

VARIATIONAL CALCULATIONS FOR THREE-BODY S-STATES WITH COULOMB INTERACTIONS

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Summary

A general purpose programme designed to deal economically with the S-states of arbitrary systems interacting only via the static Coulomb interactions is described. Its aim is to simplify the calculation of the matrices of arbitrary operators with respect to the basis chosen; these matrices are then available for use in a variety of variational calculations. A number of illustrative calculations are presented which yield both upper and lower bounds for the energy of some typical systems and expectation values for a number of operators.

I. INTRODUCTION

There have been a number of previous attempts (Kolos, Roothaan, and Sack 1960; Frost, Inokuti, and Lowe 1964) to produce a general purpose programme for treating the S-states of three-body systems interacting through Coulomb forces. These programmes have been based on the use of the Rayleigh-Ritz variation principle for the energy and, for a given choice of basis, have provided a convenient means of calculating the Hamiltonian and normalization matrices with respect to this basis set which are needed for an energy calculation.

The present programme has a similar aim. However, it differs in emphasis in two ways. Firstly, we are not primarily interested in calculations of the binding energy but in using the matrices produced by the programme to test a number of new variation principles and approximation schemes for bound and scattering states, and especially for investigating methods of calculating the expected values of operators in atomic systems. This aim requires that we produce the matrices of a large number of different operators W , including the Hamiltonian H , H^2 , and compound (though not necessarily Hermitian) operators such as $W_1 W_2$ and HW . We have made it especially easy to add new operators to the system; provided that these fall within the class of operators considered, the user has only to specify them in a formal way and is not concerned with the integrations involved.

The second difference in emphasis follows from the first. The major time in any variational calculation of the types considered is spent in performing the integrals needed to set up the Hamiltonian and other relevant matrices. We therefore gain considerable economy by computing and storing these matrices once and for all. Since we wish to vary the wave-function scale and the system parameters (the particle masses and charges), the operators H , H^2 , and HW are split into parts each of which has a simple behaviour under a scale change, and which are independent of the masses and charges.

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II. BASIS USED

We use the following unsymmetrized set of basis functions

$$\psi_{lmn}(123) = \exp[-S^{-1}\{Z^*(lr_1 + mr_2) + nr_{12}\}] \quad (1)$$

and store all matrices with respect to the symmetrized set

$$\psi_{lmn}^{\pm}(123) = \psi_{lmn}(123) \pm \psi_{lmn}(213). \quad (2)$$

Here r_1 , r_2 , and r_{12} are the three interparticle distances (with particle 3 at the origin of the centre of mass frame). S is an overall scale factor that is set equal to 1 when the matrices of all operators are produced and stored. Matrices of interest to us for which the scale is not 1 are simply related to these by some power of S . Thus if $\langle T \rangle_S$, $\langle V \rangle_S$, and $\langle 1 \rangle_S$ are the matrices for the kinetic energy, potential energy, and normalization for arbitrary scale S then

$$\langle T \rangle_S = S^4 \langle T \rangle_{S=1}, \quad \langle V \rangle_S = S^5 \langle V \rangle_{S=1}, \quad \langle 1 \rangle_S = S^6 \langle 1 \rangle_{S=1}.$$

TABLE 1
NUMBER OF COMPONENTS OF ψ_{lmn}^{\pm} AS GIVEN BY (3) FOR $N_{\min} = -1$

Q_{\max}	1	2	3	4	5	6	7	8	9	10	11	12
$Z^* > 1$												
ψ^+	1	3	7	13	22	34	50	70	95	125	161	203
ψ^-	0	1	3	7	13	22	34	50	70	95	125	161
$Z^* = 1$												
ψ^+	0	1	4	9	17	28	43	62	86	115	150	191
ψ^-	0	0	1	4	9	17	28	43	62	86	115	150

This makes it obvious how the scale can be varied during a calculation.

Z^* is a nonlinear parameter that is fixed within a given set of calculations. It is included to make some direct discrimination between the pair of particles (1, 2) and the third particle 3.

The triplets l, m, n are allowed to run through the integers subject to the restrictions

$$\left. \begin{aligned} n \geq N_{\min}, \quad l \geq m, \quad l+m+n = Q, \\ Q = N_{\min}+1, N_{\min}+2, \dots, Q_{\max}. \end{aligned} \right\} \quad (3)$$

N_{\min} in (3) is not restricted to be positive, but is considered as a nonlinear parameter. The parameter Q is conveniently used to order the triplets, all triplets of given Q being run through together. The total number of terms in the trial wave function that includes all components up to a given Q_{\max} is listed in Table 1 for the choice $N_{\min} = -1$.

The basis (1), (3) was chosen firstly to give a good representation of the wave functions of the helium sequence while minimizing the time required to construct the Hamiltonian and other matrices with the integration scheme used (see Section IV). For the ground state of the helium sequence the dominant term is expected to be $(l, m, n) = (1, 1, 0)$. However, the terms $(j, j, 0)$, $j > 1$, also appear in the sequence

as defined by condition (3), and these terms dominate for appropriate choice of the scale S . The result is that for the ground state of the helium-like ions, although not necessarily for other systems, the energy shows a marked structure as a function of the scale S , with peaks at these preferred scales. For large numbers of terms, these peaks are not well resolved and the energy is almost independent of the scale factor over a wide region. This property of the basis is illustrated in Figure 1, which plots the energy versus scale for the system He (1^1S).

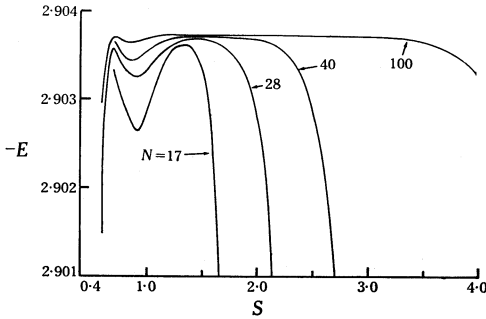


Fig. 1.—Helium ground state ($\text{He}(1^1S)$) energies calculated with the wave function (1) for various numbers of terms N . Note the structure in the dependence on the scale parameter S .

For systems other than helium and the helium-like ions we do not expect any one term to give a good approximation. The extent to which the basis (1) proves suitable for other systems is discussed in Section VI.

III. HAMILTONIAN AND OTHER OPERATORS

The S-state Coulomb Hamiltonian for three particles of mass m_1 , m_2 , and m_3 has the form (in atomic units)

$$H = -\frac{1}{2}(\mu_1^{-1} + \mu_2^{-1})T_0 + m_3^{-1}T_1 + \frac{1}{4}(\mu_1^{-1} - \mu_2^{-1})T_2 - ZV_0 + V_1,$$

where the reduced masses μ_1 and μ_2 are given by

$$\mu_1 = m_1 m_3 / (m_1 + m_3), \quad \mu_2 = m_2 m_3 / (m_2 + m_3).$$

The S-state operators T_0 , T_1 , T_2 , V_0 , and V_1 are given by

$$T_0 \equiv -\frac{1}{2}(\nabla_1^2 + \nabla_2^2)_S = -\frac{1}{2}(1 + P_{12}) \left\{ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left(r_{12}^2 \frac{\partial}{\partial r_{12}} \right) + 2 \cos \theta_1 \frac{\partial^2}{\partial r_1 \partial r_{12}} \right\},$$

$$T_1 \equiv -(\nabla_1 \cdot \nabla_2)_S = -(1 + P_{12}) \left\{ \frac{1}{2} \cos \theta_{12} \frac{\partial^2}{\partial r_1 \partial r_2} - \cos \theta_1 \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{1}{2r_{12}^2} \frac{\partial}{\partial r_{12}} \left(r_{12}^2 \frac{\partial}{\partial r_{12}} \right) \right\},$$

$$T_2 \equiv -(\nabla_1^2 - \nabla_2^2)_S = -(1 - P_{12}) \left\{ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) + 2 \cos \theta_1 \frac{\partial^2}{\partial r_1 \partial r_{12}} \right\},$$

$$V_0 \equiv r_1^{-1} + r_2^{-1}, \quad V_1 \equiv r_{12}^{-1}.$$

Here

$$\cos \theta_1 = (r_1^2 + r_{12}^2 - r_2^2) / 2r_1 r_{12}, \quad \cos \theta_{12} = (r_1^2 + r_2^2 - r_{12}^2) / 2r_1 r_2.$$

The above operators are separately Hermitian and are independent of the masses and charges of the system considered. Their matrices are stored separately in the computer programme. The operator H^2 is also split into separately Hermitian parts such as T_0^2 , $(T_1 V_0 + V_0 T_1)$, etc., which again do not depend on physical parameters such as mass and charge.

The operators W that we shall consider have the following effect when operating on the unsymmetrized basis (1)

$$W\psi_{lmn} = \left(\sum_i a_i r_1^{\alpha_i} r_2^{\beta_i} r_{12}^{\gamma_i} \right) \psi_{lmn}. \quad (4)$$

The parameters a_i , α_i , β_i , and γ_i are used in the programme to define any one operator. Product operators such as $W_1 W_2$ are generated within the programme from their separate expansions,

$$(\psi_{l'm'n'}, W_1 W_2 \psi_{lmn}) = (W_1^+ \psi_{l'm'n'}, W_2 \psi_{lmn}). \quad (5)$$

This approach makes it straightforward to include extra operators in the code, provided that they have expansions of type (4), and at present some 60 operators have been included. In addition the delta function operators $\delta(r_{12})$, $\delta(r_1)$, and $\delta(r_2)$ have been coded.

IV. INTEGRATIONS

In general, it is required to evaluate integrals of the form

$$(\psi_{l'm'n'}, W_1 W_2 \psi_{lmn}).$$

For the simpler integrals one or both of the operators W_1 , W_2 may be the unit operator 1. For the other cases we use the result (5) and the defining expansions (4) for W_1 , W_2 in order to arrive at a typical integral

$$(\alpha\beta\gamma) = \int \psi_{l'm'n'} r_1^\alpha r_2^\beta r_{12}^\gamma \psi_{lmn} d\tau. \quad (6)$$

Those integrals with $\alpha, \beta, \gamma \geq -1$ can be expanded in terms of perimetric coordinates (see Pekeris 1962) into a sum of analytic integrals. Working with single precision (48 bit word) the accuracy attained in evaluating such integrals is better than 1 part in 10^{10} on the machine used.

For some operators, for instance in parts of H^2 , one or at the most two of the exponents α, β, γ can take the values -2 . Integrals with one such exponent can also be evaluated term by term in perimetric coordinates. Those with two exponents with value -2 are reduced by a change of variables to a one-dimensional numerical integration for which the computed accuracy achieved is better than 1 part in 10^6 .

V. APPLICATIONS

Some of the calculations carried out using matrices provided by the programme have already been published (Delves 1967, 1968; Delves and Kalotas 1968). We give here some examples of their use in standard variational calculations, which demonstrate the application of the basis used to a variety of different systems.

Table 2 gives upper and lower bounds for the energy of the lowest triplet and singlet states of helium, and for the heavy mu-mesonic molecule $d-\mu-d$, the hydrogen molecule ion H_2^+ , and the positronium ion e^+e^- . These bounds explicitly include contributions coming from the finite-accuracy arithmetic used (see Delves 1968). The table also gives the expected values of a number of operators for these systems, calculated from the variational wave functions giving the upper bounds. In this table, the following parameters in (1) and (3) were used

$$N_{\min} = -1,$$

$$Z^* = \begin{array}{ll} 2 & \text{lower bounds,} \\ 1 & \text{upper bounds and expected values.} \end{array}$$

VI. DISCUSSION

The results of Table 2 show firstly that the basis (1) does provide a good representation of the lowest singlet and triplet states of helium. In addition, it provides at least a reasonably good representation of other Coulombic three-body S-states for a wide range of the relative particle masses. Indeed, the upper bound for the positronium ion e^+e^- appears to be the lowest yet published. The basis is least successful in describing systems, such as H_2^+ , containing two heavy and one light particle; this is a defect it shares with other general purpose bases that have been proposed (Kolos, Roothaan, and Sack 1960; Frost, Inokuti, and Lowe 1964), which also fail to reflect adequately the extremely sharp peaking of the H_2^+ wave function around the equilibrium position of the protons.

The lower bounds shown are interesting in that they demonstrate the flexibility of the programme. Lower-bound calculations have not been popular in the past, firstly because the bounds obtained are in general much worse than the upper bounds, and secondly because of the labour involved in deriving the necessary integrals. At least this second factor is alleviated by the method used here, the specification of the integrals of H^2 being a trivial exercise. We hope to use the programme to test a number of other variation principles that also involve the matrices of H^2 . For this purpose the lower bounds given here are very encouraging; the upper and lower bounds for helium have merged to five significant figures.

Also of interest is the technique used to deal with round-off errors in Table 2. It is well known that the errors due to the finite-accuracy arithmetic used can build up disastrously in a variational calculation. These errors can, however, be *bounded* and the bound added to the raw upper or lower bounds generated to give a rigorous bound including the round-off error (Delves 1968). This has been done in Table 2. The round-off contribution to the bounds are significant only for the lower bounds, since our matrices of H^2 are less accurate than those of H . Figure 2 illustrates the size of the round-off errors for the lower bound to the state He (2^3S). In this figure both the uncorrected and the corrected lower bounds are plotted against the scale parameter S , together with the corrected upper bound. We see that the round-off errors may be large for some values of S , but are satisfactorily small near the optimum

TABLE 2

ENERGIES AND EXPECTATION VALUES FOR SOME ATOMIC SYSTEMS

Values are expressed in electron atomic units a_0 , but for the d- μ -d system muon atomic units a_μ are used except for the energy, which is given in eV. For the upper and lower bounds the number of terms used in the expansion is shown in parentheses, and the scale factor S in equation (1) is given. Previous upper and lower bound calculations are shown for comparison

Energy or Operator	He (1 1S)	He (2 3S)	System d- μ -d	H ₂ ⁺	e ⁺ e ⁻ e ⁻
m_1	1	1	17.7511244	1836.08	1
m_2	1	1	17.7511244	1836.08	1
m_3	∞	∞	1	1	1
Z	2	2	1	1	1
E (upper bound)	-2.903724313 (100)	-2.1752267 (71)	-2988.5373 eV (100)	-0.592947 (100)	-0.2620035 (100)
S (upper bound)	1.4	3.4	2.9	3.0	9.0
E (lower bound)	-2.9037945 (50)	-2.1753306 (34)	—	—	-0.2662 (50)
S (lower bound)	2.0	4.25	—	—	10.5
Upper bound from previous calculations*	-2.903724375 (1078) ^b	-2.175229378237 (715) ^b	-2981 eV (32) ^a	-0.58305 (32) ^a	-0.2620011 (50) ^c
Lower bound from previous calculations*	-2.903726615 (1078) ^b	-2.175229379 (715) ^b	—	-0.60263 [†]	—
$\langle T_0 \rangle$	2.903724313	2.1752267	0.75397	—	0.1332387
$\langle T_1 \rangle$	0.1590695	0.0074447	-0.2665	—	-0.004472412
$\langle r_1^{-1} + r_3^{-1} \rangle$	3.376634	2.3093	1.4551	—	0.6796438
$\langle r_{12}^{-1} \rangle$	0.9458191	0.26822	0.39403	—	0.155634
$\langle r_1 + r_2 \rangle$	1.858940	5.1002	4.2478	—	10.979
$\langle r_1^2 + r_2^2 \rangle$	2.386941	22.921	11.9428	—	96.89
$\langle r_{12} \rangle$	1.422066	4.4468	2.8416	—	8.549
$\langle \delta(r_1) + \delta(r_2) \rangle$	3.620719	2.6406	0.3169	—	0.041458
$\langle \delta(r_{12}) \rangle$	0.1063434	0.0	5.5×10^{-6}	—	1.71045
$\langle \cos \theta_1 + \cos \theta_2 \rangle$	1.296036	1.1256	1.0685	—	1.183968

* References are: a, Kolos, Roothaan, and Sack (1960); b, Pekeris (1962); c, Frost, Inokuti, and Lowe (1964).

[†] Fixed nuclei approximation (Bates, Ledsham, and Stewart 1953).

value of S . The round-off corrections depend on the computed eigenvector, and this dependence accounts for the structure observed in curve C.

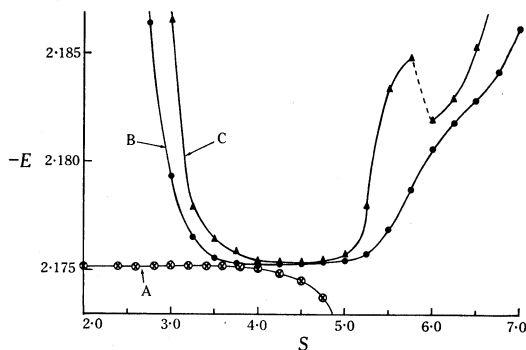


Fig. 2.—Upper and lower bounds on the energy of the $\text{He}(2^3\text{S})$ state:

- A, upper bound (71-term wave function).
- B, uncorrected lower bound (34-term wave function).
- C, lower bound corrected for the contribution from round-off errors in the computed matrix elements. The corrections depend on the computed eigenvector and hence are not necessarily smoothly varying with the scale factor S .

Also given in Tables 2 and 3 are the expected values of some representative operators, calculated from the 100-term wave function yielding the best energy upper bound. The accuracy of these values has been estimated by comparison with

TABLE 3

EXPECTATION VALUES OF POWERS OF THE INTERPARTICLE DISTANCES

Results are for operators of the form $(l, m, n) = r_1^l r_2^m r_{12}^n (2 - \delta_{lm})$. All values are expressed in electron atomic units a_0 except for the $d-\mu-d$ system, where muon units a_μ are used

l	m	n	He (1 ¹ S)	He (2 ³ S)	$d-\mu-d$	$e^+e^-e^-$	l	m	n	He (1 ¹ S)	He (2 ³ S)	$d-\mu-d$	$e^+e^-e^-$
-1	-1	-1	4.167157	0.18661	0.20821	0.0220342	-1	-1	1	2.631789	2.0644	1.0985	0.5476255
-1	0	-1	3.841888	0.64545	0.60864	0.121397	-1	0	1	4.136490	9.9298	3.9288	5.2768
-1	1	-1	2.849227	2.0932	1.2735	0.585452	-1	1	1	4.980830	45.698	10.113	46.23
-1	2	-1	2.993350	8.8639	3.3443	4.293	-1	2	1	8.009495	261.74	32.206	587.8
-1	3	-1	4.133502	44.646	10.363	43.82	-1	3	1	16.01758	1722.3	118.96	9760
0	1	-1	1.448933	1.18539	1.5526	1.384483	0	1	1	3.104986	25.829	12.937	113.97
0	2	-1	1.540627	4.5322	4.0329	9.5265	0	2	1	4.668667	134.15	39.209	1275
0	3	-1	2.129992	22.362	12.779	93.48	1	1	1	1.548576	16.893	13.304	269.78
1	1	-1	0.5653453	0.72318	1.4719	2.77406	-1	-1	2	3.406223	9.0513	3.0316	4.4497
1	2	-1	1.210745	3.9037	7.5777	34.536	-1	0	2	6.466397	50.070	11.808	53.88
1	3	-1	1.672415	17.286	24.427	314.8	-1	1	2	9.333429	266.86	33.336	613.2
2	2	-1	0.648927	3.1342	9.7665	95.045	-1	2	2	17.66658	1737.0	115.85	9860
-1	-1	0	2.708656	0.56078	0.44712	0.090935	0	0	2	2.516414	23.038	8.9262	93.23
-1	1	0	3.277818	9.0196	3.3926	4.4893	0	1	2	6.310569	150.749	43.368	1496
-1	2	0	4.354313	44.825	9.8463	44.04	-1	-1	3	5.514115	46.289	9.2794	46.93
-1	3	0	7.364284	259.91	33.409	581.7	-1	0	3	12.28134	290.728	39.103	702.77
0	3	0	3.935817	130.40	40.872	1218	-1	1	3	20.74915	1769.8	120.46	10200
1	1	0	0.8271069	3.2301	4.2030	24.174	0	0	3	5.307917	136.71	30.713	1269
1	2	0	2.043074	19.704	22.842	356.2							

the accurate results of Pekeris (1962), where available, and by observing the convergence with increasing numbers of terms (Delves and Kalotas 1968). For the expectation values the last digit quoted may be in error.

We see that except for the system H_2^+ we obtain an accuracy of from five to seven significant digits in these expected values, a very satisfactory result. For the hydrogen molecule ion the expected values we obtained behave extremely erratically and they have not been quoted here.

VII. ACKNOWLEDGMENTS

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