provement amounting to (-0.00224) reckoned from the third approximation. Adding the same value to the third approximation of the tri-electron the result is $E=-1.02984$. On the other hand, adding the contribution (-0.0030) from c_1u in the third approximation to the fourth approximation with u-independent functions the result is $E=-1.0306$. But the contribution of c_1u must be smaller in this approximation than in the third one. We therefore infer that the energy of the positronium ion is very near to $E=-1.0300$, corresponding to an electron affinity of positronium of

$$W=0.0300R'h=0.203 \text{ ev}.$$

As to the various terms of M, it is easier to evaluate $\int(\nabla_3\psi)^2d\tau$ than the difference ΔM. Putting

$$M_1=4\int\{(\nabla_1\psi)^2+(\nabla_2\psi)^2\}d\tau$$

and

$$M_2=4\int(\nabla_3\psi)^2d\tau$$

and considering only terms of the form

$$\psi_{lm}=e^{-\frac{1}{2}s}t^lu^m$$

in the eigenfunction one finds

$$(M_2)_{lm}{}^{l'm'}=\left\{\frac{l+l'+m+m'+4}{l+l'+1}+\frac{4ll'}{(l+l'-1)(l+l'+1)}\right\}\cdot\Pi(l+l'+m+m'+2),$$

where M_1, N, and L have already been given in the paper[4] on H^-. In order to have just this numerical value the volume element is taken to be $d\tau=\frac{1}{2}r_1r_2r_{12}dr_1dr_2dr_{12}=\frac{1}{16}u(s^2-t^2)dsdudt$, corresponding to $dt=r_1^2r_2^2dr_1dr_2$ when the eigenfunction is independent of r_{12}.

It is easy to find general formulae for all matrix elements but, because of the complexity of M_1, we shall not give them here but take the values from the paper cited above. The result is

$$\begin{aligned}N&=4+35c_1+48c_2+96c_1^2+308c_1c_2+576c_2^2\\ L&=11+88c_1+156c_2+218c_1^2+928c_1c_2+1992c_2^2\\ M_1&=8+50c_1+96c_2+128c_1^2+584c_1c_2+1920c_2^2\\ M_2&=8+60c_1+96c_2+144c_1^2+560c_1c_2+1920c_2^2\end{aligned}$$

$$M=\tfrac{1}{2}(M_1+M_2)=8+55c_1+96c_2+136c_1^2+572c_1c_2+1920c_2^2.$$

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Binding Energy of the Positronium Molecule

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A system of two electrons and two positrons is shown to possess dynamic stability. The variational calculation performed leads to a binding energy of at least 0.11 ev for this cluster. The approximate wave function which yields this value depends on the four electron-positron distances only. Neglect of the two distances between particles of the same kind permits an essential mathematical simplification which might be of interest in other problems.

INTRODUCTION

THE question of the stability of a compound of two electrons and two positrons is of particular interest, since it may be considered fundamental in a theoretical investigation of the stability of large poly-electrons.[1]

A first approximation calculation of the

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[1] J. A. Wheeler, Ann. New York Acad. Sci. **48**, 219 (1946).

binding energy of the quadri-electron or "positronium molecule" $(++--)$ was performed by Wheeler[1] who employed the variational method with a ground-state harmonic oscillator function. The investigations have been extended to higher approximations by Ore,[2] who considered oscillator functions of higher degree of excitation as well as functions of more "hydrogenic" character. The results failed to furnish evidence for the stability of this four-particle system with respect to dissociation into two separate bi-electrons or "positronium atoms."

These investigations were not conclusive, and there were reasons why it seemed worth while to re-examine the problem in question. The cluster $(++-)$ forms a stable particle[1,3] capable of exerting an attractive coulomb force on a distant electron. Furthermore, it is easily found that the energy arising from the attractive van der Waals force between two distant bi-electrons is appreciably larger than that for two hydrogen atoms. But an attempt to study the stability of the four-particle system from this point of view leads to a difficulty of principle, *viz.*, the combination of short range exchange forces with long range van der Waals forces when all component particles of the interacting structures are of equal mass. In point of fact, a precisely similar difficulty arises when one treats the problem of the interaction between light nuclei. It was the attempt to solve this question which led Wheeler to the invention of a "collision" matrix.[4] It would seem that the problem of interaction between two bi-electrons is of the type for which the method of resonating group structure is in principle adapted.

However, the present treatment of the quadri-electron may be considered an extension of the successful treatments of the tri-electron, which followed the scheme employed by Hylleraas for the negative hydrogen ion.[5]

THEORY

In suitable units, which differ from ordinary atomic units in that as the energy unit is taken to be $R'h=\frac{1}{2}Rh$ rather than $2Rh$, the wave equation of the four-electron may be written:

$$\{\tfrac{1}{2}[\nabla_1^2+\nabla_2^2+\nabla_a^2+\nabla_b^2]+E/4+V\}\Psi=0,$$

$$V=\frac{1}{r_{1a}}+\frac{1}{r_{2b}}+\frac{1}{r_{1b}}+\frac{1}{r_{2a}}-\frac{1}{r_{12}}-\frac{1}{r_{ab}}.$$

Here 1, 2 refer to the two electrons, and a, b to the positrons.

The motion of the center of mass of the cluster is irrelevant, and the ground state is an S state. The absence of total linear and angular momentum with respect to the center of mass reduces the number of independent variables from 12 to 6. Obviously these six variables can be taken to be the six distances appearing in the expression for the potential energy.

This means a reduction in the number of variables as compared to a total of nine scalar components of the three vectors $\mathbf{s}$, $\mathbf{t}$, and $\mathbf{u}$ employed in reference 2. It is readily seen that a function of s, t, and u involves the angle between $\mathbf{r}_{12}$ and $\mathbf{r}_{ab}$ in addition to the six interparticle distances. The ground-state harmonic oscillator function, on the other hand, contains no such irrelevant variable. Thus we see why the hydrogenic function of reference 2 turned out to be inferior to the oscillator function.

The usual procedure of minimizing the energy with respect to the parameter k, corresponding to the correct wave function $\Psi=\Psi(kr_{ij})$, $i, j=1, 2, a, b$, leads to

$$EN/4=-kL+k^2M, \quad \text{or} \quad E=-L^2/NM$$

where

$$N=\int\Psi^2d\tau, \quad L=\int V\Psi^2d\tau,$$

$$M=\tfrac{1}{2}\int\textstyle\sum_i(\nabla_i\Psi)^2d\tau, \quad i=1, 2, a, b; \quad \Psi=\Psi(r_{ij}).$$

For suitable new variables we choose

$$s_1=r_{1a}+r_{1b}, \quad t_1=r_{1a}-r_{1b}, \quad s_2=r_{2a}+r_{2b},$$

$$t_2=r_{2a}-r_{2b}, \quad u=r_{12}, \quad v=r_{ab}.$$

The ground state is non-degenerate and will have symmetry properties which follow from the symmetry of the Hamiltonian, that is, symmetry in both electrons and positrons, as well as, symmetry or anti-symmetry with respect to inter-

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[2] A. Ore, Phys. Rev. 70, 90 (1946).

[3] E. A. Hylleraas, Phys. Rev. 71, 491 (1947).

[4] J. A. Wheeler, Phys. Rev. 52, 1107 (1937).

[5] E. A. Hylleraas, Zeits. f. Physik 60, 624 (1930).

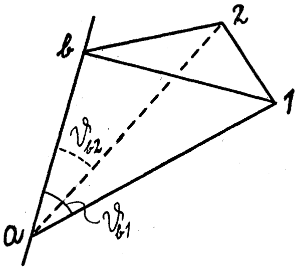

FIG. 1. Coordinate system for the positronium molecule.

change of the two electrons against the two positrons. (We are concerned with the space dependence of the wave function. The inclusion of the two anti-symmetric spin functions, one for each kind of particles, would give a total wave function in accordance with the Pauli principle.)

Thus if we consider functions of the simple form

$$\Psi=\psi_1(s_1,\,s_2)\psi_2(t_1,\,t_2)\psi_3(u)\psi_4(v)$$

the symmetry suggests

$$\psi_1=\psi_1(s_1+s_2),\quad \psi_2=\psi_2((t_1-t_2)^2)\quad \text{and}\quad \psi_3=\psi_4.$$

There will in general be no particular difficulties involved in the calculation of the integrals L, M, and N when the variational function is taken to be independent of u and v. By performing the substitution 1, $2\leftrightarrow a$, b in the terms which involve u one can see that it is proper in that case to consider the integrands independent of u. For instance, on account of this symmetry u may be replaced by v in L. We need then retain only five variables of integration, since the integration over the sixth variable, which may be chosen to be the angle φ_{12} defined below, contributes merely the same constant factor to L, M, and N.

In order to get the proper volume element consider the edge (ab) as the main axis of the tetrahedron $(ab12)$ (in Fig. 1). Then the three angles defining the direction of (ab) and the rotation of the system as a whole around this axis may be left out of the integrations. Also the relative angle φ_{12} between the triangles $(ab1)$ and $(ab2)$ is unimportant when the integrand is independent of $r_{12}=u$.

After this reduction in the number of independent variables from 9 to 6, and next to 5, we may take the volume element to be

$$\begin{aligned}d\tau&=4r_{ab}{}^2dr_{ab}r_{1a}{}^2dr_{1a}r_{2a}{}^2dr_{2a}\sin\vartheta_{b1}d\vartheta_{b1}\sin\vartheta_{b2}d\vartheta_{b2}\\&=4dr_{ab}r_{1a}dr_{1a}r_{1b}dr_{1b}r_{2a}dr_{2a}r_{2b}dr_{2b}\\&=dv\tfrac{1}{4}(s_1{}^2-t_1{}^2)ds_1dt_1\tfrac{1}{4}(s_2{}^2-t_2{}^2)ds_2dt_2,\end{aligned}$$

the limits of integration being

$$v\leqq s_1,s_2\leqq\infty;\quad -v\leqq t_1,t_2\leqq v;\quad 0\leqq v\leqq\infty.$$

If we use in a first approximation the very simple function

$$\Psi=\exp[-\tfrac{1}{2}(s_1+s_2)],$$

the integrals become

$$\begin{aligned}N_1&=\int_0^\infty e^{-2v}(\tfrac{1}{3}v^3+v^2+v)^2dv=33/8,\\L_1&=4A-2B=4\cdot21/8-2\cdot25/12=19/3,\\M_1&=2A=21/4,\\A&=\int_0^\infty e^{-2v}(\tfrac{1}{3}v^3+v^2+v)(v^2+v)dv,\\B&=\int_0^\infty e^{-2v}(\tfrac{1}{3}v^3+v^2+v)^2\frac{dv}{v}.\end{aligned}$$

Hence, in this approximation,

$$E=-\frac{19^2\cdot32}{33\cdot21\cdot9}=-1.8522R'h=-12.54\text{ ev}.$$

A better approximation is obtained when we consider a function representing each electron strongly bound to one of the two positrons and only loosely bound to the second. For instance, let

$$\begin{aligned}2\Psi=&\exp[-\tfrac{1}{2}(1+\beta)(r_{1a}+r_{2b})-\tfrac{1}{2}(1-\beta)(r_{1b}+r_{2a})]\\&+\exp[-\tfrac{1}{2}(1-\beta)(r_{1a}+r_{2b})-\tfrac{1}{2}(1+\beta)(r_{1b}+r_{2a})].\end{aligned}$$

or

$$\Psi=\exp[-\tfrac{1}{2}(s_1+s_2)]\cosh\beta/2(t_1-t_2).$$

Then $\beta=1$ will correspond to two separate bi-electrons, whereas for $\beta=0$ we have the above case of equal binding within all electron-positron pairs.

Since $\cosh^2\beta/2(t_1-t_2)=\frac{1}{2}(1+\cosh\beta(t_1-t_2))$ the integrals N, L, and M will now be

$$N=\tfrac{1}{2}(N_1+N_2),\quad L=\tfrac{1}{2}(L_1+L_2)$$

TABLE I. Numerical relation between the calculated total binding energy and the square of the parameter β.

β^2	0	0.25	0.5	0.75	1.0
$-E$	1.8522	1.98180	2.01681	2.00288	2.0000

and

$$M=\tfrac{1}{2}(M_1'+M_2),\quad M_1'=M_1-3\beta^2.$$

Here N_1, L_1, and M_1 are the integrals given above, while the integrals of index 2 can be obtained from those of index 1 by replacing $\frac{1}{3}v^3+v^2+v$ by

$$\left(v-\frac{1-\beta^2}{\beta^2}\right)\frac{\sinh\beta v}{\beta}+\frac{v\cosh\beta v}{\beta^2}$$

and by further replacement of v^2+v by

$$(v+1)(\sinh\beta v)/\beta \text{ in } L_2$$

and by

$$v((\sinh\beta v)\beta+\cosh\beta v) \text{ in } M_2.$$

Finally we get M_1' from M_1 by replacing v^2+v by $v^2+v-\frac{1}{3}\beta^2v^3$.

The result is

$$N_2=\frac{33/8-11\beta^2/4+5\beta^4/8}{(1-\beta^2)^3},$$

$$M_2=2\frac{21/8-3\beta^2/4+\beta^4/8}{(1-\beta^2)^3},$$

$$L_2=4\frac{21/8-9\beta^2/4+5\beta^4/8}{(1-\beta^2)^3}-\frac{2}{(1-\beta^2)^2}\left[1-\frac{5\beta^2}{8}-\frac{1}{4\beta^2}+\frac{7}{8\beta^2}+\frac{(1-\beta^2)^4}{4\beta^6}\log\frac{1}{1-\beta^2}\right].$$

Among the integrations leading to these expressions we need only mention the integral involved in L_2

$$\int_0^\infty e^{-2v}\left(\frac{\sinh\beta v}{\beta}\right)^2\frac{dv}{v}=\frac{1}{4\beta^2}\log\left(\frac{1}{1-\beta^2}\right).$$

The relation between the calculated total binding energy of the system and the value of the parameter β, which determines the approximate wave function, can be read from Table I. The minimum value of E appears to be roughly -2.017 for β^2 about 0.50. The binding energy of the positronium molecule with respect to dissociation into two positronium atoms is thus in fact positive, amounting in this approximation to

$$W=0.017R'h=0.11\text{ ev.}$$

The approximate calculation just presented is related to the well-known Heitler-London treatment of the hydrogen molecule or rather to Wang's modification of this treatment. In view of the excellent results obtained subsequently by James and Coolidge for the binding energy of that molecule we are inclined to believe that considerable improvement is possible in the value presented above for the positronium molecule.

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