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SOME REMARKS ON THE NEGATIVE HYDROGEN ION AND ITS ABSORPTION COEFFICIENT

S. Chandrasekhar
Yerkes Observatory

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ABSTRACT

Some remarks on the quantum theory of the negative hydrogen ion are made, and attention is drawn to certain facts which make the evaluation of its continuous absorption coefficient a problem of extreme difficulty.

This paper will consist of a few disconnected remarks on the quantum theory of the negative hydrogen ion.

1. *The wave function for the ground state of* H^-.—Since the discovery of the stability of the negative ion of hydrogen by Bethe[1] and Hylleraas[2] and the recognition of its astrophysical importance by Wildt,[3] attempts[4] have been made to determine the electron affinity of hydrogen with as high a precision as possible. In these latter attempts the energy of the ground state is determined by applications of the Ritz principle, using forms for the wave functions suggested by Hylleraas' successful treatment of the ground state of the helium atom. Thus Williamson's six-parameter wave function is of exactly the same form as the "best" wave function of Hylleraas for helium. Similarly, Henrich's eleven-parameter wave function includes terms beyond those used by Williamson. While there can hardly be any doubt that Henrich's value for the electron affinity of 0.747 electron volts can be in error by more than a fraction of 1 per cent, the relatively weak convergence of the entire process (cf., e.g., Table 7 in Henrich's paper) leaves one with a suspicion that the formal analogy between the atomic configurations of H^- and He has perhaps been taken too literally. From one point of view it would seem that the structures of these two atoms must be very different indeed; for, while helium is a stable closed structure, the negative hydrogen ion is an open structure which exists principally on account of incomplete screening and polarization (see below). This suggests that it might be possible to obtain better representations of the true wave function by seeking forms which will explicitly take into account this difference. That such attempts may not prove unsuccessful is suggested by the following preliminary considerations.

As is well known, the success of Hylleraas' investigations on helium is due principally to the circumstance that a wave function of the form

$$\psi = e^{-\alpha(r_1+r_2)} , \tag{1}$$

which ascribes a hydrogen-like wave function to each of the electrons in a suitably screened Coulomb field, already provides a good first approximation. More particularly the wave function of the form (1), which gives the lowest energy, is

$$\psi = e^{-(Z-[5/16])(r_1+r_2)} . \tag{2}$$

(In the foregoing equation r_1 and r_2 are measured in units of the Bohr radius. Similarly, in the rest of the paper we shall systematically use Hartree's atomic units.)

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[1] *Zs. f. Phys.*, **57**, 815, 1929.

[2] *Zs. f. Phys.*, **60**, 624, 1930.

[3] *Ap. J.*, **89**, 295, 1939.

[4] R. E. Williamson, *Ap. J.*, **96**, 438, 1942; and L. R. Henrich, *Ap. J.*, **99**, 59, 1943.

When $Z = 1$, the wave function (2) predicts an energy $E = -0.473$, which actually makes H^- an unstable structure and is in error by fully 12 per cent. In other words, the first approximation, which is so satisfactory for *He*, fails completely for H^-. That this should happen is not surprising in view of our earlier remarks concerning the difference between the two atoms. On the other hand, it would appear that in contrast to *He* a natural first approximation for H^- is to ignore the screening of one of the electrons and adjust the screening constant for the second electron only. In other words, the starting-point for H^- should rather be a wave function of the form

$$\psi = e^{-r_1 - b r_2} + e^{-r_2 - b r_1} , \tag{3}$$

where b is the screening constant for the second electron. More generally, we may write

$$\psi = e^{-a r_1 - b r_2} + e^{-a r_2 - b r_1} , \tag{4}$$

where a and b are constants to be appropriately chosen. The Ritz principle applied to a wave function of the form (4) showed that the lowest value of energy is attained when

$$a = 1.03925 \quad \text{and} \quad b = 0.28309 . \tag{5}$$

The corresponding value for the energy is

$$E_1 = -0.51330 , \tag{6}$$

which predicts the stability of H^-. Moreover, in confirmation of our expectations it is seen that, while the inner electron is practically unscreened, the outer one is screened considerably and to the extent of 72 per cent. In view of this, it appears that a good second approximation may be provided by considering a wave function of the form

$$\psi = (e^{-a r_1 - b r_2} + e^{-a r_2 - b r_1})(1 + c\, r_{12}) , \tag{7}$$

where a, b, and c are constants to be so chosen as to lead to a minimum value for the energy. It is found that with

$$a = 1.07478 , \quad b = 0.47758 , \quad \text{and} \quad c = 0.31214 \tag{8}$$

we minimize the energy integral and obtain for it the value

$$E_2 = -0.52592 . \tag{9}$$

This value for the energy, while inferior to those predicted by Williamson (0.5265) and Henrich (0.5276), is substantially better than the value 0.5253 given by the three-parameter wave function of Bethe and Hylleraas.

An interesting feature of the wave function (7) with the constants as given by equation (8) is that the inclusion of the term r_{12} reduces the screening of the outer electron from 0.72 to 0.52. This relatively large reduction in the screening is due to the strong polarizability of the hydrogen atom. Indeed, according to equations (6) and (9) we may say that the electron affinity of hydrogen is due about equally to the incomplete screening of the nucleus and to the polarization of the hydrogenic core.

The foregoing discussion suggests that it might be profitable to improve the wave function (7) by including further terms. This would be particularly useful for estimating the inherent uncertainty in the absorption cross-sections derived from different wave functions, all of which predict (within limits) the same value for energy. The practical importance for carrying out such a discussion will be apparent from our remarks in the following section.

2. *The absorption cross-sections for* H$^-$.—The calculations of the absorption cross-sections which have been carried out so far (Massey and Bates; Williamson; Henrich)

are based on two approximations. The first consists in the use of the wave function for describing the bound state the ones derived from the minimal calculations and the second, in the use of a plane wave representation of the ejected outgoing electron. The validity or otherwise of these approximations will depend upon whether the principal contributions to the matrix element,

$$\mu = \int \Psi_d (r_1 + r_2) \Psi_c d\tau \;, \tag{10}$$

come from those regions of the configuration space in which the two approximations may be expected to be satisfactory. In equation (10) Ψ_d denotes the normalized wave function for the ground state of H^-, and Ψ_c the wave function of the continuous state normalized to correspond to an outgoing electron of unit density.

It appears that the use of the plane-wave representation for the free electron will not introduce any very serious error, since, as has been pointed out on an earlier occasion,[5] parts of the configuration space which are only relatively far from the hydrogenic core are relevant for the absorption process. But if this be admitted, the question immediately arises as to whether the wave function for the ground state derived from the Ritz principle can be trusted to these distances. It appears that the matter can be decided in the following manner.

First, we may observe that it might prove to be an adequate approximation to use for the continuous wave function that of an electron moving in the Hartree field of a hydrogen atom. In other words, it might be sufficient to use for Ψ_c the expression

$$\Psi_c = \frac{1}{\sqrt{2\pi}} \{ e^{-r_2} \phi (r_1) + e^{-r_1} \phi (r_2) \} \;, \tag{11}$$

where $\phi(r)$ satisfies the wave equation

$$\nabla^2 \phi + \left[k^2 + 2 \left(1 + \frac{1}{r} \right) e^{-2r} \right] \phi = 0 \tag{12}$$

and tends asymptotically at infinity to a plane wave of unit amplitude along some chosen direction. If this direction in which the ejected electron moves at infinity be chosen as the polar axis of a spherical system of co-ordinates, it is readily shown that the appropriate solution for ϕ can be expressed in the form

$$\phi = \sum_{l=0}^{\infty} \frac{1}{k r} (2l+1) P_l (\cos \vartheta) \chi_l (r) , \tag{13}$$

where the radial function χ_l is a solution of the equation

$$\frac{d^2 \chi_l}{d r^2} + \left\{ k^2 - \frac{l(l+1)}{r^2} + 2 \left(1 + \frac{1}{r} \right) e^{-2r} \right\} \chi_l = 0 \;, \tag{14}$$

which tends to a pure sinusoidal wave of unit amplitude at infinity. Thus, on our present approximation Ψ_c can be written in the form

$$\left. \begin{aligned} \Psi_c = \frac{1}{\sqrt{2\pi}} \Big\{ & e^{-r_2} \sum_{l=0}^{\infty} \frac{1}{k r_1} (2l+1) P_l (\cos \vartheta_1) \chi_l (r_1; k) \\ & + e^{-r_1} \sum_{l=0}^{\infty} \frac{1}{k r_2} (2l+1) P_l (\cos \vartheta_2) \chi_l (r_2; k) \Big\} \,. \end{aligned} \right\} \tag{15}$$

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[5] S. Chandrasekhar and M. K. Krogdahl, *Ap. J.*, **98**, 205, 1943.

Using the foregoing form for Ψ_c, the standard formula for the absorption cross-section for a process in which a photoelectron with k atomic units of momentum is ejected can be reduced to the form

$$\kappa = 9.266 \times 10^{-19} \frac{k^2 + 0.05512}{k} \left| \int_0^\infty W(r) \chi_1(r) \, dr \right|^2 \text{cm}^2 , \qquad (16)$$

where $W(r)$ is a certain weight function which can be derived from and depends only on the wave function for the bound state. It is seen that, according to equation (16), the absorption cross-section depends only on the single radial function χ_1. This is to be expected, since the ground state, being an s-state, transitions can take place only to a p-state. It may be noted here that on the plane-wave representation of the free electron the appropriate form for χ_1 is

$$\chi_1 (\text{plane wave}) = \frac{\sin k r}{k r} - \cos k r . \qquad (17)$$

The function $W(r)$ corresponding to Henrich's eleven-parameter wave function has been computed and is tabulated in Table 1. The run of the function is further illustrated in Figure 1.

TABLE 1

THE WEIGHT FUNCTION $W(r)$

r	$W(r)$	r	$W(r)$	r	$W(r)$	r	$W(r)$
0..........	0	4.0.......	1.597	11.0.......	0.833	19.0.......	0.131
0.5.........	0.210	4.5.......	1.623	12.0.......	.703	20.0.......	.096
1.0.........	0.553	5.0.......	1.620	13.0.......	.585	21.0.......	.069
1.5.........	0.861	6.0.......	1.548	14.0.......	.478	22.0.......	.049
2.0.........	1.108	7.0.......	1.422	15.0.......	.383	23.0.......	.034
2.5.........	1.298	8.0.......	1.273	16.0.......	.301	24.0.......	.024
3.0.........	1.439	9.0.......	1.120	17.0.......	.233	25.0.......	0.016
3.5.........	1.538	10.0.......	0.972	18.0.......	0.177	∞	0

An examination of the values given in Table 1 discloses the somewhat disquieting fact that substantial contributions to the integral

$$\int_0^\infty W(r) \chi_1(r) \, dr \qquad (18)$$

arise from values of r up to 25, while as much as 30–40 per cent of the entire value comes from $r \geqslant 10$. This result has two consequences. The first is that the use of the p-spherical wave (17) instead of the solution derived from (cf. eq. [14])

$$\frac{d^2\chi_1}{dr^2} + \left\{ k^2 - \frac{2}{r^2} + 2 \left(1 + \frac{1}{r} \right) e^{-2r} \right\} \chi_1 = 0 , \qquad (19)$$

will not lead to any serious error; for the solution of equation (19), which tends to a sine wave of unit amplitude at infinity, has the behavior

$$\chi_1 \rightarrow \frac{\sin (k r + \delta)}{k r} - \cos (k r + \delta) \qquad (r \rightarrow \infty), \quad (20)$$

and the "phase shift" δ may be taken as a measure of the distortion of the p-spherical wave by the hydrogen atom at the origin. Integrations of equation (19) for various values of k^2 have been carried out numerically, and the resulting phase shifts for some of them are given in Table 2. It is seen that the phase shifts are indeed quite small for values of k^2, which are of astrophysical interest.

The second consequence of the run of the function $W(r)$ is not so satisfactory; for an examination of the energy integral minimized in the Ritz principle reveals that over 95 per cent of the contribution to the integral arises from regions of the configuration space which correspond to $r < 10$. Accordingly, it would appear that the choice of the wave function in accordance only with the Ritz principle cannot be expected to lead to values of $W(r)$ which are necessarily trustworthy for $r > 10$. Under these circumstances the best hope for improving the current wave functions would consist in first determining the true asymptotic forms of the wave function for large distances and later choosing functions which would lead not only to the best value for the energy but also to the correct asymptotic forms. However, such calculations are likely to be extremely laborious.

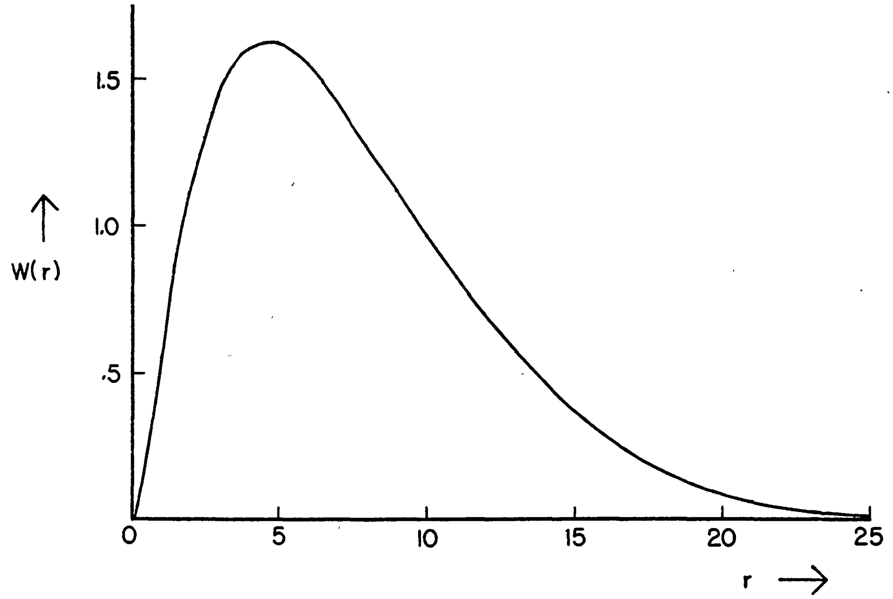

FIG. 1

TABLE 2

PHASE SHIFTS δ FOR THE p-SPHERICAL WAVES IN THE HARTREE FIELD OF A HYDROGEN ATOM

k^2	δ	k^2	δ	k^2	δ	k^2	δ
1.50.......	0.1486	0.80......	0.09244	0.25......	0.02605	0.100.....	0.007689
1.00.......	0.1115	0.50......	0.05838	0.125.....	0.01046	0.035.....	0.001709

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