

# ON THE CONTINUOUS ABSORPTION COEFFICIENT OF THE NEGATIVE HYDROGEN ION

S. CHANDRASEKHAR

Yerkes Observatory

Received June 25, 1945

## ABSTRACT

In this paper it is shown that the continuous absorption coefficient of the negative hydrogen ion is most reliably determined by a formula for the absorption cross-section which involves the matrix element of the momentum operator. A new absorption curve for  $H^-$  has been determined which places the maximum at  $\lambda$  8500 Å; at this wave length the atomic absorption coefficient has the value  $4.37 \times 10^{-17}$  cm<sup>2</sup>.

1. *Introduction.*—In earlier discussions<sup>1</sup> by the writer attention has been drawn to the fact that the continuous absorption coefficient of the negative hydrogen ion, evaluated in terms of the matrix element

$$\mu = \int \Psi_d^* (r_1 + r_2) \Psi_c d\tau \quad (1)$$

(where  $\Psi_d$  denotes the wave function of the ground state of the ion and  $\Psi_c$  the wave function belonging to a continuous state normalized to correspond to an outgoing electron of unit density), depends very much on  $\Psi_d$  in regions of the configuration space which are relatively far from the hydrogenic core. This has the consequence that the absorption cross-sections are not trustworthily determined if wave functions derived by applications of the Ritz principle are used in the calculation of the matrix elements according to equation (1). This is evident, for example, from Figure 1, in which we have plotted the absorption coefficients as determined by Williamson<sup>2</sup> and Henrich,<sup>3</sup> using wave functions of the forms

$$\Psi_d = \mathcal{N} e^{-as/2} (1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2) \quad (2)$$

and

$$\Psi_d = \mathcal{N} e^{-as/2} (1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 t^4 + \chi_7 t^6 + \chi_8 t^4 u^2 + \chi_9 t^2 u^2 + \chi_{10} t^2 u^4), \quad (3)$$

respectively. (In eqs. [2] and [3]  $\mathcal{N}$  is the normalizing factor; and  $a$ ,  $\beta$ ,  $\gamma$ , etc., are constants determined by the Ritz condition of minimum energy,

$$s = r_2 + r_1, \quad t = r_2 - r_1, \quad \text{and} \quad u = r_{12}, \quad (4)$$

where  $r_1$ ,  $r_2$ , and  $r_{12}$  are the distances of the two electrons from the nucleus and from each other, respectively.) The wide divergence between the two curves in Figure 1 is too large to be explained in terms of only the improvement in energy effected by the wave function (3): it must arise principally from the fact that in the evaluation of the matrix elements according to equation (1) parts of the wave function are used which do not contribute appreciably to the energy integral and are therefore poorly determined. Indeed, this sen-

<sup>1</sup> *Ap. J.*, 100, 176, 1944; also *Rev. Mod. Phys.*, 16, 301, 1944.

<sup>2</sup> *Ap. J.*, 96, 438, 1942.

<sup>3</sup> *Ap. J.*, 99, 59, 1944.

sitiveness of the derived absorption coefficients to wave functions effecting only relatively slight improvements in the energy makes it difficult to assess the reliability of the computed absorption coefficients. However, in this paper we shall show how these difficulties can be avoided by using a somewhat different formula for the absorption cross-section.

2. *Alternative formulae for evaluating the absorption coefficient.*—It is well known that in the classical theory the radiative characteristics of an oscillating dipole can be expressed in terms of either its dipole moment, its momentum, or its acceleration. There are, of course, analogous formulations in the quantum theory, the matrix element

$$(a | z_j | b) = \int \psi_a^* z_j \psi_b d\tau \quad (5)$$

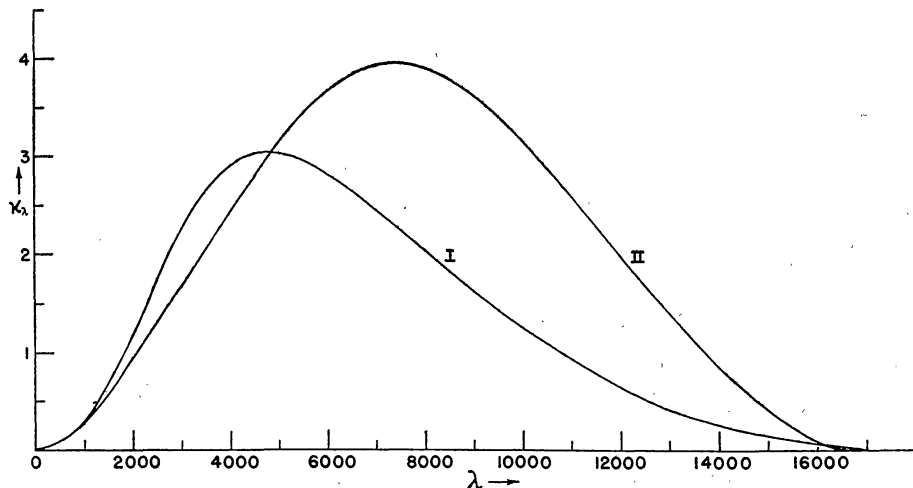


FIG. 1.—A comparison of the continuous absorption coefficient of  $H^-$  computed according to formula (I) and with wave functions of forms (2) (curve I) and (3) (curve II). The ordinates denote the absorption coefficients in units of  $10^{-17} \text{ cm}^2$ ; the abscissae, the wave length in angstroms.

for the co-ordinate  $z_j$  of the  $j$ th electron in an atom being simply related to the corresponding matrix element of the momentum operator or the acceleration. Thus, we have the relations

$$(a | z_j | b) = \frac{1}{(E_a - E_b)} \int \frac{\partial \psi_a^*}{\partial z_j} \psi_b d\tau = -\frac{1}{(E_a - E_b)} \int \psi_a^* \frac{\partial \psi_b}{\partial z_j} d\tau \quad (6)$$

and

$$(a | z_j | b) = \frac{1}{(E_a - E_b)^2} \int \psi_a^* \frac{\partial V}{\partial z_j} \psi_b d\tau \quad (7)$$

if all the quantities are measured in Hartree's atomic units and where  $E_a$  and  $E_b$  denote the energies of the states indicated by the letters  $a$  and  $b$  and where  $V$  denotes the potential energy arising from Coulomb interactions between the particles. More particularly for an atom (or ion) with two electrons, we have

$$\mu_z = \int \Psi_d^* (z_1 + z_2) \Psi_c d\tau, \quad (8)$$

$$\mu_z = -\frac{1}{(E_d - E_c)} \int \Psi_d^* \left( \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) \Psi_c d\tau, \quad (9)$$

and

$$\mu_z = \frac{1}{(E_d - E_c)^2} \int \Psi_d^* \left( \frac{z_1}{r_1^3} + \frac{z_2}{r_2^3} \right) \Psi_c d\tau. \quad (10)$$

While the foregoing formulae are entirely equivalent to each other if  $\Psi_d$  and  $\Psi_c$  are exact solutions of the wave equation, they are of different merits for the evaluation of  $\mu_z$  if approximate wave functions are used. Thus, it is evident that formula (8) uses parts of the

configuration space, which are more distant than relevant, for example, in the evaluation of the energy; similarly, formula (10) uses the wave functions in regions much nearer the origin. It would appear that formula (9) is the most suitable one for the evaluation of  $\kappa_\nu$ , particularly when wave functions derived by applications of the Ritz principle are used. The calculations which we shall present in the following sections confirm this anticipation; but before we proceed to such calculations, it is useful to have the explicit formulae for the absorption cross-sections on the basis of equations (8), (9), and (10).

In ordinary (c.g.s.) units the standard formula for the atomic absorption coefficient  $\kappa_\nu$  for radiation of frequency  $\nu$ , in which an electron with a velocity  $v$  is ejected, is

$$\kappa_\nu = \frac{32\pi^4 m^2 e^2}{3h^3 c} \nu v \left| \int \Psi_d^* (z_1 + z_2) \Psi_c d\tau \right|^2, \tag{11}$$

where  $m$ ,  $e$ ,  $h$ , and  $c$  have their usual meanings. (In writing eq. [11] it has been assumed that the electron is ejected in the  $z$ -direction; see eq. [15] below.) By inserting the numerical values for the various atomic constants equation (11) can be expressed in the form

$$\kappa_\nu = 8.561 \times 10^{-19} (\nu_{\text{at}} k |\mu_z|^2) \text{ cm}^2, \tag{12}$$

where  $k$  denotes the momentum of the ejected electron and  $\nu_{\text{at}}$  the frequency of the radiation absorbed, both measured in atomic units, and where, moreover, the matrix element  $\mu_z$  has also to be evaluated in atomic units.

If  $I$  denotes the electron affinity (also expressed in atomic units)

$$4\pi\nu_{\text{at}} = k^2 + 2I, \tag{13}$$

and depending on which of the formulae (8), (9), and (10) we use for evaluating  $\kappa_\nu$ , we have

$$\kappa_\nu = 6.812 \times 10^{-20} k (k^2 + 2I) \left| \int \Psi_d^* (z_1 + z_2) \Psi_c d\tau \right|^2, \tag{I}$$

$$\kappa_\nu = 2.725 \times 10^{-19} \frac{k}{(k^2 + 2I)} \left| \int \Psi_d^* \left( \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) \Psi_c d\tau \right|^2, \tag{II}$$

and

$$\kappa_\nu = 1.090 \times 10^{-18} \frac{k}{(k^2 + 2I)^3} \left| \int \Psi_d^* \left( \frac{z_1}{r_1^3} + \frac{z_2}{r_2^3} \right) \Psi_c d\tau \right|^2. \tag{III}$$

Finally, we may note that if  $\lambda$  denotes the wave length of the radiation measured in angstroms, then

$$\lambda = \frac{911.3}{k^2 + 2I} \text{ \AA}. \tag{14}$$

3. *The continuous absorption coefficient of H<sup>-</sup> evaluated according to formula (III).*—

As we have already indicated, in the customary evaluations of  $\kappa_\nu$  according to formula (I) the relatively more distant parts of the wave function are used. It is evident that we shall be going to the opposite extreme in using the wave function principally only near the origin if we evaluate  $\kappa_\nu$  according to formula (III). For this reason it is of interest to consider first the absorption coefficient as determined by this formula.

In evaluating  $\kappa_\nu$  according to formula (III), we shall use for  $\Psi_d$  a wave function of form (3) and for  $\Psi_c$  a plane wave representation of the outgoing electron:

$$\Psi_c = \frac{1}{\sqrt{2\pi}} (e^{-r_1 + ikz_2} + e^{-r_2 + ikz_1}). \tag{15}$$

(In § 5 we refer to an improvement in  $\Psi_c$  which can be incorporated without much difficulty at this stage.) For  $\Psi_d$  and  $\Psi_c$  of forms (3) and (15) the evaluation of the matrix element

$$\int \Psi_d^* \left( \frac{z_1}{r_1^3} + \frac{z_2}{r_2^3} \right) \Psi_c d\tau \tag{16}$$

is straightforward, though it is somewhat involved. We find

$$\int \Psi_d^* \left( \frac{z_1}{r_1^3} + \frac{z_2}{r_2^3} \right) \Psi_c d\tau = - (2048\pi^3)^{1/2} \frac{\mathcal{N}}{(1+a)^3} \frac{i}{k^2} \left[ \sum_{j=-2}^6 l_j \mathcal{L}_j^{(\alpha)} + \sum_{j=-2}^3 \lambda_j \mathcal{L}_j^{(1+2\alpha)} - \frac{1}{3} \beta (1+a)^4 \left\{ \sum_{j=-1}^3 a_j S_j^{(1+2\alpha)} + \sum_{j=-1}^3 b_j C_j^{(1+2\alpha)} \right\} \right], \quad (17)$$

where we have used the following abbreviations:

$$\mathcal{L}_j^{(p)} = \int_0^\infty e^{-py} \left( k \cos ky - \frac{\sin ky}{y} \right) y^j dy \quad (j = -2, -1, \dots),$$

$$= (j-1)! \rho^j \{ j \rho k \cos [(j+1)\xi] - \sin j\xi \} \quad (j \geq 1),$$

$$= \rho k \cos \xi - \xi \quad (j = 0),$$

$$= p\xi - k \quad (j = -1),$$

$$= \frac{1}{2} \left( pk - \frac{\xi}{\rho^2} \right) \quad (j = -2).$$

$$S_j^{(p)} = \int_0^\infty e^{-py} y^j \sin ky dy \quad (j = -1, 0, \dots),$$

$$= j! \rho^{j+1} \sin [(j+1)\xi] \quad (j = 0, 1, \dots),$$

$$= \xi \quad (j = -1).$$

and

$$C_j^{(p)} = \int_0^\infty e^{-py} y^j \cos ky dy = j! \rho^{j+1} \cos [(j+1)\xi] \quad (j = 0, 1, \dots),$$

$$= \int_0^\infty e^{-py} (e^{ay} - \cos ky) \frac{dy}{y} = \log \left( \frac{p}{p-a} |\sec \xi| \right) \quad (j = -1).$$

where

$$\rho = \frac{1}{(k^2 + p^2)^{1/2}} \quad \text{and} \quad \xi = \tan^{-1} \frac{k}{p}; \quad (21)$$

and

$$l_{-2} = 4q^2\beta,$$

$$l_{-1} = 1 + q \left( \frac{1}{3}\beta + \delta \right) + 12q^2(\gamma + \epsilon + \zeta) + 360q^4(\chi_6 + \chi_9) + 20,160q^6(\chi_7 + \chi_8 + \chi_{10}),$$

$$l_0 = (\delta + \beta) - 6q(\gamma - \epsilon) - 120q^3(2\chi_6 + \chi_9) - 5040q^5(3\chi_7 + 2\chi_8 + \chi_{10}),$$

$$l_1 = -\frac{\beta}{6q} + (\gamma + \epsilon + \zeta) + 24q^2(3\chi_6 + \chi_9) + 120q^4(45\chi_7 + 21\chi_8 + 13\chi_{10}),$$

$$l_2 = -\frac{\zeta}{3q} - 4q(3\chi_6 + 2\chi_9) - 40q^3(30\chi_7 + 13\chi_8 + 12\chi_{10}),$$

$$l_3 = (\chi_6 + \frac{7}{3}\chi_9) + 4q^2(45\chi_7 + 29\chi_8 + 21\chi_{10}),$$

$$l_4 = -\frac{\chi_9}{3q} - 2q(9\chi_7 + 12\chi_8 + 7\chi_{10}),$$

$$l_5 = \chi_7 + \frac{11}{3}(\chi_8 + \chi_{10}),$$

$$l_6 = -\frac{1}{3q}(\chi_8 + 2\chi_{10}).$$

$$\left. \begin{aligned} \lambda_{-2} &= -4\beta q^2; & \lambda_1 &= \frac{\beta}{15q}, \\ \lambda_{-1} &= -\frac{6}{5}\beta q; & \lambda_2 &= -\frac{\beta}{30q^2}, \\ \lambda_0 &= -\frac{1}{5}\beta; & \lambda_3 &= \frac{\beta}{30q^3}, \end{aligned} \right\} \quad (23)$$

where

$$q = \frac{1}{1+a}; \quad (24)$$

and

$$\left. \begin{aligned} a_{-1} &= 6\eta^4 [4\eta k^2 (5a^4 - 10a^2k^2 + k^4) + (a^4 - 6a^2k^2 + k^4)], \\ a_0 &= 6\eta^3 a [16\eta k^2 (a^2 - k^2) + (a^2 - 3k^2)], \\ a_1 &= 3\eta^2 [4\eta k^2 (3a^2 - k^2) + (a^2 - k^2)], \\ a_2 &= \eta a (8\eta k^2 + 1), \\ a_3 &= \eta k^2, \end{aligned} \right\} \quad (25)$$

$$\left. \begin{aligned} b_{-1} &= +24\eta^4 a k [\eta (a^4 - 10a^2k^2 + 5k^4) - (a^2 - k^2)], \\ b_0 &= -6\eta^3 k [4\eta (a^4 - 6a^2k^2 + k^4) - (3a^2 - k^2)], \\ b_1 &= -6\eta^2 a k [2\eta (a^2 - 3k^2) - 1], \\ b_2 &= -\eta k [4\eta (a^2 - k^2) - 1], \\ b_3 &= -\eta a k. \end{aligned} \right\} \quad (26)$$

where

$$\eta = (a^2 + k^2)^{-1}. \quad (27)$$

Putting  $\chi_6 = \chi_7 = \dots = \chi_{10} = 0$  in the foregoing equations, we shall obtain the formulae which can be used with a wave function of form (2).

By using for the constants of wave functions (2) and (3) the values determined by Williamson and Henrich, the atomic absorption coefficient  $\kappa_\nu$  has been computed according to the foregoing formulae for various wave lengths. The results of the calculations are given in Table 1 and are further illustrated in Figure 2. It is seen that, in contrast to what happened when formula (I) was used (cf. Fig. 1), wave function (2) now predicts systematically *larger* values for  $\kappa_\nu$  than does wave function (3). The divergence between the two curves must now be attributed to the overweighting of the wave function near the origin, where it is again poorly determined by the Ritz method.

4. *The continuous absorption coefficient of H<sup>-</sup> evaluated according to formula (II).*— Finally, returning to formula (II), which would appear to have the best chances for determining  $\kappa_\nu$  most reliably, the calculations were again carried through for wave functions  $\Psi_d$  of forms (2) and (3) and for  $\Psi_c$  of form (15). Before we give the results of the calculations, we may note that for  $\Psi_d$  of form (3) and for  $\Psi_c$  of form (15)

$$\left. \begin{aligned} \int \Psi_d^* \left( \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) \Psi_c d\tau &= - (2048\pi^3)^{1/2} \frac{\mathfrak{N}}{(1+a)^3} \frac{i}{k^2} \left[ \sum_{j=-1}^6 l_j \mathcal{L}_j^{(a)} \right. \\ &\quad \left. + \sum_{j=-1}^{+1} \lambda_j \mathcal{L}_j^{(1+2a)} + k^2 \left\{ \sum_{j=0}^7 s_j S_j^{(a)} + \sum_{j=0}^{+1} \sigma_j S_j^{(1+2a)} \right\} \right], \end{aligned} \right\} \quad (28)$$

TABLE 1  
 THE CONTINUOUS ABSORPTION COEFFICIENT OF  $H^-$  COMPUTED  
 ACCORDING TO FORMULA III AND WITH WAVE FUNCTIONS  
 OF FORMS (2) AND (3)

$\lambda$ (Å)	$\kappa_\lambda \times 10^{17} \text{ cm}^2$		$\lambda$ (Å)	$\kappa_\lambda \times 10^{17} \text{ cm}^2$	
	With Wave Function (3)	With Wave Function (2)		With Wave Function (3)	With Wave Function (2)
1000.....	0.225	0.241	7000.....	5.173	6.732
2000.....	0.955	1.010	7500.....	5.225	7.070
2500.....	1.459	1.538	8000.....	5.204	7.333
3000.....	2.010	2.125	8500.....	5.106	7.496
3500.....	2.580	2.752	9000.....	4.946	7.567
4000.....	3.139	3.400	9500.....	4.724	7.536
4500.....	3.657	4.046	10000.....	4.453	7.411
5000.....	4.118	4.676	12000.....	3.031	5.952
5500.....	4.505	5.271	14000.....	1.407	3.355
6000.....	4.812	5.820	16000.....	0.149	0.401
6500.....	5.036	6.310			

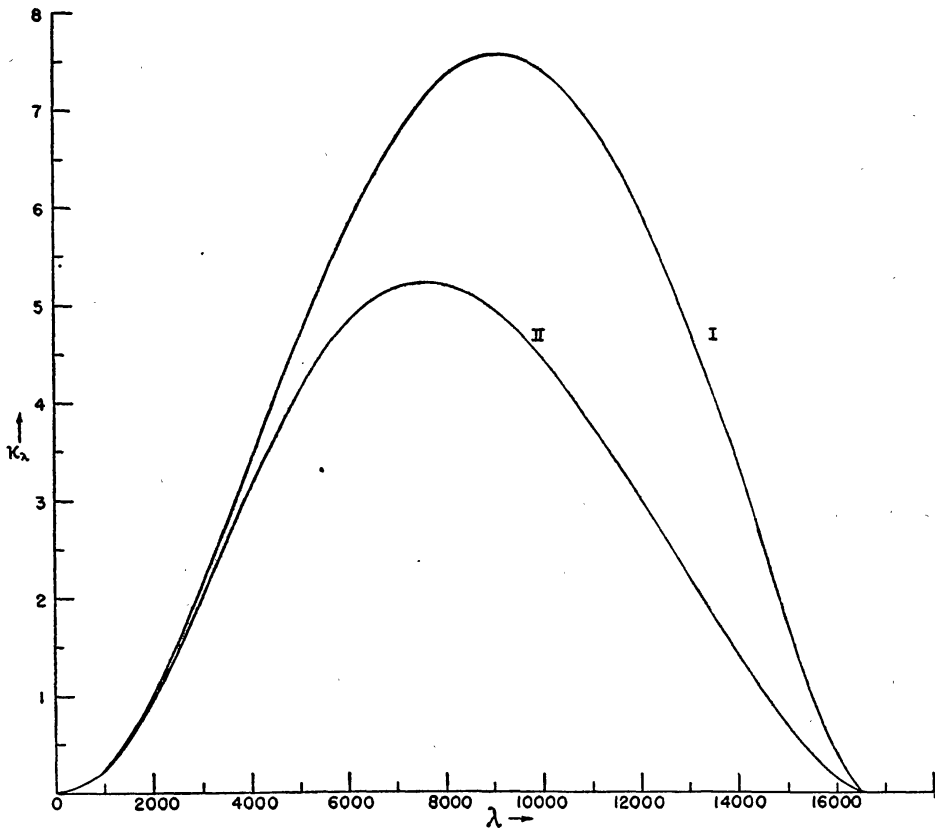


FIG. 2.—A comparison of the continuous absorption coefficient of  $H^-$  computed according to formula (III) and with wave functions of forms (2) (curve I) and (3) (curve II). The ordinates denote the absorption coefficients in units of  $10^{-17} \text{ cm}^2$ ; the abscissae, the wave length in angstroms.

where

$$\left. \begin{aligned} l_{-1} &= 4\beta q^3; & l_0 &= 0; & l_1 &= -\beta q. \\ l_2 &= -2q\zeta - 40q^3\chi_9 - 1680q^5(\chi_8 + 2\chi_{10}). \\ l_3 &= 16q^2\chi_9 + 960q^4(\chi_8 + \chi_{10}), \\ l_4 &= -2q\chi_9 - 80q^3(3\chi_8 + 2\chi_{10}). \\ l_5 &= 32q^2(\chi_8 + \chi_{10}); & l_6 &= -2q(\chi_8 + 2\chi_{10}), \end{aligned} \right\} \quad (29)$$

$$\lambda_{-1} = -4\beta q^3; \quad \lambda_0 = -4\beta q^2; \quad \lambda_1 = -\beta q, \quad (30)$$

$$\left. \begin{aligned} s_0 &= 4\beta q^2, \\ s_1 &= 1 + 3q\delta + 12q^2(\gamma + \epsilon + \zeta) + 360q^4(\chi_6 + \chi_9) + 20,160q^6(\chi_7 + \chi_8 + \chi_{10}), \\ s_2 &= (\delta + \beta) - 6q(\gamma - \epsilon) - 120q^2(2\chi_6 + \chi_9) - 5040q^5(3\chi_7 + 2\chi_8 + \chi_{10}), \\ s_3 &= (\gamma + \epsilon + \zeta) + 24q^2(3\chi_6 + \chi_9) + 120q^4(45\chi_7 + 21\chi_8 + 13\chi_{10}), \\ s_4 &= -6q(2\chi_6 + \chi_9) - 80q^3(15\chi_7 + 6\chi_8 + 5\chi_{10}), \\ s_5 &= (\chi_6 + \chi_9) + 4q^2(45\chi_7 + 21\chi_8 + 13\chi_{10}), \\ s_6 &= -6q(3\chi_7 + 2\chi_8 + \chi_{10}), \\ s_7 &= \chi_7 + \chi_8 + \chi_{10} \end{aligned} \right\} \quad (31)$$

and

$$\sigma_0 = -4\beta q^2; \quad \sigma_1 = -\beta q. \quad (32)$$

Further, in equation (28) the quantities  $\mathcal{L}_j^{(p)}$ ,  $S_j^{(p)}$ , and  $q$  have the same meanings as in equations (18), (19), (21), and (24).

TABLE 2  
THE CONTINUOUS ABSORPTION COEFFICIENT OF H<sup>-</sup> COMPUTED  
ACCORDING TO FORMULA II AND WITH WAVE FUNCTIONS  
OF FORMS (2) AND (3)

$\lambda$ (Å)	$\kappa_\lambda \times 10^{17} \text{ cm}^2$		$\lambda$ (Å)	$\kappa_\lambda \times 10^{17} \text{ cm}^2$	
	With Wave Function (3)	With Wave Function (2)		With Wave Function (3)	With Wave Function (2)
1000.....	0.271	0.270	7000.....	4.174	4.113
2000.....	0.945	0.991	7500.....	4.296	4.080
2500.....	1.335	1.461	8000.....	4.363	3.993
3000.....	1.730	1.955	8500.....	4.372	3.858
3500.....	2.119	2.437	9000.....	4.324	3.682
4000.....	2.498	2.880	9500.....	4.221	3.471
4500.....	2.860	3.265	10000.....	4.065	3.233
5000.....	3.197	3.581	12000.....	2.995	2.108
5500.....	3.504	3.822	14000.....	1.502	0.954
6000.....	3.773	3.989	16000.....	0.167	0.097
6500.....	3.998	4.084			

The absorption cross-sections, as calculated according to formula (II), and the foregoing equations are given in Table 2 and further illustrated in Figure 3. It is seen that, as anticipated, the two curves now do not diverge more than can be reasonably attributed to the betterment of the wave function in consequence of the increased number of parameters used in the Ritz method.

5. *Concluding remarks.*—A comparison of Figures 1, 2, and 3 clearly illustrates the superiority of formula (II) for the purposes of evaluating the continuous absorption coefficient of the negative hydrogen ion. The general reliability of the absorption cross

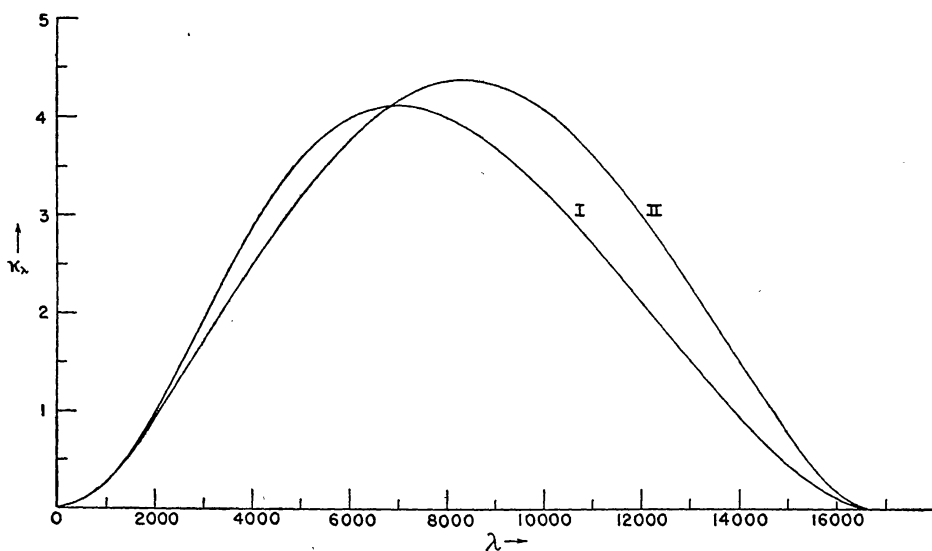


FIG. 3.—A comparison of the continuous absorption coefficient of  $H^-$  computed according to formul (II) and with wave functions of forms (2) (curve I) and (3) (curve II). The ordinates denote the absorption coefficients in units of  $10^{-17}$  cm<sup>2</sup>; the abscissae, the wave length in angstroms.

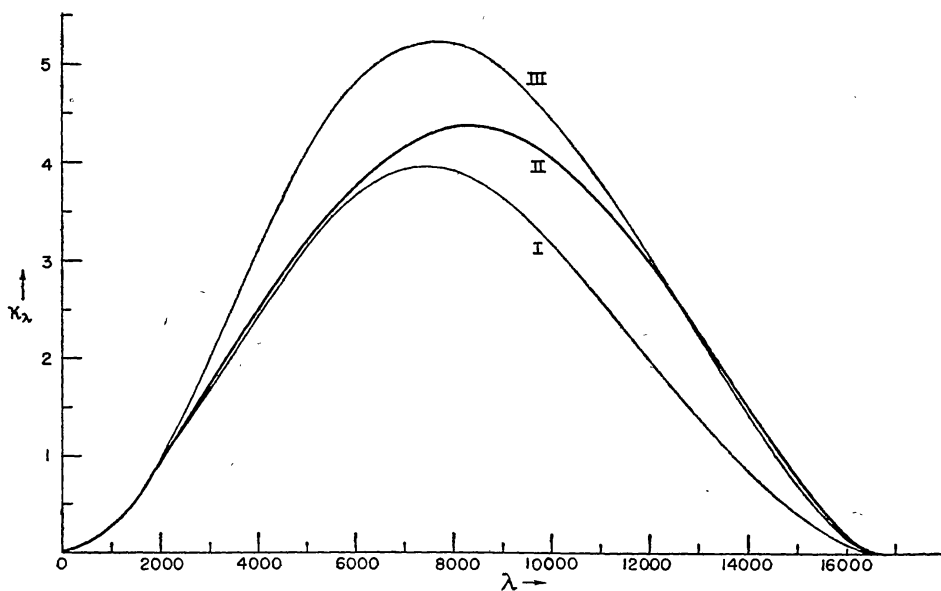


FIG. 4.—A comparison of the continuous absorption coefficient of  $H^-$  computed according to formul (I) (curve I), (II) (curve II), and (III) (curve III) with a wave function of form (3). The ordinates denote the absorption coefficients in units of  $10^{-17}$  cm<sup>2</sup>; the abscissae, the wave length in angstroms.

sections derived on the basis of formula (II) and wave function (3) can be seen in a other way. In Figure 4 we have plotted  $\kappa_{\lambda}$  as given by the three formulae and as obtain in each case with wave function (3). It is seen that, while the cross-sections given by formula (II) agree with those given by formula (I) in the visual and the violet part of t



spectrum ( $\lambda < 6000 \text{ \AA}$ ), they agree with those given by formula (III) in the infrared ( $\lambda > 12,000 \text{ \AA}$ ). This is readily understood when it is remembered that on all the three formulae the absorption cross-sections in the infrared are relatively more dependent on the wave function at large distances than they are in the visual and the violet parts of the spectrum. Accordingly, it is to be expected that, as we approach the absorption limit of  $H^-$  at  $16,550 \text{ \AA}$ , formula (III) must give less unreliable values than it does at shorter wave lengths; formula (I), of course, ceases to be valid in the infrared. It is also clear that, as we go toward the violet, we have the converse situation.

Summarizing our conclusions so far, it may be said that in the framework of the approximation in which a plane-wave representation of the outgoing electron is used, formula (II), together with wave function (3), gives sufficiently reliable values for the absorption coefficient over the entire range of the spectrum. Attention may be particularly drawn to the fact that the maximum of the absorption-curve is now placed at  $8500 \text{ \AA}$ , where  $\kappa_\lambda = 4.37 \times 10^{-17} \text{ cm}^2$ .

The question still remains as to the improvements which can be effected in the choice of  $\Psi_c$ . As shown in an earlier paper,<sup>4</sup> it may be sufficient to use for  $\Psi_c$  the wave functions in the Hartree field of a hydrogen atom. On this approximation we should use (*op. cit.*, eq. [15])

$$\Psi_c = \frac{1}{\sqrt{2\pi}} \left\{ e^{-r_1} \sum_{l=0}^{\infty} \frac{i^l}{k r_2} (2l+1) P_l(\cos \vartheta_2) \chi_l(r_2; k) + e^{-r_2} \sum_{l=0}^{\infty} \frac{i^l}{k r_1} (2l+1) P_l(\cos \vartheta_1) \chi_l(r_1; k) \right\}, \quad (33)$$

where  $\chi_l$  is the solution of the equation

$$\frac{d^2 \chi_l}{dr^2} + \left\{ k^2 - \frac{l(l+1)}{r^2} + 2 \left( 1 + \frac{1}{r} \right) e^{-2r} \right\} \chi_l = 0, \quad (34)$$

which tends to a pure sinusoidal wave of unit amplitude at infinity. We shall return to these further improvements in a later paper.

It is a pleasure to acknowledge my indebtedness to Professor E. P. Wigner for many helpful discussions and much valuable advice. My thanks are also due to Mrs. Frances Herman Breen for assistance with the numerical work.

<sup>4</sup> *A. J.*, 100, 176, 1944.

1945ApJ...102...223C