ON THE CONTINUOUS ABSORPTION OF THE NEGATIVE HYDROGEN ION IN THE ULTRAVIOLET

BY

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Through recent work on the theory of stellar atmospheres [1, 2, 3, 4] it has become clear that the continuous absorption in atmospheres of the solar type is mainly due to the negative hydrogen ion, H^-.

Making use of Hylleraas'[5] calculation of the ionisation potential of the negative hydrogen ion, and of the the estimates of its continuous absorption by Jen[6], and by Massey and Smith[7], Wildt showed that H^- probably contributed most of the continuous absorption in the case of the solar atmosphere. After the astrophysical importance of H^- had been revealed by Wildt's discovery, Massey and Bates[8] carried out a much more accurate calculation of the continuous absorption coefficient of H^- as a function of the wave length. The results of this calculation were used by Wildt[2], and by B. Strömgren[3] in work on model solar atmospheres according to the revised concept of the mechanism of continuous absorption.

The continuous absorption coefficient of the negative hydrogen ion has hitherto been calculated only for transitions to states in which the neutral atom left by the electron is in the ground-state. The fact that the integrated f-sum for these transitions is considerably smaller than the theoretical value 2 indicates, however, that we have to consider other transition processes also, namely such which leave the atom in an excited or even ionised state. Transitions of this kind, having their absorption edges in the ultraviolet, have little influence on the value of the opacity

[1] R. Wildt, Ap. J. **89**, 295, 1939.
[2] R. Wildt, Ap. J. **90**, 611, 1939.
[3] B. Strömgren, Festschrift für Elis Strömgren, p. 218, 1940.
[4] P. ten Bruggencate, V. J. S. **75**, 203, 1940.
[5] E. Hylleraas, Zs. f. Phys. **60**, 624, 1930.
[6] C. K. Jen, Phys. Rev. **43**, 540, 1933.
[7] H. S. W. Massey and R. A. Smith, Proc. Roy. Soc. A **155**, 472, 1936.
[8] H. S. W. Massey and D. R. Bates, Ap. J. **91**, 202, 1940.

of the matter in the solar atmosphere, provided that there are
no important deviations from the black body curve of emission
in the far ultraviolet. But in atmospheres where the temperature
is higher and the electron pressure is great enough to balance
the ionisation of the negative ions due to the higher temperature,
this absorption which is partly placed in the spectral "window"
on the long wave length side of the Lyman continuum may have
some influence.

The aim of the present work has been the calculation of the
transition probabilities mentioned, to see if any of them were
large enough to be responsible for the theoretically expected
remainder of the total absorption.

The formulae used for the transition probabilities and the
equations determining the eigenfunctions (Fock's equations) have
been taken from D. R. HARTREE and W. HARTREE's work on
calcium[1]. The cases are analogous, as in both cases we have
to deal with two valence electrons.

In the final state of the transition considered we have to deal
with one s- and one p-electron (one of them bound and the other
free). We therefore get the following two simultaneous FOCK-
equations which correspond to HARTREE's equations for calcium
neglecting the interaction of the valence electrons with the inner,
closed shells (with n between 1 and 3). In HARTREE's notation
—with indices s and p only instead of $4s$ and $4p$—the two
equations are as follows:

$$\left[\frac{d^2}{dr^2} + \frac{2 - 2\,Y_0\,(p,p)}{r} - \varepsilon_s\right] \cdot P(s) - \frac{2}{3}\,\frac{Y_1\,(s,p)}{r} \cdot P(p) = 0;$$
$$\left[\frac{d^2}{dr^2} + \frac{2 - 2\,Y_0\,(s,s)}{r} - \varepsilon_p - \frac{2}{r^2}\right] \cdot P(p) - \frac{2}{3}\,\frac{Y_1\,(s,p)}{r} \cdot P(s) = 0. \tag{1}$$

The negative sign of the last term in the equations is due to
the fact that we are dealing with singlet states only. ε is the
energy of the electron with its sign reversed. It is measured in
units of the Rydberg-constant equal to the ionisation energy of

[1] D. R. HARTREE and W. HARTREE, Proc. Roy. Soc. A **164**, 167, 1938.

neutral hydrogen. (In the present work we have made no distinction between the Rydberg-constant for hydrogen and for infinite mass, the difference being wholly negligible in our calculations).

$$Y_k(a, b) = \int_{r_1=0}^{r_1=r} P(a) \cdot P(b) \cdot \left(\frac{r_1}{r}\right)^k dr_1 + \int_{r_1=r}^{r_1=\infty} P(a) \cdot P(b) \cdot \left(\frac{r}{r_1}\right)^{k+1} dr_1. \qquad (2)$$

In the case that one of the two electrons is free the above equation (1) for the other electron is reduced to the simple SCHRÖDINGER-equation for a neutral hydrogen atom. The equation for the free electron itself undergoes no similar reduction, as it is homogenous in the unknown eigenfunction so that all its terms are reduced in the same way when the state of the electron approaches the free state[1]. Instead of two simultaneous equations we get only one in which beside the required eigenfunction for the free electron we have the well-known hydrogen eigenfunction for the considered stationary state of the atom.

Between the two equivalent s-electrons in the negative ion there are no exchange forces in this approximation used by HARTREE. Its two identical s-functions may therefore be determined by the ordinary self consistent field-method. These eigenfunctions are used throughout the present work because HARTREE's formulae for the transition probabilities can be utilised directly for such eigenfunctions.

For the transition probability we use HARTREE's formula for the transition between the two lowest states of neutral calcium, this transition being exactly analogous to the transitions of the hydrogen ion here considered.

The formula for the transition probability A is[2]

$$A = 2.66 \cdot 10^8 \cdot \frac{1}{3} \cdot \left(\frac{\tilde{\nu}}{R}\right)^3 \cdot S,$$

where

$$S = 2 \cdot \left[\int_0^\infty P_A(s) \cdot P_B(s) \, dr\right]^2 \cdot \left[\int_0^\infty r \cdot P_A(s) \cdot P_B(p) \, dr\right]^2. \qquad (3)$$

[1] H. BETHE: Handbuch der Physik, Kap. 3, 350, 1933.
[2] D. R. HARTREE and W. HARTREE, Proc. Roy. Soc. A **164**, 167, 1938.

r is—as in the equations—measured in atomic units. The in-
dices A and B refer to the ion-state and the state with one
s- and one p-electron respectively. $\tilde{\nu}$ is the wave-number of the
absorbed radiation and R the Rydberg-constant. The number 3
in the denominator in the formula for A is the statistical weight
of the upper state, this being a singlet P-state.

Between A and the oscillator-strength of absorption f we
have LADENBURG's relation:

$$A = \frac{g}{g'} \cdot \frac{8 \pi^2 e^2}{3 mc^2} \cdot \nu^2 \cdot f = \frac{g}{g'} \cdot 3 \cdot \left(\frac{\tilde{\nu}}{R}\right)^2 \cdot f \cdot 2.66 \cdot 10^8 \sec^{-1}. \quad (4)$$

Here g' and g denote the statistical weights of the upper and
the lower state respectively.

In our case, when we have to deal with continuous upper
states, we are interested in $\dfrac{df}{dE}$, the oscillator strength per inter-
val of energy. The eigenfunctions for the free electrons must
then be normalised in such a way that their limiting amplitudes
are $\pi^{-\frac{1}{2}} \cdot E^{-\frac{1}{4}}$, where E is the energy of the electron[1]. The
formula for $\dfrac{df}{dE}$ is then the same as for f and is written:

$$\frac{df}{dE} = \frac{1}{3} \cdot \frac{\tilde{\nu}}{R} \cdot 2 \cdot \left[\int_0^\infty P_A(s) \cdot P_B(s)\, dr\right]^2 \cdot \left[\int_0^\infty r \cdot P_A(s) \cdot P_B(p)\, dr\right]^2, \quad (5)$$

where the eigenfunction of the free electron (being an s- or an
p-electron if the atom is in a P- or a S-state respectively) is
normalised in the way described above.

The energy of the absorbed radiation is the sum of the
ionisation energy of the ion, the exitation energy of the atom
and the energy of the free electron.

The absorption coefficient $\varkappa_\nu$ is $8.06 \cdot 10^{-18} \cdot \dfrac{df}{dE}$.[2] The transi-
tion probabilities for the transitions to the ground state of the
atom calculated in the way here described may be less accurate
than the corresponding probabilities as calculated by MASSEY
and BATES[3] because the latter authors used HYLLERAAS' better

[1] J. HARGREAVES, Proc. Cambridge Phil. Soc. **15**, 75, 1929.
[2] A. UNSÖLD: Physik der Sternatmosphären (35,1), 1938.
[3] H. S. W. MASSEY and D. R. BATES, Ap. J. **91**, 202, 1940.

approximation for the ion-eigenfunction. The degree of agreement between the two sets of results may, however, serve as an indication of the accuracy of those of our results, which cannot be compared with earlier calculations, in so far as the inaccuracy is due to the uncertainty of the ion-eigenfunction.

The eigenfunction for the negative hydrogen-ion was found by successive approximations, the Z_p-function used for an approximation being calculated by means of the preceding approximation. As a rule an eigenfunction intermediate between the two last approximations was used for the calculation of the new field function, and a corresponding average field function was used for the calculation of a new eigenfunction. In this way the oscillations in the functions from one approximation to the next were considerably damped. The eigenfunction as integrated from the origin was joined with an exponential function outside the range of the Coulomb field. The difference between the energy parameters in the inner and the outer part of the function was a measure of the error in the approximation. A new field function was not calculated until an energy parameter had been found, which made the eigenfunction satisfy the two boundary conditions simultaneously. The energy parameter—not to be confused with the ionisation potential of the ion—was in the final approximation found to be 0.093 Rydberg units.

The normalised eigenfunction P for one electron in the ion found in the way here described is given in Table I together with $r \cdot P$ and the corresponding $2 Z_p = 2 - 2 Y_0$. The last figure given has in most cases an uncertainty amounting to one or two units.

The eigenfunctions of the free electrons were calculated by means of successive approximations, the first being the solution of the equations without the exchange term. When one solution had been found, the exchange integrals were calculated and used for the next approximation, which could always be started as the solution without exchange sufficiently near the origin. The calculation was carried out by numerical integration. For the first integration—as for all the integrations of the ion-eigenfunctions—NUMEROV's method[1] could þe used since the

[1] B. NUMEROV: Méthode nouvelle de la détermination des orbites et le calcul des éphémérides en tenant compte des pertubations. Ch. II.

Table I.

r	P	$r \cdot P$	$2 Z_p$	r	P	$r \cdot P$
0.0	0.0000	0.000	2.000	10.0	0.0507	0.507
0.1	.1263	. .	1.863	10.5	436	.458
0.2	.2291	. .	1.730	11.0	374	.411
0.3	.3122	. .	1.601	11.5	321	.369
0.4	.3790	. .	1.481	12.0	276	.331
0.5	.4320	.216	1.365	12.5	237	.296
0.6	.4736	. .	1.257	13.0	203	.264
0.7	.5057	. .	1.157	13.5	175	.236
0.8	.5299	. .	1.066	14.0	150	.210
0.9	.5475	. .	0.980	14.5	129	.187
1.0	.5596	.560	0.902	15.0	110	.165
1.1	.5672	. .	0.829	15.5	95	.147
1.2	.5711	. .	0.763	16.0	81	.130
1.3	.5718	. .	0.701	16.5	70	.116
1.4	.5700	. .	0.645	17.0	60	.102
1.5	.5660	.849	0.592	17.5	52	91
1.6	.5604	. .	0.547	18.0	44	79
1.7	.5533	. .	0.502	18.5	38	70
1.8	.5452	. .	0.462	19.0	33	63
1.9	.5361	. .	0.427	19.5	28	55
2.0	.5263	1.053	0.392	20.0	24	48
				20.5	21	43
				21.0	18	38
2.0	0.5263	1.053	0.392	21.5	15	33
2.5	.4713	1.178	0.266	22.0	13	29
3.0	.4143	1.243	0.175	22.5	11	25
3.5	.3607	1.262	0.119	23.0	10	22
4.0	.3122	1.249	0.080	23.5	8	20
4.5	.2694	1.212	0.055	24.0	7	17
5.0	.2320	1.160	0.037	24.5	6	15
5.5	.1996	1.098	0.026	25.0	5	13
6.0	.1716	1.030	0.017	25.5	4	11
6.5	.1474	.958	0.012	26.0	4	10
7.0	.1266	.886	0.008	26.5	3	9
7.5	.1087	.815	0.005	27.0	3	8
8.0	934	.747	0.004	27.5	2	7
8.5	802	.682	0.002	28.0	2	6
9.0	688	.619	0.001	28.5	2	5
9.5	591	.561	. .	29.0	2	4
10.0	507	.507	. .	29.5	1	4
. .	. .	. .	. .	30.0	1	3

Table II.

State of Atom	Radial eigenfunction	$\dfrac{2\,Z_p}{r} = \dfrac{2 - 2\,Y_0}{r}$
$1\,S$	$2\,r \cdot e^{-r}$	$\left(2 + \dfrac{2}{r}\right) \cdot e^{-2r}$
$2\,S$	$\dfrac{1}{\sqrt{2}} \cdot r \cdot e^{-\frac{r}{2}} \left(1 - \dfrac{1}{2}r\right)$	$\left(\dfrac{r^2}{4} + \dfrac{r}{2} + \dfrac{3}{2} + \dfrac{2}{r}\right) \cdot e^{-r}$
$2\,P$	$\dfrac{1}{2\sqrt{6}} \cdot r^2 \cdot e^{-\frac{r}{2}}$	$\left(\dfrac{r^2}{12} + \dfrac{r}{2} + \dfrac{3}{2} + \dfrac{2}{r}\right) \cdot e^{-r}$
$3\,S$	$\dfrac{2}{3\sqrt{3}} \cdot r \cdot e^{-\frac{r}{3}} \left(1 - \dfrac{2}{3}r + \dfrac{2}{27}r^2\right)$	$\left(\dfrac{8}{2187}r^4 - \dfrac{8}{729}r^3 + \dfrac{8}{81}r^2 + \dfrac{8}{27}r + \dfrac{10}{9} + \dfrac{2}{r}\right) \cdot e^{-\frac{2r}{3}}$
$3\,P$	$\dfrac{8}{27\sqrt{6}} \cdot r^2 \cdot e^{-\frac{r}{3}} \left(1 - \dfrac{1}{6}r\right)$	$\left(\dfrac{4}{2187}r^4 + \dfrac{4}{729}r^3 + \dfrac{4}{81}r^2 + \dfrac{8}{27}r + \dfrac{10}{9} + \dfrac{2}{r}\right) \cdot e^{-\frac{2r}{3}}$

ratio of the second derivative of the eigenfunction to the function itself was here a function of r alone.

The normalised radial eigenfunctions of the neutral hydrogen atom and the corresponding potential functions $\dfrac{2\,Z_p}{r} = \dfrac{2 - 2\,Y_0}{r}$ are given in Table II for the states considered. The series expansions of the $\dfrac{2\,Z_p}{r}$-functions near the origin are $\dfrac{2}{r} - 2$, $\dfrac{2}{r} - \dfrac{1}{2}$, $\dfrac{2}{r} - \dfrac{2}{9}$ for the 1-, 2- and 3-states respectively. For the S-states the first neglected term is of the second, for the P-states of the fourth order in r. In the case considered by MASSEY and BATES with the atom in the $1\,S$-state they found that the total distortion of the eigenfunctions due to electrostatic and exchange forces was negligible. This result was confirmed by the examination of one function (with $E = \dfrac{1}{2}$), the total phase difference for $r \to \infty$ between the exact solution and the field-free solution amounting to 6 degrees only. The phase effect of the exchange forces was in this case nearly three times the effect of the electrostatic forces and of the opposite sign. Then the field-free solutions were exclusively used for the calculation of the absorption coefficients in this case, so that the whole difference

Table III.

Energy of the free electron	$\dfrac{df}{dE}$	$\varkappa_\nu$
0.04	1.96	$1.58 \cdot 10^{-17}$ cm²
0.09	2.82	2.28
0.1225	2.86	2.31
0.16	2.72	2.19
0.25	2.20	1.78
0.36	1.66	1.34
0.49	1.22	0.98
0.64	0.88	0.71
0.81	0.65	0.52
1.00	0.47	0.38

found between them and MASSEY and BATES' is due to our use of another eigenfunction for the ion.

The total absorption coefficient—being the sum of the coefficients belonging to the different allowed transitions—was calculated for the limiting frequency for the absorption edges. This frequency is 1.052 Rydberg units as the binding energy of the electron in the ion is taken to be 0.052 according to HYLLERAAS. This frequency is somewhat larger than the limiting frequency for the Lyman continuum and corresponds to a wave length of 867 Å. The energy of the free electron is then $\dfrac{1}{4}$ when the atom is in a 2-state and $\dfrac{1}{9}$ when it is in a 3-state. Further the transition probability was calculated for transitions to the 2-states only with energies of the free electron of $\dfrac{1}{2}$ and 1.

The eigenfunctions for the free electrons were calculated in higher approximations (2 or 3) in the two cases only, where the atom was in the 2 S- and the 2 P-state and the energy of the free electron was $\dfrac{1}{4}$. In the other cases the transition probability was so small, that a correction of it would have no interest. For the eigenfunctions of smaller energies (near the absorption limits) the exchange terms could not in a first approximation be regarded as small and the described method of successive approximations would be of little use.

Table IV.

Final state of the atom	$\left[\int_0^\infty P_A(s) \cdot P_B \cdot (s)\,dr\right]^2$	$\left[\int_0^\infty P_A(s) \cdot P_B(p) \cdot r\,dr\right]^2$		
		$\lambda = 867\ \text{Å}$	$\lambda = 700\ \text{Å}$	$\lambda = 506\ \text{Å}$
1 S	0.865	0.781	—	—
2 S	0.137	3.846	0.266	0.060
3 S	0.002	0.153	—	—

Final state of the atom	$\left[\int_0^\infty P_A(s) \cdot P_B(p) \cdot r\,dr\right]^2$	$\left[\int_0^\infty P_A(s) \cdot P_B(s) \cdot dr\right]^2$		
		$\lambda = 867\ \text{Å}$	$\lambda = 700\ \text{Å}$	$\lambda = 506\ \text{Å}$
2 P	9.175	0.264	0.023	0.004
3 P	0.066	0.038	—	—

The absorption coefficients for the transitions directly to the ground-state are given in Table III as a function of the energy of the free electron. The integrated f-sum is found to be 1.54 while for MASSEY and BATES' absorption coefficients it is found to be 1.50. The difference is unimportant, as the uncertainty due to the extrapolation of the $\frac{df}{dE}$-curves for the integration is of the same order of magnitude. The good agreement between the two values seems to indicate, that the total absorption is better determined than the shape of the $\frac{df}{dE}$-curve.

Table IV gives the squares of the product integrals

$$\int_0^\infty P_A(s) \cdot P_B(s) \cdot dr \quad \text{and} \quad \int_0^\infty r \cdot P_A(s) \cdot P_B(p)\,dr$$

and Table V the resulting absorption coefficients.

The integrated f-sum for the transitions to the 2-states is roughly about 0.6—0.7. The number of points on the curve is not quite sufficient to determine the run of the curve with certainty especially around its maximum near the Lyman limit. The probability for the transitions to the 3-states is seen to be

Table V.

Final state of the atom	$\lambda = 867 \, \overset{\bullet}{\text{Å}}$	$\lambda = 700 \, \text{Å}$	$\lambda = 506 \, \text{Å}$
1 S	$0.38 \cdot 10^{-17} \, \text{cm}^2$	—	—
2 S	0.30	0.02	0.01
3 S	0.00	—	—
2 P	1.37	0.15	0.04
3 P	0.00	—	—
Sum: 2.0_5			

The table gives $\varkappa_\nu$ as a function of wave length for different transitions.

negligible, so that we have probably found the whole of the theoretically expected absorption. The total f-sum is found to be 2.1—2.2. The agreement with the theoretical value of 2.0 has thus been considerably improved by taking the transitions covered by our calculations into account. The greatest part of the absorption due to transitions to the 2-states is seen to belong to the transition in which the final state of the atom is the 2 P-state.