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Energies of the Lowest Singlet *S* and Triplet *S* States of Helium by the Local Energy Method

By

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The least squares local energy method is applied to the helium atom in greater detail in a formulation which can easily be extended to more complicated atoms. The energies of the $1\,{}^1S$ and 2^3S states are calculated to be — 2.9025 H and — 2.1753 H respectively. These values are in excellent agreement with the non-relativistic values of — 2.9037 H and — 2.1752 H calculated by Pekeris.

Le calcul de l'énergie locale par la méthode des moindres carrés est appliqué plus en détail à l'atome d'hélium, dans une forme qui s'étend aisément à des atomes plus compliqués. Les énergies des états $1\,{}^1S$ et $2\,{}^3S$ se calculent à — 2,9025 et — 2,1753 u. a., respectivement. Ces valeurs sont en excellent accord avec les valeurs de — 2,9037 et — 2,1752 u. a. (sans relativité) calculées par Pekeris.

Die Methode, die Varianz der „lokalen Energie" zu minimisieren, wird in einer leicht auf kompliziertere Atome zu erweiternden Form ausführlicher auf das Heliumatom angewandt. Die Energien des $1\,{}^1S$- und des $2\,{}^3S$-Zustandes werden zu — 2,9025 bzw. — 2,1753 at. E. berechnet. Diese Werte stimmen ausgezeichnet mit den von Pekeris berechneten nichtrelativistischen Werten von — 2,9037 bzw. — 2,1752 at. E. überein.

A. Introduction

The helium atom can be used as a model for testing some of the approximations we would like to make in least squares local energy calculations of the lithium atom and perhaps beyond. Details of the method can be found elsewhere [*3*]. This report describes the calculation of the energies of both the ground state (1^1S) and the first excited state ($2\,{}^3S$). The triplet state of helium is a particularly good model of more complicated atoms since the two electrons are definitely in different shells. In excited singlet states the electrons are also in different shells but the variance minimization equations are difficult to solve for the higher roots which correspond to these levels.

Although the formulation used here is not the natural one for helium it is capable of being extended to atoms containing more electrons.

B. Wave Functions

The spin part of the wave function for two electrons simply factors out, leaving only the space part φ to be considered. We can write this as

$$\varphi = \varphi(1,2) \pm \varphi(2,1) \tag{1a}$$

$$= (1 \pm P_{12})\varphi(1,2) \tag{1b}$$

$(+) =$ singlet,

$(-) =$ triplet,

$P_{12} =$ interchange coordinates of electrons 1 and 2.

The function $\varphi(1,2)$ can be constructed of products of Slater-type orbitals multiplied by a function of the interelectronic distance;

$$\begin{aligned}\varphi(1,2) &= a_1 b_2 \chi_{12} \\ &= (r_1{}^{n_1} e^{-\zeta_1 r_1})(r_2{}^{n_2} e^{-\zeta_2 r_2}) r_{12}^{n_3} \end{aligned} \tag{2}$$

Notice that when a = b ($n_1 = n_2$ and $\varphi_1 = \varphi_2$) the triplet function vanishes.

A more general trial function would be

$$\varphi = \sum_{i}^{n} c_i \varphi_i \tag{3}$$

where the φ_i's are defined by Eq. (1) and Eq. (2) and the c_i's are variation parameters determined by finding the minimum in the variance of the local energy with respect to each c_i.

C. Local Energy Formulas

The formulas listed below for the helium atom local energy are equivalent to those used by others and follow directly from the many-particle equation derived by Frost [2], assuming infinite nuclear mass.

$$\varepsilon(1,2) = -\frac{1}{2}(A_1 + A_2) - A_3 + B_1 B_3 \cos\theta_{13} + B_2 B_3 \cos\theta_{23} + \boldsymbol{V},$$

$$\text{where } A_i = \zeta_i^2 + (n_i + 1)\left(\frac{n_i}{r_i^2} - \frac{2\zeta_i}{r_i}\right)$$

$$B_i = \zeta_i - \frac{n_i}{r_i}\,;\; i = 1 \textit{ or } 2;$$

$$A_3 = n_3(n_3 + 1)/r_3^2;\; B_3 = n_3/r_3$$

$$\cos\theta_{i3} = (r_i^2 + r_3^2 - r_j^2)/2r_i r_3$$

$$\boldsymbol{V} = -q\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}$$

$q =$ nuclear charge.

$$\text{If } \varepsilon(1,2) = \frac{\boldsymbol{H}\varphi(1,2)}{\varphi(1,2)}$$

$$\text{then } \boldsymbol{H}\varphi(1,2) = \varepsilon(1,2) \cdot \varphi(1,2)$$

$$\text{and } \boldsymbol{H}\varphi = \boldsymbol{H}\varphi(1,2) \pm \boldsymbol{H}\varphi(2,1) \tag{4a}$$

$$= (1 \pm P_{12})\,\boldsymbol{H}\varphi(1,2) \tag{4b}$$

Equations (1b) and (4b) express quantities which must be evaluated over a set of points.

D. Coordinates and Points

In a previous calculation on helium we selected a set of points and weighting coefficients in interparticle coordinates by the method of Gauss quadrature [4]. Since one can easily write trial functions and the Hamiltonian in interparticle coordinates, this system is a natural one to choose. Unfortunately, for an atom with more than two electrons the non-differential part of the volume element, which we use as part of the total weighting factor for each point, turns out to be unbearably complicated in interparticle coordinates. To avoid this we chose the

Gauss quadrature points in spherical coordinates and evaluated the weighting factors using

$$d\tau = r_1{}^2 r_2{}^2 \sin\theta_{12}\, dr_1\, dr_2\, d\theta_{12},$$

and determined the value of the interelectronic distance $r_{12} = r_3$ for each point from

$$r_3{}^2 = r_1{}^2 + r_2{}^2 - 2r_1 r_2 \cos\theta_{12}.$$

Actually we compute points in r_1 and r_2 from the Gauss-Laguerre quadrature tabular data and points in θ_{12} from the Gauss-Legendre data by means of simple transformations [*4*, *6*].

Because the points $\pi \leq \theta_{12} \leq 2\pi$ are merely the reflection of those $0 \leq \theta_{12} \leq \pi$ we considered only the latter group. We also eliminated all points where $r_1 < r_2$, weighting those where $r_1 > r_2$ doubly since symmetry tells us that the two groups yield identical configurations.

If P_r = number of points in radial coordinates,
P_θ = number of points in angular coordinate,

then the total number of points N_{tot} is given by

$$N_{tot} = P_r{}^2 P_\theta$$

The number of points, reduced by the symmetry discussed above, is

$$N_{SR} = \frac{1}{2} P_r (P_r + 1) P_\theta.$$

In these calculations the point distributions $P_r = 5$, $P_\theta = 4$ and $P_r = 6$, $P_\theta = 6$ were used to produce sets of 60 and 126 symmetry reduced points respectively.

E. Results

I. Singlet State

1. Same ζ for Same Shell. Using a wave function of exactly the same form as that of our previous He atom calculation [*4*] and using the same distribution of points among the coordinates, we now get $E = -2.8968$ Hartrees, $V = 1.51 \times 10^{-2}$ compared with $E = -2.8971$ H, $V = 1.79 \times 10^{-2}$ before, which is good agreement considering the different treatment of Gauss points and weights.

In the present calculation many additional terms were included in the trial function to aim at higher accuracy and to study the convergence of the computed energy toward the observed as more terms are added. Tab. 1 shows these results. The c_i's are the coefficients of the unnormalized wave function and n_1, n_2, n_3 are the powers of r_1, r_2, r_3 respectively.

In the calculations of Tab. 1 the exponential parameter $\zeta = 1.816$ was not optimized with respect to the variance. Later an attempt was made to find an approximate optimum value. The results of this search were:

a) The optimum value of ζ does not change smoothly as more terms are added to the wave function.

b) For long wave functions (10 terms or more) the energy and variance are rather insensitive to changes in ζ. A reasonable value seems to be $\zeta = \sqrt{-E(^1S)} =$

Table 1. *1 ^1S Helium Atom Energy and Wave Function, 60 Gauss Points*

$\zeta_1 = \zeta_2 = 1.816$

$E_{calc} = -2.9025$ Hartrees, $V = 1.6 \times 10^{-4}$ H^2, $E_{obs} = -2.9037$*

i	$n_1n_2n_3$	C_i	i	$n_1n_2n_3$	C_i
1	0 0 0	1.000	16	2 2 0	—0.0392
2	0 0 1	0.4849	17	2 2 1	—0.0561
3	0 0 2	—0.2694	18	2 2 2	—0.0924
4	1 0 0	—0.1380	19	3 0 0	0.0261
5	1 0 1	—0.0384	20	3 0 1	0.0277
6	1 0 2	0.3070	21	3 0 2	0.0088
7	2 0 0	0.2673	22	3 1 0	—0.0499
8	2 0 1	—0.1923	23	3 1 1	—0.0035
9	2 0 2	—0.0861	24	3 1 2	—0.0279
10	1 1 0	—0.2841	25	3 2 0	0.0382
11	1 1 1	0.2628	26	3 2 1	—0.0021
12	1 1 2	—0.5384	27	3 2 2	0.0138
13	1 2 0	—0.0255	28	3 3 0	—0.0117
14	1 2 1	0.0680	29	3 3 1	0.0028
15	1 2 2	0.2093	30	3 3 2	—0.0022

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* C. L. PEKERIS, Phys. Rev., **112**, 1649 (1958).

1.7040, which is based on the asymptotic solution of the wave equation for an atom

$$\sum_i \zeta_i^2 = -2E \qquad (5)$$

with $\zeta_1 = \zeta_2$. No extensive calculations were carried out using this value.

2. Different ζ's for Same Shell. HYLLERAAS [*5*] and ECKART [*1*] were the first to show that using different exponential parameters for electrons in the same shell produced an improvement in the calculated energy. SHULL and LOEWDIN [*7*] explained this as adding some measure of correlation to the wave function. In the present work an attempt was made to study this effect with the least squares local energy method using correlated wave functions. The results indicate that for shorter wave functions one does indeed obtain lower variances and improved energies when one includes different ζ's in the two ground state orbitals, but for longer wave functions (10 terms or more), the effect is no longer important; in fact minimum variance occurred when $\zeta_1 = \zeta_2$. This is easily explained by the fact the wave functions used here already contained all important correlation effects from the numerous r_{12} terms.

II. Triplet State

1. Same ζ for Different Shells. Requiring $\zeta_1 = \zeta_2$, a search was made for an approximately optimum single ζ for the lowest ^3S state. The results are similar to those of the ^1S case: here a good value seemed to be $\zeta = \sqrt{-E(^3S)} = 1.4749$. Further calculations employed this value. The results, using a 30 term trial function and 126 points, were $E = -2.1691$ Hartrees, $V = 4.9 \times 10^{-4}$ while the observed result is $E = -2.1752$ H. Notice that the error in the energy computed here is large compared with that of the ^1S calculation, yet the averages were made over more than twice as many points and the wave function included terms of fourth power in the radial coordinates.

2. Different ζ's for Different Shells. Calculations showed that for the ^3S state using different ζ's for the different orbitals lowers the variance and improves the energy, even for long wave functions.

At this point another interesting problem was solved. The formula for the Gauss-Laguerre quadrature is

$$\int_0^\infty e^{-x} f(x)\, dx = \sum_{j=1}^{n} H_j f(a_j) \tag{6}$$

where H_j = Gauss weighting coefficient for abscissa a_j and f(x) is a polynomial in x. Notice that the exponential appearing on the left of Eq. (6) is included in the weighting coefficients on the right. The functions φ (1,2) are exponentials times polynominals but after antisymmetrization and if different ζ's are used for the two orbitals the exponential part cannot be factored out completely.

$$\begin{aligned} \varphi &= e^{-\zeta_1 r_1} e^{-\zeta_2 r_2} r_1^{n_1} r_2^{n_2} - e^{-\zeta_2 r_1} e^{-\zeta_1 r_2} r_1^{n_2} r_2^{n_1} \\ &= e^{-\zeta_1 (r_1+r_2)} [e^{-(\zeta_2-\zeta_1) r_2} r_1^{n_1} r_2^{n_2} - e^{-(\zeta_2-\zeta_1) r_1} r_1^{n_2} r_2^{n_1}] \end{aligned} \tag{7a}$$

or

$$= e^{-\zeta_2 (r_1+r_2)} [e^{-(\zeta_1-\zeta_2) r_1} r_1^{n_1} r_2^{n_2} - e^{-(\zeta_1-\zeta_2) r_2} r_1^{n_2} r_2^{n_1}] \tag{7b}$$

If one persists in using different ζ's beyond this point one must include part of the exponential in the f(x) and ignore the fact that the equality in Eq. (6) no longer holds. The question is: Which ζ should be factored out? Should we follow 7a or 7b? After some reflection one would favor the smaller of ζ_1 and ζ_2. If $\zeta_1 < \zeta_2$, then $e^{-\zeta_1} > e^{-\zeta_2}$ and the Gauss weighting factors would take care of the larger part of the whole exponential while the $e^{-(\zeta_2-\zeta_1)}$ remaining with the polynomial will be small. A test calculation, using the scheme of Eq. (7a), gave values of the energy which tended toward the observed energy quite smoothly, as additional terms were added to the wave function, while erratic oscillations were obtained by procedure 7b.

A search for approximate optimum values of ζ_1 and ζ_2 with respect to the variance was simplified by considering the useful Eq. (5). Requiring Eq. (5) to hold for $\zeta_1 \neq \zeta_2$, the optimization problem reduces to one in a single parameter, really $\Delta\zeta = \zeta_2 - \zeta_1$. Using 12 term functions the minimum variance was found near $\Delta\zeta \sim$ or $= 1$ and in further computation the values $\zeta_1 = 0.86603$ and $\zeta_2 = 1.8975$ were used. Tab. 2 contains the results of these calculations. The energy is in excellent agreement with experiment.

F. Conclusions

Some interesting conclusions can be drawn from the results of this works:

1. The least squares local energy method is capable of producing energies which are in remarkably good agreement with the observed values, particularly when many terms are included in the trial function.

2. Different ζ's should be used in writing orbitals for electrons in different shells. One should not think of this as a simple correlation effect but as a genuine improvement in the orbital description.

3. The least squares local energy method, selecting points by Gaussian quadrature, is capable of handling the different ζ's even though the sums over the Gauss points do not correspond to the integrals.
4. A useful device for selecting reasonable values of the exponential parameters is the result of the asymptotic solution of the wave equation for an atom.

G. Computations

The actual computations were carried out on the IBM 709 computer at the Northwestern University Computing Center using programs written in the FORTRAN language.

As an example of the computing time: it took about 14 minutes to go through the complete calculation, summarized in Tab. 2, of the best 30 term ^3S function over 126 points.

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Table 2. *2 ^3S Helium Atom Energy and Wave Function 126 Gauss Points*

$\zeta_1 = 0.86603$, $\zeta_2 = 1.8975$

$E_{calc} = -2.1753$ Hartrees, $V = 1.5 \times 10^{-6}$ H^2, $E_{obs} = -2.1752$*

i	$n_1 n_2 n_3$	C_i	i	$n_1 n_2 n_3$	C_i
1	0 0 0	1.0000	16	2 2 0	—0.0090
2	0 0 1	0.6214	17	2 2 1	0.0028
3	0 0 2	0.0645	18	2 2 2	—0.00016
4	1 0 0	—1.0705	19	3 0 0	—0.0582
5	1 0 1	—0.6711	20	3 0 1	—0.0191
6	1 0 2	—0.0226	21	3 0 2	0.00041
7	2 0 0	—0.1045	22	3 1 0	—0.0093
8	2 0 1	0.1950	23	3 1 1	0.0042
9	2 0 2	0.00025	24	3 1 2	—0.00009
10	1 1 0	—0.0558	25	3 2 0	0.0011
11	1 1 1	—0.0390	26	3 2 1	—0.00054
12	1 1 2	0.0103	27	3 2 2	0.00004
13	2 1 0	0.1602	28	3 3 0	—0.00003
14	2 1 1	—0.0239	29	3 3 1	0.00002
15	2 1 2	—0.0011	30	3 3 2	—0.000002

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* C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

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