ON THE CONTINUOUS ABSORPTION COEFFICIENT OF
THE NEGATIVE HYDROGEN ION. IV

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ABSTRACT

The photoionization cross-sections of the negative ion of hydrogen are revised by making use of
Hart and Herzberg's 20-parameter wave function for the ground state. The improvements over the
earlier calculations based on Henrich's 11-parameter wave function are not very great.

I. INTRODUCTION AND RESULTS

During the early and the middle 1940's the writer and his associates (Williamson
1942; Chandrasekhar and Krogdahl 1943; Henrich 1944a, b; Chandrasekhar 1944a, b,
1945a, b, 1947; Chandrasekhar and Breen 1946; for brief accounts of these investiga-
tions from the point of view of atomic physics see Massey 1950, pp. 36–39, and Bethe
and Salpeter 1957, pp. 151, 155, 252, 316–318) spent considerable time and effort on the
determination of the continuous absorption coefficient of the negative hydrogen ion.
The results of these calculations have since become incorporated in the developments
in the theory of stellar atmospheres which have taken place in the intervening decade
(see Unsöld 1955, p. 165, and Sec. 48, pp. 174–176); and they have further received
strong confirmation in laboratory experiments (Lochte-Holtegreven 1951; Smith and
Branscomb 1955a, b).

A re-examination of the photoionization cross-sections for H− (Chandrasekhar 1945a,
b; these papers will be referred to hereafter as “Paper I” and “Paper II,” respectively)
which are currently in use was suggested by the recent advances relative to the ground-
state energies and wave functions of two-electron systems. These advances followed on
the realization that, to attain spectroscopic precision in the theoretically predicted
values for the ground-state energies, one must include a very large number of parameters
in the basic variational calculations. This was a reversal of the views previously held;
and it came about when it was pointed out (Chandrasekhar, Elbert, and Herzberg 1953)
that the results of Hylleraas’ calculations on an 8-parameter wave function for the
ground state of helium (on the basis of which the earlier contrary view had been held)
were unfortunately vitiated by an error. Once this was realized, results of calculations
with increasing numbers of variational parameters quickly followed: Chandrasekhar,
Elbert, and Herzberg (1953) with 10 parameters; Chandrasekhar and Herzberg (1955)
with 18 parameters; Hart and Herzberg (1957) with 20 parameters; Hylleraas and
Midtal (1956) with 24 parameters; and, finally, Kinoshita (1957) with 39 parameters.1
The bearing of these advances on the problem of the photoionization cross-sections of
H− is the following:

The sensitiveness of the computed cross-sections on the accuracy of variationally
determined wave functions for the ground state of H− is well known (Chandrasekhar

1 It was supposed for some time that Hylleraas and Midtal (1956), by their judicious selection of
their 24 parameters, had actually succeeded in obtaining an energy value lower than even Kinoshita
with 39 parameters. However, by repeating the calculations with the same 24 parameters, Herzberg dis-
covered that Hylleraas and Midtal's calculation was in error; that the correct values are only very slightly
different from what Hart and Herzberg had derived from a 20-parameter wave function; and that
Kinoshita's value is, indeed, the best. These facts have since been confirmed by Hylleraas and Midtal
(1958).
1944a, b; in this connection see also Geltman 1956). This had been taken into account in the earlier calculations by evaluating the required cross-sections not only in terms of the matrix elements of the dipole length but also in terms of the matrix elements of the dipole velocity and dipole acceleration (which weight different parts of the wave function differently) and comparing them. Nevertheless, in view of the central role which the continuous absorption coefficient of H− plays in the theory of stellar atmospheres, it appeared worthwhile to repeat the 1945 calculations with the most accurate wave function now available for the ground state of H−, namely, Hart and Herzberg’s 20-parameter wave function. The results of the present calculations are given in Table 1 and illustrated in Figure 1; comparisons with the results of the earlier calculations are made in Figures 2 and 3.

### Table 1

Continuous Absorption Coefficient of Negative Hydrogen Ion Computed According to Dipole-Length and Dipole-Velocity Formulae Using Hart and Herzberg’s 20-Parameter Wave Function for Ground State

<table>
<thead>
<tr>
<th>λ (A)</th>
<th>( \kappa_\lambda \times 10^{17} ) Cm(^{-2}) from Dipole-Length Formula</th>
<th>( \kappa_\lambda \times 10^{17} ) Cm(^{-2}) from Dipole-Velocity Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0.07522</td>
<td>0.06315</td>
</tr>
<tr>
<td>1000</td>
<td>0.2945</td>
<td>0.1747</td>
</tr>
<tr>
<td>1500</td>
<td>0.5761</td>
<td>0.5902</td>
</tr>
<tr>
<td>2000</td>
<td>0.8888</td>
<td>0.9463</td>
</tr>
<tr>
<td>2500</td>
<td>1.251</td>
<td>1.324</td>
</tr>
<tr>
<td>3000</td>
<td>1.666</td>
<td>1.713</td>
</tr>
<tr>
<td>3500</td>
<td>2.115</td>
<td>2.106</td>
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<tr>
<td>4000</td>
<td>2.567</td>
<td>2.495</td>
</tr>
<tr>
<td>4500</td>
<td>2.989</td>
<td>2.870</td>
</tr>
<tr>
<td>5000</td>
<td>3.352</td>
<td>3.220</td>
</tr>
<tr>
<td>5500</td>
<td>3.638</td>
<td>3.335</td>
</tr>
<tr>
<td>6000</td>
<td>3.838</td>
<td>3.807</td>
</tr>
<tr>
<td>6500</td>
<td>3.950</td>
<td>4.028</td>
</tr>
<tr>
<td>7000</td>
<td>3.977</td>
<td>4.193</td>
</tr>
<tr>
<td>7500</td>
<td>3.927</td>
<td>4.300</td>
</tr>
<tr>
<td>8000</td>
<td>3.810</td>
<td>4.346</td>
</tr>
<tr>
<td>8500</td>
<td>3.638</td>
<td>4.334</td>
</tr>
</tbody>
</table>

#### II. BASIC FORMULAE

The necessary formulae from atomic physics are given in Paper I, equations (11)–(14). Revising the numerical coefficients in them in accordance with the most recent values of the fundamental physical constants (Cohen and DuMond 1958), we have

\[
\kappa_\nu = 6.8113 \times 10^{-20} k \left( k^2 + 2I \right) \int \Psi^* \left( z_1 \right) \Psi \, d\tau \quad \text{cm}^2
\]

and

\[
\kappa_\nu = 2.7245 \times 10^{-19} \frac{k}{k^2 + 2I} \int \Psi^* \left( \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) \Psi \, d\tau \quad \text{cm}^2,
\]

where \( \kappa_\nu \) is the atomic absorption coefficient for radiation of frequency \( \nu \) in which an electron with a momentum \( k \) (in atomic units) is ejected; \( I \) is the electron affinity, also measured in atomic units; \( \Psi \) are the wave functions describing the ground
Fig. 1.—A comparison of the continuous absorption coefficient of $H^-$ computed on the basis of the dipole-length (curve 1) and the dipole-velocity (curve 2) formulae, using Hart and Herzberg's 20-parameter wave function for the ground state. The ordinates denote the absorption coefficients in units of $10^{-17}$ cm$^2$; the abscissae, the wave length in angstroms.

Fig. 2.—A comparison of the continuous absorption coefficient of $H^-$ computed on the basis of the dipole-length formula with Hart and Herzberg's 20-parameter wave function (curve 1) and Henrich's 11-parameter wave function (curve 2). The relatively close agreement between the two curves suggests that the improvement in the relevant parts of the wave function by going to 20 parameters is not very significant. The ordinates denote the absorption coefficients in units of $10^{-17}$ cm$^2$; the abscissae, the wave length in angstroms.
state of \( \text{H}^- \) and the continuum, respectively. Equations (1) and (2) are, respectively, the dipole-length and the dipole-velocity formulae; in these formulae the matrix elements are to be evaluated in atomic units.

The wavelength, \( \lambda \), of the incident radiation measured in thousand-angstrom units is given by

\[
\lambda \text{ (in 1000-A unit)} = \frac{0.9112671}{k^2 + 2I}. \tag{3}
\]

In evaluating \( \kappa \), in accordance with the foregoing formulae, we shall use for \( \Psi_d \) the

20-parameter wave function of Hart and Herzberg (1955); their wave function is of the form

\[
\Psi_d = \Re e^{-as/2} \left( 1 + \cos^2 + \cos^3 + \cos^4 + \cos^5 + \cos^6 + \cos^7 + \cos^8 + \cos^9 + \cos^{10} + \cos^{11} + \cos^{12} + \cos^{13} + \cos^{14} + \cos^{15} + \cos^{16} + \cos^{17} + \cos^{18} + \cos^{19} + \cos^{20} \right) \tag{4}
\]

where \( \Re \) is the normalization factor; \( a, c_1, c_2, \ldots, c_{19} \) are the twenty constants determined by the Ritz condition of minimum energy:

\[
s = r_1 + r_2, \quad t = r_1 - r_2, \quad \text{and} \quad u = r_{12}, \tag{5}
\]

where \( r_1, r_2, \) and \( r_{12} \) are the distances of the two electrons from the nucleus and from each other, respectively. For convenience, we give in Table 2 the values of the various constants as determined by Hart and Herzberg.
The energy for the ground state which Hart and Herzberg’s wave function gives is
\[ E = -0.5276446692 \text{ atomic unit}. \]  
(6)

This value should be contrasted with the values
\[ -0.527559 \quad \text{and} \quad -0.527717 \]  
(7)

obtained by Henrich (1944a) and Hylleraas and Midtal (1958) with 11 and 24 parameters, respectively. Hylleraas and Midtal have not published the coefficients of their wave function; moreover, since they have used fractional powers and logarithms of s, t, and u in their variational expansion, the evaluation of the cross-sections using their wave function would be excessively complicated. In any event, the improvement effected by going from Henrich’s 11-parameter wave function to Hart and Herzberg’s 20-parameter wave function is not sufficiently great to justify further efforts along these directions.

**TABLE 2**

VALUES OF COEFFICIENTS IN HART AND HERZBERG’S WAVE FUNCTION FOR GROUND STATE OF H⁻

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>c₀</td>
<td>1</td>
</tr>
<tr>
<td>c₁</td>
<td>+0 337294236</td>
</tr>
<tr>
<td>c₂</td>
<td>+0 080833954</td>
</tr>
<tr>
<td>c₃</td>
<td>-0 213129754</td>
</tr>
<tr>
<td>c₄</td>
<td>+0 020038545</td>
</tr>
<tr>
<td>c₅</td>
<td>-0 0287160073</td>
</tr>
<tr>
<td>c₆</td>
<td>-0 0154381194</td>
</tr>
<tr>
<td>c₇</td>
<td>-9 21896695×10⁻³</td>
</tr>
<tr>
<td>c₈</td>
<td>+4 32904670×10⁻³</td>
</tr>
<tr>
<td>c₉</td>
<td>+7 86976451×10⁻⁴</td>
</tr>
<tr>
<td>c₁₀</td>
<td>-1 77558678×10⁻⁴</td>
</tr>
<tr>
<td>c₁₁</td>
<td>-7 40841223×10⁻⁴</td>
</tr>
<tr>
<td>c₁₂</td>
<td>+1 63058368×10⁻⁵</td>
</tr>
<tr>
<td>c₁₃</td>
<td>-2 73106176×10⁻⁴</td>
</tr>
<tr>
<td>c₁₄</td>
<td>+6 27409440×10⁻⁴</td>
</tr>
<tr>
<td>c₁₅</td>
<td>-6 38293145×10⁻⁴</td>
</tr>
<tr>
<td>c₁₆</td>
<td>+6 84423133×10⁻⁴</td>
</tr>
<tr>
<td>c₁₇</td>
<td>+1 55857013×10⁻⁵</td>
</tr>
<tr>
<td>c₁₈</td>
<td>+6 48350632×10⁻⁴</td>
</tr>
<tr>
<td>c₁₉</td>
<td>+6 88602440×10⁻⁴</td>
</tr>
<tr>
<td>c₂₀</td>
<td>-6 38293145×10⁻⁴</td>
</tr>
</tbody>
</table>

Returning to equations (1) and (2), we shall use, for a plane-wave representation of the outgoing electron,
\[ \Psi_e = \frac{1}{\sqrt{(2\pi)}} \left( e^{−r₁+ikz₁} + e^{−r₂+ikz₂} \right). \]
(8)

In Section V we shall refer to an improvement in \( \Psi_e \) which we shall incorporate in a later paper.

**III. DIPOLE-LENGTH MATRIX ELEMENT**

For \( \Psi_d \) and \( \Psi_e \) of the forms given in Section II, we find, after some very lengthy calculations, that
\[ \int \Psi_d^* \left( z₁ + z₂ \right) \Psi_e d\tau = -i \left( 2048 \pi² \right) \frac{\eta q^2}{K^2} \left[ \sum_{j=-1}^8 \sum_{j=-1}^2 \lambda_j Q_j^{(a)} - \sum_{j=-1}^2 \lambda_j Q_j^{(1+2\alpha)} \right], \]
(9)
where

\[ q = \frac{1}{1 + \alpha} = 0.5970024; \]

\( \Omega_j^{(p)} \) are functions of \( k \) which are defined in Paper I, equation (18); and

\[ L_1 = 24q^4c_1 + 168q^6c_6 + 1344q^8c_8 + 576q^8c_8 + 28800q^8c_{14} \]
\[ + 51840q^8c_{16} + 12096q^8c_{18} \]
\[ = +0.54504286, \]
\[ L_0 = 24q^4c_6 - 336q^6c_7 - 10368q^8c_{16} - 1344q^8c_{18} \]
\[ = +0.166279695, \]
\[ L_1 = 24q^4c_7 - 72q^6c_8 - 5760q^8c_{14} - 3456q^8c_{15} - 168q^8c_{18} \]
\[ = -0.0676090978, \]
\[ L_2 = 1 + 12q^2c_2 + 3qc_3 + 12q^2c_4 + 4q^2c_5 + 120q^4c_9 + 60q^2c_{10} \]
\[ + 60q^2c_{11} - 6720q^4c_{12} - 120q^4c_{13} + 1008q^6c_{15} + 360q^4c_{16} \]
\[ + 360q^4c_{17} + 24q^4c_{18} + 360q^4c_{19} \]
\[ = +1.013384721, \]
\[ L_3 = c_1 - 6qc_2 + c_3 + 6qc_4 + 3qc_5 + 12q^2c_7 + 12q^2c_8 - 40q^2c_9 \]
\[ - 12q^2c_{10} + 36q^2c_{11} + 1680q^4c_{12} + 2880q^4c_{15} + 240q^4c_{17} \]
\[ + 60q^2c_{18} - 240q^2c_{19} \]
\[ = -0.179174932, \]
\[ L_4 = c_2 + c_4 + c_6 - 6qc_7 + 16q^2c_9 - 3qc_{10} + 9qc_{11} + 600q^4c_{12} \]
\[ + 24q^2c_{13} - 120q^2c_{15} - 24q^2c_{16} + 72q^2c_{17} - 12q^2c_{18} \]
\[ + 72q^2c_{19} \]
\[ = +0.109770777, \]
\[ L_5 = c_7 + c_8 - 6qc_9 + c_{10} + c_{11} - 240q^4c_{12} + 40q^2c_{14} + 24q^2c_{15} \]
\[ + 12qc_{17} - 3qc_{18} - 12qc_{19} \]
\[ = -1.67478325 \times 10^{-2}, \]
\[ L_6 = c_9 + 36q^2c_{12} + c_{13} - 6qc_{15} + c_{16} + c_{17} + c_{18} + c_{19} \]
\[ = +1.93154519 \times 10^{-3}, \]
\[ L_7 = -6qc_{12} + c_{14} + c_{15} \]
\[ = -6.33959945 \times 10^{-8}, \]
\[ L_8 = c_{12} \]
\[ = +1.63058368 \times 10^{-6}, \]
\[ \lambda_{-1} = 24q^4c_1 + 168q^6c_6 + 1344q^8c_7 + 576q^6c_8 + 28800q^8c_{14} + 51840q^8c_{16} + 12096q^8c_{18} \\
= +0.54504286 , \]

\[ \lambda_0 = 24q^4c_1 + 192q^6c_6 + 1008q^8c_7 + 576q^6c_8 + 28800q^8c_{14} + 41472q^8c_{16} + 10752q^8c_{18} \\
= +1.07924559 , \]

\[ \lambda_1 = 12q^6c_1 + 108q^8c_6 + 360q^6c_7 + 216q^6c_8 + 8640q^6c_{14} + 12096q^8c_{16} + 4536q^8c_{18} \\
= +0.97554017 , \]

\[ \lambda_2 = 2q^6c_1 + 32q^8c_6 + 40q^6c_7 + 24q^6c_8 + 720q^6c_{14} + 1008q^8c_{16} + 960q^8c_{18} \\
= +0.244827969 , \]

\[ \lambda_3 = 4q^6c_1 + 80q^8c_6 + 1008q^8c_{16} - 0.0258299591 . \]

Making use of equations (3) and (9), we find that equation (1) for \( \kappa_r \) becomes

\[ \kappa_r = \frac{9.1588}{\lambda k^3} \left| \sum \right| \times 10^{-19} \text{ cm}^2 , \quad (11) \]

where \( \lambda \) is the wave length in 1000-A units and \( \Sigma \) stands for the summations in brackets in equation (9). The results of the calculations based on the formulae of this section are given in Table 1.

IV. THE DIPOLE-VELOCITY MATRIX ELEMENT

We find:

\[ \int \Psi_d^* \left( \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) \Psi_c \, d\tau = -i \left( 2048 \pi^2 \right)^{1/2} \frac{9! q^3}{k^3} \left[ \sum_{j=1}^{2} (p_j + j s_{j+1} - a s_j) \psi_j^{(e)} \right. \\
- \left. \sum_{j=1}^{2} (\alpha_j + j s_{j+1} - \left[ 1 + 2a \right] s_j) \psi_j^{(1+2a)} \right] , \quad (12) \]

where

\[ p_{-1} = 4q^6c_1 + 24q^6c_6 + 168q^6c_7 + 72q^6c_8 + 2880q^7c_{14} + 5184q^7c_{16} \\
+ 1344q^7c_{18} \\
= +0.177188866 , \]

\[ p_0 = 4q^6c_6 - 48q^6c_7 - 1152q^6c_{16} - 168q^6c_{18} \\
= +0.0381409776 , \]
NEGATIVE HYDROGEN ION

\[ p_1 = - q c_1 - 4 q^2 c_6 - 16 q^3 c_7 - 24 q^3 c_8 - 1080 q^5 c_{14} - 936 q^6 c_{15} \]
\[ \quad - 144 q^7 c_{19} \]
\[ = -0.177920494 , \]

\[ p_2 = - 2 q c_6 - q c_6 + 8 q^2 c_7 - 40 q^3 c_9 - 3360 q^5 c_{12} - 80 q^6 c_{13} \]
\[ + 288 q^6 c_{15} + 24 q^7 c_{18} \]
\[ = +0.0157287428 , \]

\[ p_3 = - q c_7 - 3 q c_8 + 16 q^2 c_9 + 960 q^4 c_{12} - 180 q^5 c_{14} - 84 q^5 c_{15} \]
\[ + 4 q^7 c_{18} \]
\[ = +4.26191106 \times 10^{-3} , \]

\[ p_4 = - 2 q c_9 - 160 q^5 c_{12} - 4 q c_{13} + 24 q^6 c_{15} - q c_{18} \]
\[ = -1.27604161 \times 10^{-3} , \]

\[ p_5 = 32 q^2 c_{12} - 5 q c_{14} - 3 q c_{15} \]
\[ = +1.14187619 \times 10^{-4} , \]

\[ p_6 = -4 q c_{12} \]
\[ = -3.89384963 \times 10^{-6} , \]

\[ \omega_{-1} = 4 q^3 c_1 + 24 q^4 c_6 + 168 q^5 c_7 + 72 q^6 c_8 + 2880 q^7 c_{14} + 5184 q^7 c_{15} \]
\[ + 1344 q^7 c_{19} \]
\[ = +0.177188866 , \]

\[ \omega_0 = 4 q^3 c_1 + 28 q^4 c_6 + 120 q^4 c_7 + 72 q^4 c_8 + 2880 q^5 c_{14} + 4032 q^5 c_{15} \]
\[ + 1176 q^7 c_{18} \]
\[ = +0.334938544 , \]

\[ \omega_1 = q c_1 + 12 q^2 c_6 + 20 q^2 c_7 + 12 q^3 c_8 + 360 q^4 c_{14} + 504 q^5 c_{15} \]
\[ + 360 q^5 c_{18} \]
\[ = +0.134540148 , \]

\[ \omega_2 = 2 q c_6 + 40 q^3 c_{18} \]
\[ = -0.0129149795 , \]

\[ s_0 = 4 q^2 c_1 + 20 q^2 c_6 + 120 q^4 c_7 + 72 q^4 c_8 + 2880 q^5 c_{14} + 4032 q^5 c_{15} \]
\[ + 840 q^6 c_{18} \]
\[ = +0.344697028 , \]

\[ s_1 = 1 + 12 q^2 c_2 + 3 q c_3 + 12 q^2 c_4 + 12 q^2 c_5 + 4 q^3 c_6 - 40 q^3 c_7 \]
\[ + 360 q^4 c_9 + 60 q^5 c_{10} + 60 q^5 c_{11} + 20160 q^5 c_{12} + 360 q^6 c_{13} \]
\[ - 1008 q^6 c_{15} + 360 q^6 c_{16} + 360 q^6 c_{17} - 120 q^7 c_{18} + 360 q^7 c_{19} \]
\[ = +0.995185094 , \]

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Making use of the foregoing equations, we find that equation (2) for \( \kappa_\nu \) becomes

\[
\kappa_\nu = 4.41172 \frac{\lambda}{h^3} \left( \sum_{i=0}^{2} \right) \times 10^{-18} \text{ cm}^2, \tag{13}
\]

where \( \lambda \) is again the wave length in 1000-A units and

\[
\sum = \sum_{j=-1}^{7} L_j \mathcal{Q}_j^{(a)} + \sum_{j=-1}^{2} S_j \mathcal{Q}_j^{(1+2a)}, \tag{14}
\]
where

\[
L_{-1} = +0.167508162, \quad L_6 = -4.86841726 \times 10^{-5},
\]
\[
L_0 = +0.194541608, \quad L_7 = +1.10070118 \times 10^{-6},
\]
\[
L_1 = +1.043720208,
\]
\[
L_2 = -0.373116012, \quad S_{-1} = -0.167508162,
\]
\[
L_3 = +0.12353804, \quad S_0 = -0.475123656,
\]
\[
L_4 = -0.0179842718, \quad S_1 = -0.194553619,
\]
\[
L_5 = +1.5129296 \times 10^{-3}, \quad S_2 = +0.0174361284.
\]

The results of the calculations based on the formulae of this section are given in Table 1; for reasons which have been elaborated in the earlier papers, the present results derived from the dipole-velocity matrix elements are to be preferred to those derived from either the dipole-length or the dipole-acceleration matrix elements.

V. CONCLUDING REMARKS

From an examination of Figures 2 and 3 it would appear that no further improvement in the computed cross-sections are to be expected by going to wave functions for the ground state more accurate than Hart and Herzberg's. An improvement in the representation of the wave function for the continuum could, of course, be considered, though it is unlikely that it will bring any substantial changes. In any event, it is hoped to publish soon the results of calculations based on the Hartree wave functions for the free electron in the field of a neutral hydrogen atom.

In conclusion I wish to record my indebtedness to Miss Donna Elbert for carrying out all the numerical calculations based on the formulae of Sections III and IV; to Dr. W. H. Reid for carefully checking the formulae for the matrix elements; and most of all to Dr. G. Herzberg, to whom we owe, more than to anyone else, the current renewed interest in the two-electron systems.

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