

Upper and Lower Bounds to Eigenvalues

III. Comparison with Löwdin's Method

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Received January 14, 1969

A comparison between lower bounds to the He ground state by the method proposed in I and by the method by Löwdin is presented.

Ein Vergleich der unteren Grenzen des Heliumgrundzustandes, die nach der in I vorgeschlagenen Methode und nach der Methode von Löwdin ermittelt wurden, wird durchgeführt.

Comparaison entre les limites inférieures de l'état fondamental de He obtenues par la méthode proposée dans l'article I et par la méthode de Löwdin.

Of the non-variational approaches to determining lower bounds of eigenvalues [1, 2, 5] the method of Löwdin [5], which is based on perturbation theory, has received a great deal of attention. It is the purpose of this note to make a direct comparison between a variational method proposed recently [6] and the method of Löwdin, by considering the results of the two methods for the case of the ground state of the He atom.

The trial functions used for the variational method are of the general type

$$\Phi = \sum_{lmn} C_{lmn} \chi_{lmn} \quad (1)$$

where the C_{lmn} are coefficients to be determined by the variational calculation and will be such that Φ gives the maximum value of the lower bound.

$$\chi_{lmn} = N_{lmn} s^l t^m u^n e^{-s/2} \quad (2)$$

where N_{lmn} is a normalization factor, $s = k(r_1 + r_2)$, $t = k(r_2 - r_1)$ and $u = k r_{12}$, m is an *even* integer and k is a scaling factor. The form of the Hamiltonian and all the necessary integrals are discussed in the paper of Wilets and Cherry [9]. For the calculations presented here the values of lmn taken in the summation for the three trial functions considered are presented in Table 1. The latter are also the same functions used for the "inner projection" space in the Löwdin method calculations presented here. A summary of Löwdin's method is given in the paper of Choi and Smith [3] and the necessary integrals have also been given [4].

In Table 2 the results of the two methods are compared with the results of the Temple method for three basis sets. The basis functions listed in column one of

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Table 1 were used for the 6-function basis set. The functions of the second column were added for the 10-function calculations and all of the functions shown to Table 1 were used for the 18-function calculations. In Table 2 the numbers in parentheses are the optimum values of the scaling factor k .

Table 1. *Basis functions for calculations*

l	m	n	l	m	n	l	m	n
0	0	0	0	2	0	1	0	1
0	0	1	0	2	1	1	2	0
0	0	2	0	2	2	2	0	0
0	0	3	0	2	3	2	2	0
0	0	4	0	2	4	3	0	0
0	0	5	1	0	0	4	0	0

Table 2. *Comparison of lower bound values^c*

Basis functions	Present method ^a	Löwdin method ^b	Temple method ^a
6	-2.9147 (3.34)	-2.9098 (3.46)	-2.9260 (3.64)
10	-2.9080 (3.91)	-2.9060 (3.50)	-2.9132 (3.54)
18	-2.9041 (4.02)	-2.9039 (3.92)	-2.9055 (3.85)

^a $\tilde{E}_1 = -2.1460$ was used as the lower bound to the true eigenvalue of the 2^1S state of He [8].

^b $\epsilon = -2.9037$ was used as the upper bound to the true eigenvalue of the 1^1S state of He [3].

^c All values are in Hartrees.

The results show that both the present method and Löwdin's method give a considerably better lower bound than does the usual Temple method. The difference between the present method and that of Löwdin for 18 basis functions is not very great and from the trend of Table 2 larger basis sets would probably give almost identical results. This is a rather important point since the present method can be extended to handle many electron atoms without much difficulty, whereas Löwdin's method is of a simple form only for two electron systems, since the perturbation term is simply $V = 1/r_{12}$. For many electron atoms the perturbation is much more complicated and the integrals which would arise as a result of this are quite intractable at present.

For the bounds determined here, the associated wave functions have proved to be useless for the calculation of physical properties [7]. In the Löwdin method for lower bounds the corresponding wave function cannot be written in a tractable form. However it would most certainly suffer from the same characteristic lack of utility, which seems to be the fate of wave functions associated with a bound value. Hence the variation method for bounds is quite useful in determining bounds but should not in any way be considered as a way to determine a valid approximation to an eigenfunction. The reason is that the bound formulations add contributions from other configurations to the trial wave functions which do not help in the description of the wave function associated with the state under consideration. This is most clearly seen in Löwdin's formulation for lower bounds,

where contributions to the reference function are added from functions projected from another subspace. It is also true for the method proposed here. To obtain good bounds one must add in parts of function space which are not suited to the description of the eigenfunction.

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