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Upper and Lower Bounds to Eigenvalues

II. Excited States of He

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The variational method based on the Temple-Kato formulae is applied to the determination of bounds for some ${}^{1,3}P(1snp)$ states of He.

Die Variationsmethode, die auf der Temple-Kato Formel beruht, wird angewandt zur Bestimmung der Grenzen für einige ${}^{1,3}P(1s\,np)$-Zustände des He.

La méthode variationnelle basée sur la formulation de Temple-Kato est appliquée à la détermination de limites pour certains états ${}^{1,3}P(1snp)$ de He.

1. Introduction

In paper I [3] a variational method, based on the Temple-Kato formulae, was developed for the determination of upper and lower bounds to eigenvalues. This method, which will be referred to as the Bound Method will be used here to determine bounds to eigenvalues for some excited states of He.

The upper bounds obtained by the Bound Method will be compared to those obtained by a method proposed by Davidson. The latter method, however, is valid only in special cases; the He system treated here being such a case.

2. Application to Some He Excited States

In these calculations, basis functions of the type used by Davidson [1] were employed. The basis functions for the excited states were taken as

$$\chi_{s,n}=\frac{(2\eta)^{\frac{3}{2}}}{(n+1)!\,2^{n+1}}(2\eta_s r)^{n-1}\exp(-\eta_s r)\,Y_{0,0}(\theta,\phi)\qquad n=1,2,3,4\,, \tag{1}$$

$$\chi_{p,n}=\frac{(2\eta_p)^{\frac{3}{2}}}{(n+1)!\,2^{n+1}}(2\eta_p r)^{n}\exp(-\eta_p r)\,Y_{1,M}(\theta,\phi)\qquad n=2,3,4,5 \tag{2}$$

where the $\chi_{s,n}$ are the basis functions for the s orbital and the $\chi_{p,n}$ those for the p orbital. The s and p orbitals were each represented by four basis functions and those functions used for the calculations are given in Eqs. (1) and (2) by the n values.

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Although the $\chi_{s,n}$ and $\chi_{p,n}$ are the same, except for the choice of η_s and η_p, for all the excited state calculations reported here, the $c_{s,n}$ and $c_{p,n}$ of course differ for each calculation. They are determined by the direct application of the method developed in paper I for the determination of the best bounds. Further the η's were varied such that their optimum values give the best bounds obtainable from a wave function of the type considered here. The expansion coefficients and the optimum values of the η's are given in Tables 1 and 2 for the singlet and triplet states respectively. The U or L in parentheses after the state designation in the tables indicate whether the wave function corresponds to that of an upper or lower bound value respectively.

Table 1. *Singlet excited state wave functions – bound method*

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
		^1P 1s 2p(L)			
1	2.19	0.87274	2	0.368	−0.02899
2	2.19	0.13117	3	0.368	0.02990
3	2.19	0.01544	4	0.368	0.99266
4	2.19	0.00195	5	0.368	0.00057
		^1P 1s 3p(U)			
1	2.19	0.87274	2	0.364	−0.04185
2	2.19	0.13117	3	0.364	0.00600
3	2.19	0.01544	4	0.364	1.03134
4	2.19	0.00195	5	0.364	−0.00699
		^1P 1s 3p(L)			
1	2.13	0.90986	2	0.269	0.01350
2	2.13	0.09619	3	0.269	−0.02806
3	2.13	0.00800	4	0.269	−0.94830
4	2.13	0.00068	5	0.269	1.86615
		^1P 1s 4p(L)			
1	2.13	0.90986	2	0.180	−0.07002
2	2.13	0.09619	3	0.180	1.10376
3	2.13	0.00800	4	0.180	−3.40898
4	2.13	0.00068	5	0.180	3.30019

The values of the upper and lower bounds calculated from these wave functions are given in Table 3 along with the experimental energies and the values obtained by using Davidson's method with the basis set discussed above ($E_{\text{variational}}$), and with a larger basis set ($E'_{\text{variational}}$). A few comments on Davidson's method should be made now before continuing.

Davidson's method makes use of Roothaan's equations [5] to formulate an SCF method for obtaining upper bounds. An essential element is the choice of the type of basis functions. With his choice, he is able to make use of a theorem given by MacDonald [2]. By using this method which gives upper bounds to eigenvalues from the solution of the secular equation when the wave function is expanded in a truncated set of complete functions, he then obtains an upper bound to W_k, where W_k is the true k^{th} eigenvalue of H. Thus one is provided with a variational principle for excited states in this simple case which insures an upper bound to the true eigenvalue. This method provides a convenient comparison between upper bounds calculated by an ordinary variational treatment and the bounds calculated by the Bound Method.

Davidson's method provided the means of obtaining the values listed in Table 3 in the fifth and sixth columns. The values in the fifth column were obtained by

Table 2. *Triplet excited state wave functions – bound method*

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
			^3P 1s 2p(L)		
1	1.76	1.21140	2	0.377	−0.07442
2	1.76	−0.28595	3	0.377	0.23490
3	1.76	0.05236	4	0.377	0.84289
4	1.76	−0.00705	5	0.377	−0.00950
			^3P 1s 3p(U)		
1	1.76	1.21140	2	0.376	−0.10792
2	1.76	−0.28595	3	0.376	0.26166
3	1.76	0.05237	4	0.376	0.78938
4	1.76	−0.00706	5	0.376	0.04704
			^3P 1s 3p(L)		
1	1.85	1.12406	2	0.276	0.03428
2	1.85	−0.15784	3	0.276	−0.17941
3	1.85	0.01740	4	0.276	−0.60847
4	1.85	−0.00153	5	0.276	0.16616
			^3P 1s 4p(L)		
1	1.86	1.11500	2	0.186	−0.12947
2	1.86	−0.14535	3	0.186	1.27357
3	1.86	0.01489	4	0.186	−3.73863
4	1.86	−0.00122	5	0.186	3.45304

Table 3. *Upper and lower bounds to some* He *excited states*[a]

State	Exp. energy	Lower bound	Upper bound	$E_{\text{variational}}$	$E'_{\text{variational}}$
$^1P(1s\,2p)$	−2.12387	−2.12630	−2.12246	−2.12246	−2.12246
$^1P(1s\,3p)$	−2.05517	−2.05553	−2.05442	−2.05473	−2.05474
$^1P(1s\,4p)$	−2.03110	−2.03159		−2.03089	−2.03089
$^3P(1s\,2p)$	−2.13320	−2.13618	−2.13134	−2.13134	−2.13143
$^3P(1s\,3p)$	−2.05811	−2.05851	−2.05727	−2.05750	−2.05759
$^3P(1s\,4p)$	−2.03235	−2.03272		−2.03199	−2.03208

[a] In all cases the bounds were calculated using experimental energies for $\tilde{E}_y$ [4]; the values for the $^1P(1s\,5p)$ and $^3P(1s\,5p)$ states are −2.02009 and −2.02073 Hartrees, respectively.

direct application of Davidson's method using the basis sets described above and optimizing the η's. The wave functions corresponding to these energies are given in Tables 4 and 5. The sixth column of Table 3 contains the results obtained by Davidson using larger basis sets; these results should be close to the Hartree-Fock limit.

Table 4. *Singlet state upper bound wave functions – Davidson's method*

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
^1P 1s 2p(A)					
1	1.64	1.34383	2	0.624	0.46829
2	1.64	−0.50259	3	0.624	0.48996
3	1.64	0.14015	4	0.624	−0.03214
4	1.64	−0.02830	5	0.624	0.12795
^1P 1s 3p(A)					
1	1.80	1.17168	2	0.355	−1.25864
2	1.80	−0.22546	3	0.355	1.13821
3	1.80	0.03362	4	0.355	0.76193
4	1.80	−0.00449	5	0.355	−0.03427
^1P 1s 4p(A)					
1	1.88	1.10042	2	0.257	1.97148
2	1.88	−0.12536	3	0.257	−4.84864
3	1.88	0.01121	4	0.257	2.61793
4	1.88	−0.00113	5	0.257	0.96264

Table 5. *Triplet state upper bound wave functions – Davidson's method*

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
^3P 1s 2p(A)					
1	1.76	1.20304	2	0.710	0.68640
2	1.76	−0.27858	3	0.710	−0.10798
3	1.76	0.05158	4	0.710	0.50040
4	1.76	0.00094	5	0.710	0.00028
^3P 1s 3p(A)					
1	1.79	1.17834	2	0.437	−1.17537
2	1.79	−0.23779	3	0.437	1.42767
3	1.79	0.03893	4	0.437	−0.79388
4	1.79	−0.00328	5	0.437	1.17645
^3P 1s 4p(A)					
1	1.85	1.12427	2	0.257	2.28960
2	1.85	−0.15873	3	0.257	−6.40743
3	1.85	0.01798	4	0.257	5.01656
4	1.85	−0.00101	5	0.257	−0.21458

It should be noted that the bounds calculated give quite good limits on the true eigenvalues. The difference between the upper and lower bound values being, in the worst cases, only 0.005 a.u. For the lowest states of a given symmetry the upper bound value and the $E_{\text{variational}}$ value are identical, since the upper bound equation reduces to the ordinary variational principle in these cases.

The fact that the upper bounds given by the Davidson method ($E_{\text{variational}}$ of Table 3 are better than those of the Bound Method for the $^1P(1s\,3p)$ and $^3P(1s\,3p)$ states is explained by a simple argument. In the special case treated by Davidson, his method is equivalent to a variational principle which determines the function which gives a stationary value to E, i.e., it satisfies the equation, $\delta E = 0$. This is the same form as the ground state variational principle and it is only because of the nature of the trial functions chosen and the form of the problem which allows this equation to be valid for the determination of excited state functions also. As was shown previously the Bound Method gives an equation of the form $\delta E + \omega\,\delta\Delta = 0$.

The latter equation may be considered as a constrained variational problem with former being the unconstrained problem. These problems are well known and it is a fact that the constrained problem cannot have a minimum which is as low as the minimum for the unconstrained problem. Hence Davidson's values are better upper bounds. However in the general case, when Davidson's method is not applicable, the other method is still valid and will yield values for an upper bound which would be otherwise unavailable.

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