Schrödinger equation. In [23] Sochilin and Ermolaev firstly proposed using the powers of the function $w = r_{12}/R$ for the determination of excited $2S^3$ state energy of helium atom. In this approach, the Hylleraas coordinates were used and it is not clear from their article, how they used the proposed function w in actual calculations.

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As a first step the variational method has been used. We want to show that this (or similar) proposed basis sets open new possibilities in finding of the proper wave function that satisfies all cusp conditions. We believe that this knowledge will increase a chance to construct general few electron (with number of electrons more than two) atomic (or molecular) wave functions, because of a pairwise character of electron-electron and nuclear-electron interactions.

2. Hamiltonian transformation and basis set construction

The Hamiltonian for helium atom in S basic state in coordinates r_1, r_2 and r_{12} can be written as

$$H = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{1}{2}\frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{1}{2}\frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{1}$$

As it was already mentioned in the introduction, a function constructed with the powers of r_1, r_2 and r_{12} is not an exact eigenfunction of the Hamiltonian (1) due to the cross terms $\frac{r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}}$ and $\frac{r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}$. Let us make the following transformation of the coordinate system:

$$R = \sqrt{r_1^2 + r_2^2} \tag{2}$$

$$t = \frac{r_2^2 - r_1^2}{r_2^2 + r_1^2} \tag{3}$$

so the r_1 and r_2 coordinates can be expressed as

$$r_1 = \frac{R\sqrt{1-t}}{\sqrt{2}} \tag{4}$$

$$r_2 = \frac{R\sqrt{1+t}}{\sqrt{2}} \tag{5}$$

After somehow lengthy manipulations we obtain the following transformed Hamiltonian

$$H = -\frac{1}{2}\frac{\partial^2}{\partial R^2} - \frac{5}{2R}\frac{\partial}{\partial R} - \frac{2(1-t^2)}{R^2}\frac{\partial^2}{\partial t^2} + \frac{6t}{R^2}\frac{\partial}{\partial t} - \frac{r_{12}}{R}\frac{\partial^2}{\partial R \partial r_{12}} - \frac{2t}{r_{12}}\frac{\partial^2}{\partial t \partial r_{12}} + \frac{2t.r_{12}}{R^2}\frac{\partial^2}{\partial t \partial r_{12}} - \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{Z\sqrt{2}}{R\sqrt{1-t}} - \frac{Z\sqrt{2}}{R\sqrt{1+t}} + \frac{1}{r_{12}} \tag{6}$$

We see that the cross terms that caused problems in (1) are now transformed to somewhat more convenient expressions, namely, the differential terms now always contain at most a single singularity factor [compared with double singularity factors $(r_1 r_{12})^{-1}, (r_2 r_{12})^{-1}$ in (1)] with all the unconvenient double singularity factors occurring now only in nuclear potential terms. It seems rather natural to include some combinations of the powers of R, r_{12} and t into the wave function. Moreover, we must carefully treat the singularities in potentials and the antisymmetry of the wave function. If we could expand the potential term

$$V_{nuc} = -\frac{Z\sqrt{2}}{R}\left(\frac{1}{\sqrt{1-t}} + \frac{1}{\sqrt{1+t}}\right) \tag{7}$$

in a Taylor series around $t = 0$ in the whole range of t, the solution in the form of linear combinations of $R^i r_{12}^j t^{2k} \exp -\zeta R$ would indeed be sufficient. Our analysis showed (see Appendix A) that in this case we can eliminate all the singularities when we also include – similar to Kinoshita [3] – combinations with negative powers i for R^i. Restricting the Taylor expansion to even powers of t guarantees the required symmetry with respect to the particle interchange, moreover, odd powers of t mutually cancel in the Taylor expansion of (7) anyway. However, this Taylor expansion evidently diverges for $t = \pm 1$. The modified expansion

$$V_{nuc} = -\frac{2\sqrt{2}Z}{R\sqrt{1-t^2}}\left(1 - \sum_{k=1}^{\infty}\frac{(4k-3)!!}{4k!!}t^{2k}\right) \tag{8}$$

already correctly reproduces the singular behaviour for $t = \pm 1$, however, the convergence of the series in the vicinity of the singularities is slower. On the other hand, the alternative expansion

$$V_{nuc} = -\frac{2Z}{R\sqrt{1-t^2}}\left(1 + \frac{1}{2}\sqrt{1-t^2} + \sum_{k=2}^{\infty}\frac{(-1)^{k+1}(2k-3)!!}{2k!!}\sqrt{1-t^2}^{\,k}\right) \tag{9}$$

works well anywhere except the vicinity of $t = 0$. Based on these potential expansion considerations we suggested the following form for our wave function (para case)

$$\Psi_1 = \sum_{i,j}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{1} C_{ijkl} R^i r_{12}^j t^{2k} \sqrt{1-t^2}^{\,l} e^{-\zeta R}\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}. \tag{10}$$

With this form a function we have a chance to eliminate the potential term $1/\sqrt{1-t^2}$. Summations over l in (10) are restricted to 0 and 1 in order to avoid redundancies caused by combinations of powers of t^{2k}.

By linear combinations of the functions of the type (10) a formally simpler form can be obtained

$$\Psi_2 = \sum_{i,j}^{\infty}\sum_{k=0}^{\infty} C_{ijk} R^i r_{12}^j \sqrt{1-t^2}^{\,k} e^{-\zeta R}\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}. \tag{11}$$

As (10) can be transformed into (11) it is not surprising that also for a finite truncation of infinite sums in (10), (11) these two functions give for a comparable basis sets almost the same results. In our test calculations the wave functions of the type (10) gave slightly better results, so we decided to work further with Ψ_1 rather than Ψ_2 (we will refer to this type of function as Basis A in the text).

For even better cancellation of the nuclear potential we suggested a wave function of a little more complex form,

$$\Psi_3 = \left(\sum_{i}^{\infty}\sum_{j=0}^{\infty} R^i r_{12}^j e^{-\zeta R}\left(\sum_{k=0}^{\infty} A_{i,j,k} t^{2k}(\sqrt{1-t} + \sqrt{1+t}) + \sum_{k=1}^{\infty} B_{i,j,k} t^{2k-1}(\sqrt{1-t} - \sqrt{1+t})\right) + \sum_{i}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty} R^i r_{12}^j e^{-\zeta R}\sum_{l=0}^{1} C_{ijkl} t^{2k}\sqrt{1-t^2}^{\,l}\right)\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}. \tag{12}$$

Expansion in this basis set (denoted as Basis B) has the advantage that for properly chosen coefficients $A_{ijk}, B_{ijk}, C_{ijkl}$ acting with (6) on (12) results in the same type of functions on both sides of the Schrödinger equation. Until now we did not find anything that would contradict the statement that (12) is a formal solution of the Schrödinger equation.

In addition, we considered also a modification of (12) with more complex exponential factor $\exp\{-\zeta R(\sqrt{1-t} + \sqrt{1+t})/\sqrt{2}\}$ instead of the simple $\exp(-\zeta R)$. This function we denoted as Basis C.

Notice that each of the suggested forms of wave function (10)–(12) is also automatically antisymmetric with respect to particle interchange.