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Note on the Hylleraas-Eckart Split-Shell Description of the Groundstate of Atomic Two-Electron Systems

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When the space part of the wavefunction of the groundstate of atomic two-electron systems is taken to be $\phi(1,2)=u(1)v(2)+v(1)u(2)$, where $u=\exp(-ar)$ and $v=\exp(-br)$, the parameters a and b as well as the energy associated with $\phi(1,2)$ can be determined in the form of power series involving the nuclear charge Z. For small values of Z the convergence of these series is rather slow. The quantities mentioned, however, may be determined to any degree of accuracy by a method of stepwise approximation.

1. Introduction

In the split-shell treatment of the groundstate of atomic two-electron systems the spatial wavefunction has the form

$$\phi(1,2)=u(1)\,v(2)+v(1)\,u(2) \tag{1}$$

where u and v are one-electron functions. If these functions are taken to be simple exponentials,

$$u=\exp(-ar), \qquad v=\exp(-br) \tag{2}$$

one obtains the original form of the split-shell idea, suggested by Hylleraas [1] and Eckart [2] about forty years ago. Since then the functions (2) have been used by several authors [3–5] who obtained the optimum values of the parameters, at least in part, by trial and error. Scherr and Silverman [6] gave a rough analysis of these numerical results in terms of the nuclear charge Z. Their work can easily be extended by a slightly different approach and the accuracy of the results is only limited by the patience of the calculator.

For the calculations involved it is convenient to introduce a scale factor k and a splitting parameter s such that

$$\left.\begin{matrix}a\\b\end{matrix}\right\}=k(1\pm\sqrt{s})\,. \tag{3}$$

The optimum values of the scale factor and the energy are given by [6]

$$k=\frac{(16Z-5)\,[1+(1-s)^3]+s(6-s)}{16(1-s)\,[1+(1-s)^3]+32s} \tag{4}$$

and

$$E=-k^2\frac{(1-s)\,[1+(1-s)^3]+2s}{1+(1-s)^3}\,, \tag{5}$$

respectively, in which the optimum value of the splitting parameter s must be determined from the relation

$$\begin{aligned}&16Zs[24-90s+169s^2-201s^3+162s^4-91s^5+36s^6-9s^7+s^8]\\&\quad=48+32s-414s^2+1013s^3-1388s^4+1188s^5-644s^6+224s^7-48s^8+5s^9\,.\end{aligned} \tag{6}$$

2. Determination of the Power Series Involving Z

From (6) one obtains by division

$$
\begin{aligned}
s = \frac{1}{8Z}\Bigg[& 1+\frac{53}{12}s+\frac{43}{48}s^2+\frac{1001}{576}s^3+\frac{3529}{2304}s^4-\frac{7237}{27648}s^5 \\
& -\frac{1\,58117}{1\,10592}s^6-\frac{8\,06287}{13\,27104}s^7+\frac{59\,37361}{53\,08416}s^8 \\
& +\frac{1097\,10227}{637\,00992}s^9+\cdots\Bigg].
\end{aligned} \tag{7}
$$

Substituting for every s in the right hand side of (7) the whole expression (7) one finds the following Z-expansion

$$
\begin{aligned}
s = \frac{1}{8Z}\Bigg[& 1+\frac{53}{96Z}+\frac{2938}{(96Z)^2}+\frac{1\,72391}{(96Z)^3}+\frac{107\,66326}{(96Z)^4} \\
& +\frac{7137\,09290}{(96Z)^5}+\frac{4\,97679\,15652}{(96Z)^6}+\frac{360\,94587\,85775}{(96Z)^7} \\
& +\frac{26948\,87779\,22470}{(96Z)^8}+\frac{20\,55175\,97465\,29166}{(96Z)^9}+\cdots\Bigg].
\end{aligned} \tag{8}
$$

The convergence of this expansion is rather slow for small values of Z. With the number of terms given an accuracy of ten non-zero figures is only obtained if $Z \geqq 7$. For smaller values of Z, s may be determined by a method to be outlined in the next section. In this way extrapolation of the missing coefficients of the Z-expansion is avoided.

For any value of Z the splitting parameter can thus be accurately determined and the values of the other parameters and the energy may then be calculated from the relations (3), (4) and (5).

From (8) it is easy, though troublesome, to find the $Z^{-1/2}$-expansions of a and b, and the Z-expansions of k and E. For example, the Z-expansion of the energy is found to be

$$
\begin{aligned}
-E = \left(Z-\frac{5}{16}\right)^2+\frac{3}{128}\Bigg[& 1+\frac{26}{96Z}+\frac{1513}{(96Z)^2}+\frac{89162}{(96Z)^3} \\
& +\frac{53\,51290}{(96Z)^4}+\frac{3286\,64612}{(96Z)^5}+\frac{2\,07256\,73029}{(96Z)^6} \\
& +\frac{134\,39597\,19458}{(96Z)^7}+\frac{8959\,17977\,63014}{(96Z)^8}+\cdots\Bigg].
\end{aligned} \tag{9}
$$

With the number of terms given the energy can be obtained to ten significant figures if $Z \geqq 4$.

Another approach to the solution of the Hylleraas-Eckart split-shell problem has been made by Hibbert and Coulson [7]. These authors make use of the saddle-point character of the Hartree-Fock energy and base an iteration scheme on the possibility of expanding the split-shell energy around this point by Taylor's theorem. From the saddle-point the direction of steepest descent is along the line $a+b=$ constant, from the local minimum thus reached along the line $a-b$ $=$ constant, and so on. After two iterations the energy is found to six decimal places and the parameters a and b to three decimal places. After four iterations the parameters are obtained to five decimal places.

The drawback of this method is, of course, that it has to be repeated for every value of Z one is interested in.

3. A Method of Stepwise Approximation of s

For small values of Z one can obtain the value of the splitting parameter s from (7) to a degree of accuracy which is only limited by the length of that expansion. To first order s is found from $8Zs-\left(1+\frac{53}{12}s\right)=0$, to second order s is determined as that root of the quadratic $8Zs-\left(1+\frac{53}{12}s+\frac{43}{48}s^2\right)=0$ which is closest to the result of the first order approximation, and so on.

Table 1. *Estimates of the optimum value of s*

Order of the approximation	$Z=2$ Eq. (6)	$Z=2$ Eq. (7)	$Z=10$ Eq. (6)	$Z=10$ Eq. (7)
1	0.065217	0.086331	0.012605	0.013230
2	0.096270	0.086912	0.013250	0.01323250
3	0.086360	0.087016	0.01323229	0.0132325586
"exact"	0.08702290456		0.01323255922	

Table 2. *Optimum values of the splitting parameter and the energy*

Z	s	Order of the approximation	$-E$ (a.u.)
1	0.32680 89615		0.51330 28855
2	0.08702 29045 6	9	2.87566 1331
3	0.05119 61680 1	7	7.24874 7862
4	0.03629 96799 6	6	13.62296 493
5	0.02812 40707 3	5	21.99753 880
6	0.02295 58744 0	5	32.37227 078
7	0.01939 28878 7		44.74708 665
8	0.01678 75940 1		59.12195 233
9	0.01479 95351 6		75.49685 003
10	0.01323 25592 2		93.87176 951
25	0.00511 30310 34		609.49635 39
50	0.00252 79269 08		2468.87122 2

Scherr and Silverman [6] determined the value of s approximately by regressive neglect of higher order terms in (6). Thus, to first order they found s from $384Zs-(48+32s)=0$, to second order from $16Zs(24-90s)-(48+32s-414s^2)=0$, and so on. In this way, however, approximations are made in both the r.h.s. and the l.h.s. of (6), whereas in our method approximations are only made in the r.h.s. of (7). In Table 1 the results of both methods are given for two values of Z.

Comparison with the correct values shows that our method yields better estimates. Whereas with the method of Scherr and Silverman the estimates oscillate around the correct value, using our method this value is, at least to third order, smoothly approximated from below.

The values of s which have been determined using the method of stepwise approximation are presented in Table 2. For $Z < 7$ the order of approximation needed to obtain at least ten non-zero figures is also given. Only for $Z = 1$ this accuracy could not be reached in this way and here Eq. (6) was used directly. For $Z \geqq 7$ Eq. (8) was used.

The values of the energy have been calculated from (9) for $Z \geqq 4$. For smaller values of Z Eq. (5) was used.

4. Conclusion

The Hylleraas-Eckart split-shell problem concerning the groundstate of atomic two-electron systems has been generally solved in terms of the nuclear charge Z. The accuracy obtained is higher than has been found by other methods. The energy values may be used to test the accuracy of different extrapolation schemes to obtain "experimental" energies in those cases where direct measurement is difficult. This problem shall not be considered here, for details we refer to [5] and references contained therein.

A similar analysis as has been given for the groundstate would be possible for the lowest triplet state described by the spatial wavefunction $u(1)v(2) - v(1)u(2)$, where u and v are given by (2). Since, however, the energy associated with this function is necessarily worse than that which can be obtained from a similar function where u and v are a 1s-type and a 2s-type orbital [3], respectively, such an analysis does not seem to be worth-while.

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