High-accuracy eigenvalues for the static screened Coulomb potential

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A relatively simple variational wave function is proposed for the ground state of two particles bound by a static screened Coulomb potential. It is shown that it gives eigenvalues of high accuracy in the low- and medium-screening regions, and of fair accuracy in the high-screening region.

I. INTRODUCTION

The energy eigenvalues for a particle bound in a static screened Coulomb potential,

$$V(r) = -e^2 e^{-\alpha r}/r , \tag{1}$$

where α is a screening parameter, have been calculated by a variety of methods.[1-5] While no error estimates are quoted in these papers, it would appear that the calculated values are of four-significant-figure accuracy, except when α is very small, in which case the accuracy is greater.

In a previous paper,[2] the authors showed that by using Hulthén-type wave functions, with a single parameter, one can get energy eigenvalues for s states of comparable accuracy to those obtained by Rogers *et al.*[1] by numerical methods. Greene and Aldrich[6] have extended this approach by using solutions to a Hulthén-like effective potential as variational trial functions for calculating the energy levels of the nonzero angular momentum states. Roussel and O'Connell[4] have pointed out the advantages of the variational method over the numerical-integration technique used in Ref. 1.

In this paper we present a relatively simple variational wave function for the ground state of two particles bound by the potential (1), and we show by error bound calculations that the results obtained by this wave function are of high accuracy, except when the screening parameter is very large.

We shall use atomic units, where the unit of length is $a_0 = \hbar^2/me^2$ and the unit of energy is equal to $-me^4/\hbar^2$. Also $\delta = \alpha a_0$, a dimensionless screening parameter.

The proposed wave function is

$$\Phi = r\psi = a_1\phi_1 + a_2\phi_2 , \tag{2}$$

where

$$\phi_1 = (1/\mu)[\nu(4\nu^2 - \mu^2)]^{1/2}[e^{-(\nu-\mu/2)r} - e^{-(\nu+\mu/2)r}]$$

and

$$\phi_2 = 2\eta^{3/2} r e^{-\eta r} .$$

Here μ, ν, and η are variational parameters. ϕ_1 and ϕ_2 are, respectively, a $1s$-state Hulthén type two-parameter wave function and a one-parameter hydrogen-type wave function. In variational calculations, of practical importance is the economy of parameters necessary to achieve a given accuracy of the eigenvalues. Our aim was to obtain a wave function which has the right qualitative shape and involves a minimum number of parameters. The choice of the wave function was further constrained by the requirement that it should be simple enough so that it may be possible to calculate the quantity $\langle HH\rangle$. Several wave functions were tried, only the best one is reported here.

II. RESULTS AND DISCUSSION

The optimized values of the parameters are shown in columns 2–4 and the corresponding energies in column 5 of Table I. Values of δ below 0.1 are not considered, because in this region, to seven-significant-figure accuracy, the results obtained by the variational function (2) are identical to those obtained by the one-parameter wave function proposed in Ref. 2.

In the variation method, the energy obtained is an upper bound to the true ground-state energy. However, one does not know how far the calculated value is from the exact value. Methods for obtaining a lower bound have also been developed. Three of the best known ones are due to Temple,[7] Weinstein,[8] and Stevenson and Crawford.[9,10] If one could obtain the two bounds within a narrow interval, one has succeeded in bracketing the true eigenvalue. Among the three lower bound formulas, the Temple one is usually considered to be the best. It is given by

$$E_T = \langle H\rangle - \frac{\langle HH\rangle - \langle H\rangle^2}{E_2 - \langle H\rangle} , \tag{3}$$

where

$$\langle H\rangle = \int \psi H \psi \, d\tau ,$$

and

$$\langle HH\rangle = \int (H\psi)^2 \, d\tau .$$

TABLE I. Optimized values of parameters μ, ν, and η in the wave function (2), corresponding energy eigenvalues, and Temple's lower bounds.

Screening parameter δ	Parameters μ	ν	η	$\langle H\rangle$	E_T
0.1	0.226 68	1.019 98	1.068 80	0.407 058 0	0.407 058 0
0.2	0.478 58	1.046 77	1.177 08	0.326 808 5	0.326 808 5
0.25	0.603 51	1.061 97	1.232 09	0.290 919 6	0.290 919 6
0.3	0.714 26	1.072 18	1.273 39	0.257 638 6	0.257 638 6
0.4	0.916 68	1.085 92	1.340 13	0.198 376 1	0.198 376 2
0.5	1.108 97	1.096 95	1.400 74	0.148 117 0	0.148 117 6
0.6	1.293 22	1.105 98	1.456 90	0.106 135 9	0.106 137 9
0.7	1.470 82	1.113 46	1.509 70	0.071 833 5	0.071 839 5
0.8	1.642 78	1.119 72	1.559 90	0.044 704 3	0.044 720 1
0.9	1.809 86	1.125 01	1.608 09	0.024 314 2	0.024 354 6
1.0	1.972 66	1.129 51	1.654 68	0.010 285 8	0.010 392 8
1.05	2.053 42	1.131 91	1.678 27	0.005 552 0	0.005 733 4
1.10	2.131 66	1.133 36	1.700 01	0.002 287 2	0.002 649 5
1.15	2.209 72	1.135 01	1.722 14	0.000 455 9	0.001 470 9

Here E_2 is the exact energy of the first excited state of the same symmetry. In column 6 of Table I we show the lower bounds obtained from Temple's formula. For E_2 we have used the values given by Rogers *et al.*[1]; in some cases, interpolated values were used, interpolation being made for the difference $[E(\text{Rogers}) - E(\text{variational})]$. We may note here that all the calculations reported in this paper were carried out in "double precision" and the energy minimum was determined correct at least to the eighth decimal place.[11]

It will be noticed from Table I that for $\delta \leq 0.3$, the lower bounds calculated from the formula of Temple are identical to the variationally calculated energies to seven significant figures and thus the latter are accurate to that extent. Though E_2 is known only to four-figure accuracy, its impreciseness affects the lower bound in the Temple case only beyond seven significant figures as the second term in Eq. (3) is quite small, so long as the $2s$ state is bound. The $2s$ state becomes unbound for $\delta \geq 0.3103$ and above this value of δ, the Temple bound becomes increasingly less useful as a practical tool. For $\delta > 0.3$, a comparison of our results with those of Rogers *et al.*[1] and the lower bounds from the Temple formula leads us to estimate the accuracy of our values as follows: (accuracy given in number of significant figures): $\delta = 0.3$–0.5, accuracy six; $\delta = 0.5$–0.7, accuracy five; $\delta = 0.7$–1.0, accuracy four; $\delta > 1.0$, accuracy three.

The accuracy of a wave function itself is usually measured by the Eckart criterion,[12] according to which the overlap

$$S = \langle \psi_{\text{approx}} | \psi_{\text{exact}} \rangle \tag{4}$$

has the lower bound given by

$$S^2 \geq (E_2 - \langle H\rangle)/(E_2 - E_1)\,, \tag{5}$$

where E_1 is the energy of the ground state. In our case the right-hand side of the inequality (5) is equal to 1 (to four-figure accuracy) for $\delta \leq 0.25$ which shows that the wave function (3) is a very good approximation to the exact wave function, for such values of δ.

In conclusion, we find that the wave function (3) proposed here gives eigenvalues of high to fair accuracy, depending on the value of δ. The present investigation also serves to emphasize the need for improving on Temple's lower bound formula or developing a better one for a situation where the next excited state of the same symmetry is unbound. Also, for such a situation, development of a practically useful criterion for the accuracy of a wave function would be desirable.

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[1]F. J. Rogers, H. C. Graboske, Jr., and D. J. Harwood, Phys. Rev. A 1, 1577 (1970).
[2]C. S. Lam and Y. P. Varshni, Phys. Rev. A 4, 1875 (1971), and the references given therein. We take this opportunity to correct some transcription errors in this paper. The conditions in Eqs. (4.2), (4.3), (4.4), and (4.5) should read $\mu-\delta<2$, $2\mu-\delta<1$, $9\mu-3\delta<2$, and $8\mu-2\delta<1$, respectively, rather than what are printed.
[3]B. I. Dunlap and L. Armstrong, Jr., Phys. Rev. A 6, 1370 (1972).
[4]K. M. Roussel and R. F. O'Connell, Phys. Rev. A 9, 52 (1974).
[5]N. Bessis, G. Bessis, G. Corbel, and B. Dakhel, J. Chem. Phys. 63, 3744 (1975).
[6]R. L. Greene and C. Aldrich, Phys. Rev. A 14, 2363 (1976).
[7]G. Temple, Proc. R. Soc. London 119, 276 (1929).
[8]D. H. Weinstein, Proc. Natl. Acad. Sci. 20, 529 (1934).
[9]A. F. Stevenson, Phys. Rev. 53, 199 (1938).
[10]A. F. Stevenson and M. F. Crawford, Phys. Rev. 54, 375 (1938).
[11]J. A. Nelder and R. Mead, Comput. J. 7, 308 (1965).
[12]C. Eckart, Phys. Rev. 36, 878 (1930).