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Electron Affinity of Positronium

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By use of the variational method as previously applied to the mathematically similar problem of the negative atomic hydrogen ion, the energy of a compound of two electrons and one positron has been calculated. The resulting (third approximation) value of roughly 0.19 ev binding energy of this system with respect to dissociation into a free electron and a system of one electron and one positron corresponds to the value already found by J. A. Wheeler. On the basis of higher approximations obtained for H^- the exact binding energy of the tri-electron has been estimated to be 0.203 ev.

1.

THE properties of the hypothetical *positronium* atom or *bi-electron*, a compound of one electron and one positron, have been studied by various physicists.¹ Thus, for example, the energy levels of this system are

$$E_n = -R'h/n^2, \quad R' = \frac{1}{2}R,$$

where R is the Rydberg constant.

J. A. Wheeler first extended the investigations to electron-positron clusters of higher complexity.¹ Wheeler concludes that the three-particle system $(++-)$ or $(+--)$ is stable by at least 0.19 ev against dissociation of any kind.

Shortly after the calculations which are presented below had been completed the author was informed about the method employed and the numerical results obtained by Wheeler. The two treatments are very much the same, both being based on that previously developed by the

present author for the negative atomic hydrogen ion.² As a matter of fact, the eigenfunctions used by the two investigators are identical up to the third approximation, which is the highest approximation considered by Wheeler.

Nevertheless, I believe the present publication to be of some interest in demonstrating the agreement between the numerical results, and, furthermore, because of the attempt which has been made in this paper to estimate the exact value of the binding energy of the tri-electron on the basis of the higher approximations previously found by the author for the hydrogen ion. Again, the results recently reported³ on the dynamic stability of the four-electron system might also make the publication of this paper desirable.

2.

A compound of two electrons and one positron (or two positrons and one electron) is closely related to the negative hydrogen ion. In atomic

¹ The name 'positronium' has been proposed by A. E. Ruark, *Phys. Rev.* **68**, 278 (1945) and the name 'bi-electron' by J. A. Wheeler, *Ann. New York Acad. Sci.* **48**, 219 (1946).

² E. A. Hylleraas, *Zeits. f. Physik* **60**, 624 (1930).

³ E. A. Hylleraas and A. Ore, *Phys. Rev.* **71**, 493 (1947).

units, with e , m , and \hbar as fundamental units and a_H and $2Rh$ the corresponding units of length and energy, the wave equation for such systems may be written as

$$\left\{ \frac{1}{2} \left(\nabla_1^2 + \nabla_2^2 + \frac{m}{m_3} \nabla_3^2 \right) + E + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} \right\} \psi = 0,$$

r_1 and r_2 being the distances of the two electrons from the positive particle of mass m_3 .

For the hydrogen ion we take $m_3 = \infty$ and change the unit of length from a_H to $\frac{1}{2}a_H$, the unit of energy becoming $4Rh$. In energy units Rh , the wave equation of H^- then reads

$$\left\{ \nabla_1^2 + \nabla_2^2 + \frac{E}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} \right\} \psi = 0$$

compared to

$$\left\{ \frac{1}{2} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + \frac{E}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} \right\} \psi = 0$$

for the tri-electron in units a_H and $\frac{1}{2}Rh$.

Considering only states of zero total linear and angular momentum it is easily seen that the wave function depends only on the three distances appearing in the potential energy of the particles. As shown in reference 2 the energy of the ground state is given by the minimum value of $E = -L^2/4NM$, where

$$N = \int \psi^2 d\tau, \quad L = 4 \int \left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} \right) \psi^2 d\tau,$$

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

$$\text{or } 4 \int \frac{1}{2} \{ (\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 + (\nabla_3 \psi)^2 \} d\tau.$$

It is understood, however, that in the function $\psi(r_1, r_2, r_{12})$ used here we have to replace each r by kr in order to get the actual eigenfunction. The expression for E given above has been obtained by minimizing E with respect to k in the expression $NE = -kL + k^2M$.

The two expressions for M refer to the hydrogen ion and the tri-electron, respectively. The

difference in the two M -values

$$\Delta M = 4 \int \frac{1}{2} \{ (\nabla_3 \psi)^2 - (\nabla_1 \psi)^2 - (\nabla_2 \psi)^2 \} d\tau$$

vanishes when ψ is independent of r_{12} . Consequently, in that case there is no mathematical difference at all between the two problems—apart from the difference in energy units.

If we consider a function

$$\psi = e^{-\frac{1}{2}s} (1 + c_1 u + c_2 t^2 + c_4 t^4 + c_6 t^6 + \dots),$$

$$s = r_1 + r_2, \quad t = -r_1 + r_2, \quad u = r_{12},$$

and put $c_1 = c_4 = c_6 = 0$, we get in the first and second approximation $E = -0.9453$ and $E = -1.0246$ when we take $c_2 = 0$, and $c_2 = 0.05$, respectively. For the hydrogen ion this value is better than the second approximation $E = -1.0176$ obtained by variation of c_1 only. The corresponding variation for the tri-electron leads to the value $E = -0.9607$; hence it is evident that the variable $u = r_{12}$ plays a less important role in the case of the tri-electron.

In order to investigate the convergence by r_{12} -independent functions the third and fourth approximations have been calculated, giving

$$E = -1.02665 \text{ for } c_2 = 0.045,$$

$$c_4 = 0.00025 \text{ and } E = -1.02762 \text{ for } c_2 = 0.048,$$

$$c_4 = 0.00011, \quad c_6 = 0.0000011.$$

On the other hand the wave function

$$\psi = e^{-\frac{1}{2}s} \cosh \beta t / 2$$

gives $E = -1.02660$, with $\beta = 0.33$, corresponding approximately to the above third approximation. The difference between the third and fourth approximations is rather astonishing, but certainly does not mean that the limiting value is still far away.

Postponing the evaluation of ΔM , we give at once the third approximation minimum value when $c_4 = c_6 = 0$. Putting $c_1 = 0.05$, $c_2 = 0.05$, the result is $E = -1.0276$, the corresponding value for H^- being (-1.0506) . Thus the contributions of the term $c_1 u$ are (-0.0030) and (-0.0260) , respectively. Now the minimum energy value of H^- has been found⁴ to be (-1.05284) , an im-

⁴ E. A. Hylleraas, Zeits. f. Physik 65, 209 (1930).

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 $\int (\nabla_3\psi)^2 d\tau$ than the difference ΔM . Putting

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

and

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

and considering only terms of the form

$$\psi_{lm} = e^{-\frac{1}{2}st} u^m$$

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 paper⁴ 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

$$\begin{aligned} N &= 4 + \frac{35c_1 + 48c_2}{96c_1^2 + 308c_1c_2 + 576c_2^2} & L &= 11 + \frac{88c_1 + 156c_2}{218c_1^2 + 928c_1c_2 + 1992c_2^2} \\ M_1 &= 8 + \frac{50c_1 + 96c_2}{128c_1^2 + 584c_1c_2 + 1920c_2^2} & M_2 &= 8 + \frac{60c_1 + 96c_2}{144c_1^2 + 560c_1c_2 + 1920c_2^2} \\ M &= \frac{1}{2}(M_1 + M_2) = 8 + \frac{55c_1 + 96c_2}{136c_1^2 + 572c_1c_2 + 1920c_2^2} \end{aligned}$$

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).