LETTER TO THE EDITOR

The wavefunction for the ground state of H⁻

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Abstract. We investigate the ground-state energy of H⁻ using a variational function recently proposed by Wu and Tsai. Contrary to their conclusions, we find that their function produces results comparable with a previous calculation of Williamson. Furthermore, the explicit formulae given in the present paper can easily be applied to the helium isoelectronic series.

In a recent letter in this journal, Wu and Tsai (1985) proposed a four-parameter variational function to approximate the ground state of H⁻. Their function was obtained by considering a term proportional to st^2 in a previous ansatz due to Chandrasekhar; in other words, they proposed the function

$$\psi(s, u, t) = e^{-s/2} \cosh(\tfrac{1}{2}\varepsilon t)(1 + x_1 u + x_2 st^2) \tag{1}$$

where as usual $\Psi(s, u, t) = \psi(ks, ku, kt)$; s, u and t are Hylleraas' coordinates and k, ε and x_i are variational parameters. The particular case $\varepsilon = 0$ corresponds to the well known expansion introduced by Hylleraas (see, for example, Bethe and Salpeter 1957). Wu and Tsai compared the energy obtained from ψ in equation (1) with the energy obtained in an early investigation by Williamson (1942) using the six-parameter Hylleraas-type ansatz

$$\psi(s, u, t) = e^{-s/2}(1 + x_1 u + x_2 t^2 + x_3 s + x_4 s^2 + x_5 u^2). \tag{2}$$

According to the results in their table 1, the energies obtained from equation (1) should be much superior to the corresponding ones from equation (2).

We believe the suggestion of Wu and Tsai to be interesting in two respects. The first is the obvious one of reducing the total number of variational parameters (in spite of using a basis which is more difficult to deal with) but the second is more subtle: it gives us hope that the correlation terms might not, after all, play such a crucial role. This last point is of special significance for those wishing to investigate properties of two-electron atomic systems in the presence of angle-dependent potentials such as the Zeeman diamagnetism in helium-like atoms. Actual calculations of the properties of two-electron atomic systems in the presence of strong magnetic fields would be very much simplified if one could eventually find good trial functions not involving correlation (i.e. angular dependence). With this purpose in mind we reviewed the calculation of Wu and Tsai (1985), since we had been somewhat surprised by the numbers reported

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in their table 1. Contrary to the conclusions of these authors, we find that equation (1) produces results comparable with those from equation (2). Furthermore, since it is easier to evaluate the matrix elements in Hylleraas' basis than in that of Chandrasekhar, we believe the real gain in using equation (1) instead of equation (2) to be rather small. In the remaining part of this letter we present the explicit analytical results of our investigation of the ground-state energy, as well as an application to the helium isoelectronic series.

The evaluation of the eigenenergies, although quite laborious in the present case, is straightforward (see Bethe and Salpeter (1957) for details). Assuming the eigenfunction to be an even function of t, we write $\psi = e^{-s/2}\varphi(s, u, t)$ and use the definitions

$$N = \tfrac{1}{8} \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-s} u(s^2 - t^2)\varphi^2 \tag{3}$$

$$L = 2 \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-s} us\varphi^2 \tag{4}$$

$$L' = \tfrac{1}{2} \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-s}(s^2 - t^2)\varphi^2 \tag{5}$$

$$M' = \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-s}[u(s^2 - t^2)(\varphi_s^2 + \varphi_u^2 + \varphi_t^2)$$
$$+ 2s(u^2 - t^2)\varphi_s\varphi_u + 2t(s^2 - u^2)\varphi_u\varphi_t] \tag{6}$$

$$M = L - 2N - M'. \tag{7}$$

Our task is now to solve the generalised eigenvalue problem $H\psi_k = E_k S\psi_k$ where H and S are the symmetrical matrices

$$H_{ij} = k^2 M_{ij} - k(L_{ij} - L'_{ij}/Z) \tag{8}$$

$$S_{ij} = N_{ij}. \tag{9}$$

Equations (3)–(9) above have here been given explicitly because they are simpler to apply than the results presented by Bethe and Salpeter. Our normalisation agrees with that in equation (23) of Hylleraas (1929).

Taking

$$\varphi = (1 - \varepsilon^2)^{3/2} \cosh(\tfrac{1}{2}\varepsilon t)(1 + x_1 u + x_2 st^2)$$

corresponding to the ansatz of equation (1), and definining $a \equiv 1 - \varepsilon^2$ we find, after a long and tedious calculation,

$$
\begin{aligned}
&N_{11} = 2 + 2a^3 \qquad N_{12} = \tfrac{1}{4}(35a^3 - a - 12 + 48/a) \\
&N_{13} = 96(a^3 - 9/a^2 + 10/a^3) \qquad N_{22} = 48(a^3 - 1/a + 2/a^2) \\
&N_{23} = 3(231a^3 + 5 + 50/a + 656/a^2 - 4320/a^3 + 3840/a^4) \\
&N_{33} = 2880(11a^3 - 33/a^3 + 660/a^4 - 1512/a^5 + 896/a^6)
\end{aligned}
\tag{10}
$$

$$
\begin{aligned}
&L_{11} = 8 + 8a^3 \qquad L_{12} = 30a^3 - 2a - 16 + 48/a \\
&L_{13} = 48(7a^3 + 7/a - 80/a^2 + 80/a^3) \\
&L_{22} = 48(3a^3 - 5/a + 8/a^2) \\
&L_{23} = 80(28a^3 + 1 + 3/a + 168/a^2 - 720/a^3 + 576/a^4) \\
&L_{33} = 11\,520(9a^3 - 99/a^3 + 836/a^4 - 1624/a^5 + 896/a^6)
\end{aligned}
\tag{11}
$$

$$L'_{11} = \tfrac{1}{2}(5a^3 + a^2 + 4a) \qquad L'_{12} = 8(1 + a^3)$$
$$L'_{13} = 3(21a^3 - 3a - 16 - 88/a + 128/a^2)$$
$$L'_{22} = 35a^3 - a - 12 + 48/a \tag{12}$$
$$L'_{23} = 384(a^3 - 9/a^2 + 10/a^3)$$
$$L'_{33} = 360(39a^3 + 2 + 13/a + 40/a^2 + 816/a^3 - 2624/a^4 + 1792/a^5)$$

$$M_{11} = 4a^4 - 4a + 8$$
$$M_{12} = \tfrac{1}{2}(35a^4 - 10a^3 - a^2 + 2a - 72 + 96/a)$$
$$M_{13} = 48(4a^4 - a^3 + 27/a - 104/a^2 + 80/a^3)$$
$$M_{22} = 32(3a^4 - a^3 + 2 - 12/a + 12/a^2) \tag{13}$$
$$M_{23} = 6(231a^4 - 56a^3 - a - 12 - 324/a + 4672/a^2 - 11\,840/a^3 + 7680/a^4)$$
$$M_{33} = 1152(55a^4 + 6a^3 + 111/a^2 - 2690/a^3 + 12\,160/a^4 - 18\,480/a^5 + 8960/a^6).$$

It is interesting to observe that equation (2) had already been used in an early investigation of helium by Hylleraas (1929). Indeed, in equation (23) of his paper Hylleraas gives analytical expressions for N, M and $L - L'/2$ (denoted by L in his equation (23)). To check the energy result of Williamson we recalculated the expressions for L and L' using ψ of equation (2). These results generalise the equations of Hylleraas to the full isoelectronic series. In the notation of equation (23) of Hylleraas we find

$$
\begin{aligned}
L = 16 &+ 120c_1 + 192c_2 + 160c_3 + 960c_4 + 576c_5 \\
&+ c_1(288c_1 + 1120c_2 + 720c_3 + 5040c_4 + 3360c_5) \\
&+ c_2(2304c_2 + 1344c_3 + 10\,752c_4 + 7680c_5) + c_3(480c_3 + 6720c_4 + 4032c_5) \\
&+ c_4(26\,880c_4 + 32\,256c_5) + 11\,520c_5^2
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
L' = 5 &+ 32c_1 + 36c_2 + 50c_3 + 300c_4 + 140c_5 \\
&+ c_1(70c_1 + 192c_2 + 192c_3 + 1344c_4 + 768c_5) \\
&+ c_2(312c_2 + 252c_3 + 2016c_4 + 1232c_5) + c_3(150c_3 + 2100c_4 + 980c_5) \\
&+ c_4(8400c_4 + 7840c_5) + 2520c_5^2.
\end{aligned}
\tag{15}
$$

For $\varepsilon = 0$ ($a = 1$) the 2×2 minors in equations (10)–(13) agree with equations (14) and (15) and with equation (23) of Hylleraas (1929).

Table 1 presents the results of the generalised eigenvalue problem mentioned above. We believe all of the digits in our eigenvalues to be exact. Dimension 2 refers to energies obtained neglecting the term st^2 in equation (1), while dimension 3 refers to the case $x_1 \neq 0$ and $x_2 \neq 0$. Since we are diagonalising matrices we have, in fact, a one- or two-parameter minimisation problem corresponding to whether $\varepsilon = 0$ or $\varepsilon \neq 0$, respectively. All parameters x_i are automatically fixed by the diagonalisation procedure and are therefore not quoted here.

In table 2 the best eigenvalue obtained from ψ in equation (1) is compared with eigenvalues obtained by other authors. We have recalculated the values quoted by Bethe (1929), Chandrasekhar (1944) and Williamson (1942). They agree with the values in the original publications. Our value ought to agree with that of Wu and Tsai, but it does not. We first note that there is a discrepancy of a factor of two between μ as defined in equation (5) of Wu and Tsai and that reported in their table 1. The same discrepancy appears in the paper by Williamson. In addition, the value 0.478 attributed by Wu and Tsai to Chandrasekhar is incorrect: the correct value of μ obtained by

Table 1. Ground-state energies for the first five members of the helium isoelectronic series as obtained from equation (1) with (dimension = 3) and without (dimension = 2) the term proportional to st^2.

Dimension	Z	E (Z^2 Ryd)	E (au)	k	ε^2
2	1	−1.017 5609	−0.508 7805	0.825 726	0.0
	2	−1.445 5604	−2.891 1207	0.924 842	0.0
	3	−1.615 1460	−7.268 1572	0.952 144	0.0
	4	−1.705 5065	−13.644 0521	0.964 795	0.0
	5	−1.761 5635	−22.019 5437	0.972 114	0.0
3	1	−1.051 7010	−0.525 8505	0.812 287	0.0
	2	−1.450 5305	−2.901 0609	0.923 733	0.0
	3	−1.616 9203	−7.276 1413	0.951 434	0.0
	4	−1.706 3922	−13.651 1372	0.964 164	0.0
	5	−1.762 0893	−22.026 1161	0.971 543	0.0
2	1	−1.051 8375	−0.525 9187	0.776 158	0.148 116
	2	−1.450 7099	−2.901 4197	0.911 163	0.044 887
	3	−1.617 1497	−7.277 1737	0.943 541	0.027 430
	4	−1.706 5682	−13.652 5455	0.958 472	0.019 877
	5	−1.762 2207	−22.027 7593	0.967 112	0.015 620
3	1	−1.052 9793	−0.526 4896	0.801 324	0.029 766
	2	−1.450 7569	−2.901 5137	0.908 427	0.055 352
	3	−1.617 1902	−7.277 3557	0.941 093	0.036 705
	4	−1.706 5984	−13.652 7875	0.956 419	0.027 739
	5	−1.762 2435	−22.028 0436	0.965 372	0.022 360

Table 2. Ground-state energy of H⁻ as calculated by several authors. The calculation of Pekeris was based on a 444-parameter trial function.

	k	E (Z^2 Ryd)	E (au)
Bethe (1929)	0.768 8499	−1.050 6194	−0.525 3097
Chandrasekhar (1944)	0.776 1583	−1.051 8375	−0.525 9187
Williamson (1942)	0.701 1856	−1.052 9287	−0.526 4644
Wu and Tsai (1985)	0.801	−1.053 26	−0.526 63
Present result	0.801 3237	−1.052 9793	−0.526 4896
Pekeris (1962)		−1.055 5020	−0.527 7510

Chandrasekhar is $\frac{1}{2}(1.07478 + 0.47758) = 0.77618$, which agrees with the value 0.7761583 recalculated by us. With the factor of two taken properly into account, the relation between the parameters μ and β of Wu and Tsai and our k and ε is given by $k = \frac{1}{2}\mu(\beta + 1)$, $\varepsilon = (\beta - 1)/(\beta + 1)$. Therefore, Wu and Tsai find the minimum energy at $(k, \varepsilon^2) = (0.8008, 0.03045)$ while we find it at $(0.8013, 0.02977)$. We have considered the possibility of the existence of more than one minimum and have found that in the region $0.5 \le k \le 1.2$ and $0.015 \le \varepsilon^2 \le 0.050$ there is only one, centred at $(0.8013, 0.02977)$. We have no explanation for the difference between the energies.

In summary, the four-parameter variational function of equation (1) and the six-parameter function of equation (2) produce about the same energy eigenvalue for H⁻. The matrix elements are much more easily calculable using the function in equation (2) than with the function in equation (1).

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