On the use of Chandrasekhar's basis for helium and its isoelectronic series

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We report a systematic investigation of the ability of Chandrasekhar's basis to produce energy eigenvalues for the helium isoelectronic sequence and compare it with the standard Hylleraas' basis. The basis is found to be extremely useful to obtain fast and accurate energy approximations for H^-. In addition, we also investigate the dependence of energy eigenvalues on the interelectronic u coordinate and find it to be more important for $Z\geqslant 2$.

In 1929 Hylleraas[1,2] introduced the coordinates s,u,t and the wave function

$$\psi_{\rm H}(s,u,t)=e^{-s/2}\sum_{i,j,k} c_{i,j,k}\,s^i u^j t^k, \qquad (1)$$

as an *ansatz* to describe properties of helium. The basic reason of introducing these coordinates was their simplicity in dealing with the explicit electronic correlation u of two-electron systems. Essentially, the coordinates reduced variational calculations involving Eq. (1) above to the evaluation of integrals of the generic type

$$I_{\rm H}=\int_0^\infty e^{-s}ds\int_0^s du\int_0^u dt\, s^i u^j t^k=\frac{(i+j+k+2)!}{(k+1)(j+k+2)}. \qquad (2)$$

While such calculations produced good results for atoms with $Z\geqslant 2$, their success was not so great for $Z=1$, the negative hydrogen ion. The poor convergence for $Z=1$ induced Chandrasekhar[3] to suggest using

$$\psi_{\rm C}(s,u,t)=e^{-s/2}\cosh(\tfrac{1}{2}\epsilon t)\sum_{i,j,k} d_{i,j,k}\,s^i u^j t^k, \qquad (3)$$

where ϵ should account for "missing" screening and polarization. Obviously, for $\epsilon=0$, $\psi_{\rm C}\equiv\psi_{\rm H}$. In addition to $I_{\rm H}$, energy calculations with Eq. (3) imply having to deal with the family of integrals

$$I_{\rm C}=\int_0^\infty e^{-s}ds\int_0^s du\int_0^u e^{\alpha t}s^i u^j t^k dt=\frac{(-1)^{k+1}k!(i+j+1)!}{(j+1)\alpha^{k+1}}+\sum_{n=0}^{k}\frac{(-1)^{j+k+1}k!(k+j-n)!i!}{(k-n)!\alpha^{j+k+2}}$$
$$+\sum_{n=0}^{k}\sum_{m=0}^{j+k-n}\frac{(-1)^{n+m}k!(j+k-n)!(i+j+k-n-m)!}{(k-n)!(j+k-n-m)!\alpha^{n+m+2}(1-\alpha)^{i+j+k-n-m+1}}. \qquad (4)$$

Chandrasekhar showed that Eq. (3) indeed produces better results for H^-. His function could have well been used to calculate properties of the whole helium isoelectronic series. However, while Hylleraas' wave function was applied in many investigations of properties of two-electron systems, Chandrasekhar's wave function was essentially forgotten. A reason for this could be the quite complicate nature of $I_{\rm C}$. The situation did not change with the advent of modern computers; the general approach has mainly been to use long expansions involving configurations producing simple integrals rather than looking for "better basis," i.e., basis allowing one to obtain the same numerical accuracy but using much less configurations. The price to be paid for reducing the number of configurations is an increase in the complexity of integrals. But, when is it convenient to pay the price? Would it be convenient to replace Hylleraas' by Chandrasekhar's basis in general?

The purpose of the present note is to present results of a systematic investigation of how the inclusion of the $\cosh[\frac{1}{2}\epsilon t]$ term in Hylleraas' *ansatz* influences variational energies obtained for the helium isoelectronic sequence. Another objective is to study the relative importance of terms involving the u coordinate ("explicit correlations") in variational trial functions. Good u-independent *ansätze* for two-electron systems are of importance in studies of noncentral potentials like, e.g., the quadratic Zeeman effect, in the same spirit that allowed the introduction of a convenient basis to describe with very high accuracy properties of hydrogen atoms in magnetic fields of arbitrary strength.[4] The "noncentral" nature of the potential, i.e., its

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TABLE I. Energies (a.u.) obtained by adding the term in the first column to the expansion $\varphi(s,u,t)=\cosh(\frac{1}{2}\epsilon t)(1+x_1s+x_2u+x_3t^2)$. The terms in the first column were ordered according their effectiveness in lowering the energy for $Z=1$, downwards from best to worst term. The numbers in parenthesis in the last two columns indicate the order that is obtained for $Z=2$ and 10. The terms are separated into three groups, according to the sum of their exponents.

Term	$E(Z=1)$	$E(Z=2)$	$E(Z=10)$
u^2	−0.527 151 4	−2.902 963 1(1)	−93.905 351 7(1)
s^2	−0.527 142 5	−2.902 797 6(2)	−93.904 652 1(2)
su	−0.527 029 3	−2.902 590 4(3)	−93.904 364 6(3)
st^2	−0.527 175 1	−2.902 629 3(6)	−93.904 288 9(5)
s^3	−0.527 159 3	−2.902 793 9(1)	−93.904 579 8(3)
u^3	−0.527 061 3	−2.902 744 0(2)	−93.904 855 9(1)
su^2	−0.527 031 4	−2.902 632 4(5)	−93.904 556 4(4)
s^2u	−0.527 048 5	−2.902 637 4(4)	−93.904 284 0(6)
ut^2	−0.527 026 0	−2.902 705 9(3)	−93.904 745 8(2)
s^2t^2	−0.527 331 7	−2.902 691 8(2)	−93.904 333 6(5)
sut^2	−0.527 152 9	−2.902 593 0(8)	−93.904 310 3(7)
s^4	−0.527 152 0	−2.902 743 4(1)	−93.904 452 3(2)
t^4	−0.527 121 2	−2.902 611 2(5)	−93.904 289 4(9)
s^3u	−0.527 087 3	−2.902 653 1(3)	−93.904 293 6(8)
u^2t^2	−0.527 048 2	−2.902 606 7(6)	−93.904 438 2(4)
s^2u^2	−0.527 035 9	−2.902 590 0(9)	−93.904 330 6(6)
u^4	−0.527 027 7	−2.902 632 5(4)	−93.904 528 0(1)
su^3	−0.527 025 2	−2.902 605 7(7)	−93.904 442 2(3)

dependence on the angular coordinates entangles integrals needed to evaluate quantities like, e.g., energies. Such entangling would be avoided if trial functions did not explicitly depended on u. Therefore, it would be of great help to find a basis not involving directly the u-coordinate but that, in spite of this, could yield good eigenvalues. These are our main motivations.

We start by considering the trial function

$$\varphi(s,u,t)=\cosh(\tfrac{1}{2}\epsilon t)(1+x_1s+x_2u+x_3t^2), \tag{5}$$

which contains the lowest-order terms in s,u, and t. The notation and method is the same we used before.[5] By diagonalizing and minimizing the 4×4 matrix corresponding to Eq. (5) we obtained the energies −0.527 025 2, −2.902 589 6, and −93.904 283 8 a.u. for $Z=1$, 2, and 10, respectively. The problem now is to determine from the multitude of possible terms, which are the most relevant ones to be added to the expansion of Eq. (5). To this end we follow Chandrasekhar and Herzberg;[6] we consider the effect of adding further terms, one at a time, in the expansion. "Good" terms are those which produce the biggest individual decrease of the energy. The several terms selected in this way are then all added to the fixed expansion and a new energy is calculated from the new function. The Z-dependent ordering of subsequent terms obtained for $Z=1$, 2, and 10 is shown in Table I. By trial and error we conclude a fair compromise for all Z to be

$$\begin{aligned}\varphi(s,u,t)=\cosh(\tfrac{1}{2}\epsilon t)(&1+x_1s+x_2u+x_3t^2+x_4s^2+x_5u^2\\&+x_6su+x_7st^2+x_8ut^2+x_9s^3+x_{10}s^2u+x_{11}su^2\\&+x_{12}u^3+x_{13}s^2t^2+x_{14}sut^2+x_{15}s^4).\end{aligned} \tag{6}$$

This function contains the first 12 terms in the first column of Table I. For low Z, u terms seem to be less important than terms with s,t, and powers of st. Table II shows the energies obtained by minimizing the energy functional[5] involving κ and $a\equiv 1-\epsilon^2$. Table II also contains "exact" energies, i.e., the most accurate energy values available in the literature, obtained by Frankowski and Pekeris[7] and, more recently, by Freund *et al.*[8] Frankowski and Pekeris used 246 terms of the generic form

$$\varphi(s,u,t)=s^nt^lu^m(s^2+t^2)^{i/2}(\ln s)^j, \tag{7}$$

while Freund *et al.* considered 230 terms of the form

$$\varphi(s,u,t)=s^nt^lu^m(\ln s)^j. \tag{8}$$

TABLE II. Energies (a.u.) for $Z=1$, 2, and 10 for increasing dimension of the matrix generated with Eq. (6). E_H and E_C refer to the energies as obtained using the wave functions of Hylleraas [Eq. (1)] and Chandrasekhar [Eq. (3)], respectively. Exact values are from Refs. 7 and 8.

	$Z=1$		$Z=2$		$Z=10$	
Dimension	E_H	E_C	E_H	E_C	E_H	E_C
2	−0.472 656	−0.513 302	−2.847 656	−2.875 663	−93.847 65	−93.871 76
3	−0.509 590	−0.526 097	−2.891 232	−2.901 419	−93.895 49	−93.903 29
4	−0.526 262	−0.527 025	−2.902 473	−2.902 589	−93.903 65	−93.904 28
5	−0.526 275	−0.527 142	−2.902 774	−2.902 797	−93.904 51	−93.904 65
6	−0.526 464	−0.527 417	−2.903 329	−2.903 364	−93.905 75	−93.906 03
7	−0.526 594	−0.527 433	−2.903 425	−2.903 429	−93.906 22	−93.906 30
8	−0.526 633	−0.527 467	−2.903 441	−2.903 453	−93.906 24	−93.906 33
9	−0.526 807	−0.527 481	−2.903 502	−2.903 506	−93.906 41	−93.906 41
10	−0.526 808	−0.527 492	−2.903 523	−2.903 536	−93.906 52	−93.906 54
11	−0.526 875	−0.527 581	−2.903 590	−2.903 616	−93.906 58	−93.906 59
12	−0.526 893	−0.527 611	−2.903 628	−2.903 639	−93.906 64	−93.906 65
13	−0.526 893	−0.527 611	−2.903 640	−2.903 659	−93.906 70	−93.906 71
14	−0.526 906	−0.527 695	−2.903 684	−2.903 688	−93.906 72	−93.906 73
15	−0.526 967	−0.527 711	−2.903 693	−2.903 694	−93.906 73	−93.906 74
16	−0.526 967	−0.527 712	−2.903 700	−2.903 701	−93.906 75	−93.906 76
Exact		−0.527 751		−2.903 724		−93.906 80

In the precision used in Table II, the numbers of Frankowski and Pekeris and of Freund *et al.* agree in all digits. For H^- Frankowski and Pekeris obtain the "extrapolated" value $-0.527\,751\,016\,38$ while Freund *et al.* obtain $-0.527\,751\,015\,3$.

From Table II, it is easy to see that for $Z=1$ Chandrasekhar's wave function is much more efficient in producing converged energies than the simple *ansatz* of Hylleraas. In view of the relative complexity of I_C when compared with I_H, this table also convincingly shows that Hylleraas' wave function is a more convenient basis to be used for $Z \geqslant 2$. Although Table II presents results for the specific sequence of configurations given in Eq. (6), we also minimized the energy functional for several other orders and possible combinations of terms in Table I. Based in Table I it is reasonable to expect terms like s^2t^2 or sut^2 to be more important than, for example, u^3, su^2, s^2u or ut^2. However, when included in the trial function, the last terms optimize the convergence in a better fashion than when skipping them. Note however the increased convergence in passing from dimension 13 to 14, i.e., when explicitly considering the s^2t^2 term. This effect is also seen for $Z=2$ and 10. $Z=1$ tends to prefer s^kt^2 terms while $Z=2$ and 10 prefer s^{k+2} and u^{k+2}. u-terms are much more important at higher Z than at $Z=1$.

An interesting fact to be observed during the minimization of κ and ϵ^2 was the possibility of having $\epsilon^2<0$ for $Z \geqslant 2$, exactly when the energy functional seems to be less sensitive to ϵ. This changes the hyperbolic function in Eq. (3) into a simple trigonometric function. Since imaginary ϵ are quite unexpected here, a reason for their appearence could be a numerical instability coming from handling high-dimensional matrices involving as elements several powers of the variable a, i.e., $a^6, a^7, \ldots, a^{12}$. In any case, if indeed real, such instabilities only show up for large Z, where we already know Hylleraas basis (i.e., $\epsilon=0$) to be a much better choice.

In conclusion, we find Chandrasekhar's *ansatz* to be an extremely effective basis set to calculate the energy of H^-. The significant gain can be easily seen by comparing columns E_H and E_C in Table II. Although Chandrasekhar's basis can also be used for $Z \geqslant 2$ with no great problem, the final results are of the same quality as those obtained by using Hylleraas' basis. In view of the simpler nature of the matrices involved when using Hylleraas' basis, this set is to be preferred for $Z \geqslant 2$. This makes Chandrasekhar's basis a promising candidate to be used in investigations of noncentral potentials like, for example, the quadratic Zeeman effect in H^-. We hope to report about such calculation soon.

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