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DETERMINATION OF CONTINUOUS  
ABSORPTION COEFFICIENTS IN  
THE SPECTRUM OF NA I

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In certain astrophysical problems it is of importance to know the continuous absorption coefficients of the metals. The metals contribute a part of the continuous absorption coefficients of the stellar atmospheres. Therefore, knowledge of the metal continuous absorption is essential in the theory of stellar atmospheres.<sup>1</sup> Further, these quantities are of importance for the determination of the state of ionisation of the interstellar matter.<sup>2</sup>

For some neutral alkali atoms the continuous absorption coefficients from the ground-states have been calculated according to the laws of quantum mechanics.<sup>3, 4, 5</sup> The results showed that, in all cases investigated, the continuous absorption is smaller than for hydrogen. Until now, however, continuous absorption coefficients have not been calculated for the excited states of any metal. It has been the aim of the present investigation to determine some of these absorption coefficients for sodium.

The continuous absorption coefficient corresponding to a so-called bound-free transition of the valence electron of an alkali atom is given by

<sup>1</sup> A. UNSÖLD: Ph. d. Sternatmosphären. Kap. VI.

<sup>2</sup> B. STRÖMGREN: *Astroph. Journ.* **89**, 526, 1939.

<sup>3</sup> B. TRUMPY: *Z. f. Ph.* **71**, 720, 1931.

<sup>4</sup> J. HARGREAVES: *Cambridge Phil. Soc.* **25**, 75, 1929.

<sup>5</sup> M. PHILLIPS: *Phys. Rev.* **39**, 905, 1932.

$$\kappa_{\nu} = \frac{\pi e^2}{mc} \cdot \frac{1}{Rc} \cdot \frac{df}{dE} = 8.02 \times 10^{-18} \cdot \frac{df}{dE}$$

where

$$\frac{df}{dE} = \sum \frac{1}{3} \cdot \frac{l''}{2l+1} \cdot \frac{\nu}{Rc} \cdot \left[ \int_0^{\infty} r R_1 R_2 dr \right]^2.$$

In these formulae

$l$  means the azimuthal quantum number of the valence electron in its bound state.

$l''$   $l$  or  $l+1$  according to the cases, where the quantum number of the free electron takes the values  $l-1$  or  $l+1$  respectively.

$\nu$  the frequency of the absorbed radiation.

$R$  the Rydberg wave-number.

$e, m, c$  have their usual meaning.

The functions  $R_1$  and  $R_2$  under the integral are radial eigenfunctions for the valence electron in the two states. They satisfy differential equations of the form:

$$\frac{d^2 R}{dr^2} = \left( -E - \frac{2Z_p}{r} + \frac{l(l+1)}{r^2} \right) \cdot R.$$

Here  $E$  means the energy of the state measured in units of  $\frac{2\pi^2 m e^4}{h^2}$ , the value of  $E$  at the series' limits being taken as zero. The unit of  $r$  is  $\frac{h^2}{4\pi^2 m e^2}$ .  $-\frac{2Z_p}{r}$  is the potential energy of an (negative) electron in the field of the nucleus.

The units are those used by TRUMPY.<sup>1</sup> The so-called "atomic" units correspond to these, with the exception that the atomic unit of energy is twice our unit. For a bound state  $-E$  is the term value divided by the Rydberg

<sup>1</sup> B. TRUMPY: Z. f. Ph. 71, 720, 1931.

constant. (The Rydberg constant for infinite mass is used throughout).

In the formula for  $\frac{df}{dE}$  the summation is extended over all transitions involving absorption of radiation of the same frequency. Therefore we will usually have to add two quantities corresponding to transitions of  $l$  to  $l-1$  and  $l+1$  respectively.

These formulae are not exact. FOCK<sup>1</sup> has been able to set up equations determining the radial eigenfunctions of an atom taking account of forces due to exchange of coordinates of the electrons in the atom, his  $Z_p$ -functions therefore differing from those of HARTREE's "self-consistent field" potentials. In these approximations the influence of the valence electron on the inner 10 electrons has been neglected, as has the influence of the non-spherical distribution of the electrons around the nucleus. Furthermore smaller quantities as e. g. relativistic (spin-) and retardation effects have been neglected.

FOCK and PETRASCHEN<sup>2</sup> have calculated the eigenfunctions of the electrons for the ground-state of Na II and the eigenfunctions of the valence electron for the two lowest  $s$ - and the two lowest  $p$ -states of Na I taking account of the exchange forces. In the calculation of the continuous absorption coefficients FOCK's eigenfunctions for the electron in the bound states have been used, as they were considered the best approximations available at present.

NUMEROV's<sup>3</sup> method has been used for the numerical integration of the differential equations for the free elec-

<sup>1</sup> V. FOCK: Z. f. Ph. **61**, 126, 1930.

<sup>2</sup> V. FOCK and M. J. PETRASCHEN: Ph. Z. d. Sowjetunion **6**, 368, 1934.

<sup>3</sup> B. NUMEROV: Méthode nouvelle de la détermination des orbites et le calcul des éphémérides en tenant compte des perturbations. Ch. II.

trons, this method being particularly well suited for integration with the aid of a calculating machine of differential equations of the form here considered. It can not be used for the integration of FOCK's equations in their exact form, and therefore the following procedure was adopted:

First, a potential field-function was constructed, which made the  $3d$ -state eigenfunction nearly satisfy the boundary conditions, when the spectroscopical value of  $E$  was used. The numerical values of the eigenfunction for  $r \infty 20$  were computed with the aid of the asymptotic series given in WHITTAKER and WATSON: "Modern Analysis".<sup>1</sup> This series gives correct values in the case of a Coulomb field. One of the boundary conditions was in this way automatically satisfied. As a first approximation to the  $Z_p$ -function TRUMPY's<sup>2</sup> field was used. This has been constructed in a similar way, TRUMPY having used only  $s$ - and  $p$ -functions, however. TRUMPY's field was left unchanged for small values of  $r$  ( $r < 0.5$ ). For larger values of  $r$  the new field bears more resemblance to PROKOFJEW's<sup>3</sup> field, as was to be expected, since PROKOFJEW used the  $3d$ -state also in determining his field.

MCDUGALL<sup>4</sup> has calculated the  $E$ -values for an atom using approximate eigenfunctions for the correction of the approximate eigenvalues for effects neglected in the first approximation. His final eigenvalues differed only slightly from the experimental ones. The corrections tended to zero for increasing term-numbers and increased the  $E$ -values

<sup>1</sup> E. T. WHITTAKER and G. N. WATSON: Modern Analysis. Kap. XVI, p. 337.

<sup>2</sup> B. TRUMPY: Z. f. Ph. **61**, 54, 1930.

<sup>3</sup> W. K. PROKOFJEW: Z. f. Ph. **58**, 255, 1929.

<sup>4</sup> MCDUGALL: Proc. Roy. Soc. **138**, 550, 1932.

numerically. Therefore our use of the experimental eigenvalues has certainly led to too high values of  $Z_p$ . The  $\kappa_\nu$ -values calculated are therefore probably somewhat too small.

The field determined as described above was thought to be a useful approximation in the case of  $d$ -states only, because the ratio of exchange forces to electrostatic forces is more dependent upon  $l$  than upon the value of  $E$ .

The calculations of the eigenfunctions for the free electrons were started with the aid of series, which were determined by an approximation of  $Z_p$  as a polynomial of the third degree in  $r$ . From 0.2 to 0.3 22 terms had to be retained in these series in order to obtain 6-figure accuracy.

The eigenfunctions for the bound electrons as calculated according to Fock's method are mutually orthogonal, when they have the same quantum number  $l$ . Therefore it was thought a better approximation to replace the calculated  $p$ -functions for the free electron by linear combinations of these and the "bound"  $p$ -functions. Because the latter were mutually orthogonal, the numerical coefficients in the linear combinations could be determined simultaneously.

The  $s$ -functions were not corrected. The reason was partly that the integrals of the products of the functions, which enter in the formula for  $\frac{df}{dE}$  for transitions from the  $p$ -states, do not as the corresponding integrals for the transitions from the ground-state and the  $4s$ -state contain nearly equal positive and negative parts, and partly that the part of the total absorption which is due to transitions to the  $s$ -states is small in comparison with the part due to transitions to the  $d$ -states. The  $d$ -functions, however, can not be corrected in a similar way, because no  $d$ -functions have been calculated according to Fock's method.

The eigenfunctions belonging to states with positive  $E$ -values have to be normalised in such a way, that the limiting amplitude for  $r \rightarrow \infty$  is  $\pi^{-1/2} E^{-1/4}$ .

The method here used has been indicated by Dr. B. STRÖMGREN. It is partly based upon a method due to JEFFREYS<sup>1</sup> for approximative solution of differential equations. It is easy to use and especially for  $E \rightarrow 0$  the method is very much simpler than the method formerly used.

We will write the differential equation in this way:

$$\frac{d^2 R}{dr^2} + \lambda \cdot R = 0.$$

In the interval concerned  $\lambda$  is positive.

If a solution of the equation is written in the form:

$$R = f \cdot \sin \varphi,$$

where  $f$  and  $\varphi$  are functions of  $r$ , then we must have:

$$\sin \varphi \left[ \frac{d^2 f}{dr^2} - f \left( \frac{d\varphi}{dr} \right)^2 + \lambda \cdot f \right] + \cos \varphi \left[ 2 \frac{df}{dr} \cdot \frac{d\varphi}{dr} + f \frac{d^2 \varphi}{dr^2} \right] = 0.$$

This equation is satisfied for all values of  $\varphi$  if we put the coefficients of  $\sin \varphi$  and  $\cos \varphi$  equal to zero separately. If  $\frac{d\varphi}{dr}$  is denoted by  $z$ , one of the two new equations can be written as follows:

$$2 \frac{df}{dr} \cdot z + f \frac{dz}{dr} = 0$$

with the solution  $f^2 \cdot z = c$ , where  $c$  is an arbitrary constant.

If we use this to eliminate  $f$  from the other equation, we find:

<sup>1</sup> H. JEFFREYS: Proc. London Math. Soc. (2) 23, 428, 1925.



$$z^2 = \lambda + \frac{1}{z^{-1/2}} \cdot \frac{d^2(z^{-1/2})}{dr^2},$$

where  $c$  has disappeared.

If the last term is neglected, we have JEFFREYS's approximation:  $z^2 = \lambda$ .

In our case the solution for great values of  $r$  can easily be found by iteration, the first  $\frac{1}{z^{-1/2}} \cdot \frac{d^2(z^{-1/2})}{dr^2}$  being calculated from JEFFREYS's approximation.

When  $r \infty 20-30$  this second approximation needs no further correction.

When  $z$  is found in this way from the known function  $\lambda$ ,  $\varphi_2 - \varphi_1 = \int_{r_1}^{r_2} \frac{d\varphi}{dr} dr = \int_{r_1}^{r_2} z dr$  is calculated numerically.

The eigenfunction found by the numerical integration starting from the origin can be written as

$$C \cdot z^{-1/2} \sin \varphi$$

the arbitrary constant  $c^{1/2}$ , which determines the ratio of  $f$  to  $z^{-1/2}$  forming a part of  $C$ .

As the limit of  $\lambda$  for  $r \rightarrow \infty$  is  $E$ , the limit of  $z^{-1/2}$  is  $E^{-1/4}$ . The limiting amplitude of the eigenfunction is  $C \cdot E^{-1/4}$ . Therefore, normalising the eigenfunction means dividing it by  $\pi^{1/2} \cdot C$ , or dividing the square of the integral, which determines  $\kappa_v$ , by  $\pi C^2$ . This process is analogous to the normalisation process for the eigenfunctions of the bound electrons.

$C$  can be found from the values in two points of the eigenfunction as calculated by numerical integration from the origin.

We have  $C \sin \varphi_1 = \frac{R_1}{z_1^{-1/2}}$  and  $C \sin \varphi_2 = \frac{R_2}{z_2^{-1/2}}$ . When  $\varphi_2 - \varphi_1$  has been found as described above,  $C$  is easily calculated.

This method is just as easy to use for  $E = 0$  as for positive values of  $E$ .

Eigenfunctions have been calculated for the two values of  $E$ :  $-0$  and  $+0.05$ , and for the three values of  $l$ :  $-0, 1, 2$ .

With the aid of these six eigenfunctions I have calculated  $\frac{df}{dE}$  in two points in each of the series' continua, which correspond to the bound states denoted by  $3s, 4s, 3p, 4p$ .

The following results were obtained:

Initial state	Transition of $l$	$E = 0$		$E = + 0.05$ [0.677 e.V.]	
		$\frac{df}{dE}$	$\frac{v}{c \cdot R}$	$\frac{df}{dE}$	$\frac{v}{c \cdot R}$
3s.....	$0 \rightarrow 1$	0.020	0.3777	< 0.001	0.4277
4s.....	$0 \rightarrow 1$	0.020	0.1432	< 0.001	0.1932
3p.....	$1 \rightarrow 0$	0.13		0.08	
	$1 \rightarrow 2$	0.82		0.31	
		0.95	0.2231	0.39	0.2731
4p.....	$1 \rightarrow 0$	0.22		0.10	
	$1 \rightarrow 2$	1.79		0.48	
		2.0	0.1019	0.58	0.1519

The absorption coefficients of the  $s$ -states are rather uncertain, because, as was mentioned above, the integral of the product of  $r$  and the eigenfunctions in these cases is the sum of two nearly equal parts of opposite sign. The very small (and uncertain) values of  $\frac{df}{dE}$  for  $E = 0.05$  only indicate, that we are here in the neighbourhood of the point, where the two parts exactly cancel each other. On the opposite side of this point  $\frac{df}{dE}$  will again increase. The phenomenon is probably of the same nature as that found experimentally for potassium in the ground-state.<sup>1</sup>

<sup>1</sup> E. O. LAWRENCE and N. E. EDLEFSEN: Phys. Rev. **34**, 1056, 1929.

The numerical value of  $\frac{df}{dE}$  at the principal series' limit can also be found from experimental results. When the  $f$ -values of the high members of the series can be expressed as  $\frac{C}{n^3}$ ,  $\frac{df}{dE}$  at the limit is  $\frac{C}{2}$ . Here  $n$  denotes the so-called effective quantum number defined by the equation  $\tilde{\nu}$  (the term value) equal to  $\frac{R}{n^2}$ . The same law is of course followed also when the number of the line in the series or of the upper term is used, but the effective quantum number alone gives the right  $C$ -value for reasonably low  $n$ -values. [At the term-number 16 e. g. the effective quantum number is  $\approx 15.1$ , and the number of the line in the series is 14. The ratios of the cubes of these three numbers are nearly as 6:5:4]. When the first  $f$ -value is put equal to 1 in the results of FILIPPOV and PROKOFJEV<sup>1</sup> the  $\frac{df}{dE}$ -value at the series' limit is found to be 0.020, very nearly. The good agreement with the calculated value may be accidental.

TRUMPY<sup>2</sup> has found the value 0.038 at the same limit. The difference is not greater than might be expected. Both values are calculated as the squares of small differences between nearly equal quantities.

When the  $\frac{df}{dE}$ -values are compared with the corresponding values for hydrogen, the latter are usually modified as follows:

$$\left(\frac{df}{dE}\right)_{\text{mod}} = \left(\frac{df}{dE}\right)_H \cdot \left(\frac{\nu_H}{\nu}\right)^3 \cdot \left(\frac{n}{n_{\text{eff}}}\right)^3.$$

Introducing a correcting factor  $F$ , we may write for the true value of  $\frac{df}{dE}$

<sup>1</sup> A. FILIPPOV and W. PROKOFJEV: Z. f. Ph. **56**, 458, 1929.

<sup>2</sup> B. TRUMPY: Z. f. Ph. **71**, 720, 1931.

$$\frac{df}{dE} = \left(\frac{df}{dE}\right)_H \cdot \left(\frac{\nu_H}{\nu}\right)^3 \cdot \left(\frac{n}{n_{\text{eff}}}\right)^3 \cdot F.$$

$n_{\text{eff}}$  is defined by  $\nu = \frac{c \cdot R}{n_{\text{eff}}^2}$ . We can therefore conveniently express the values of  $\frac{df}{dE}$  determined above with the aid of the corresponding correcting factor  $F$  given by

$$F = \frac{\left(\frac{df}{dE}\right)}{\left(\frac{df}{dE}\right)_H} \cdot \left(\frac{\nu}{c \cdot R}\right)^{3/2} \cdot n^3.$$

At the four series' limits here considered, the  $\left(\frac{df}{dE}\right)_H$  values are taken from the limiting formulae for the  $f$ -values as given by BETHE.<sup>1</sup> For these states we have:

Initial state	$\left(\frac{df}{dE}\right)_H$	$F$
3s .....	3.1	0.040
4s .....	4.65	0.015
3p .....	3.2	0.84
4p .....	4.9	0.85

The results obtained in the case of sodium may thus be summarised as follows. For the excited states 3p and 4p, the continuous absorption at the series' limit is slightly smaller than that calculated with the aid of the modified hydrogen-formula. For the ground-state 3s, and the excited state 4s, the continuous absorption at the series' limit is much smaller than that given by the formula mentioned.

Evidently it is only in the case of absorption from the s-states, that the interference-phenomenon plays a rôle. It

<sup>1</sup> H. BETHE: Handbuch d. Physik XXIV/1, p. 443.

is probable, as mentioned before, that  $\frac{df}{dE}$  for greater values of  $\nu$  is greater than at the series' limit.

For the absorption from  $d, f, \dots$ -states the hydrogen-absorption coefficients are probably good approximations. These states correspond to what has been called "non-penetrating orbits" for the valence electron.

### Appendix.

The following tables give the  $Z_p$ -function used and the normalised radial eigenfunctions  $R(r)$ . The number of decimals given does not indicate the degree of accuracy, because even small alterations in  $Z_p$  may cause considerable displacements of the nodes of the eigenfunctions.

$r$	$2 \cdot Z_p$	$l = 1$ $E = 0$	$l = 1$ $E =$ $+ 0.05$	$r$	$2 \cdot Z_p$	$l = 1$ $E = 0$	$l = 1$ $E =$ $+ 0.05$
0.0	22.00	0.000	0.000	2.0	2.30	+ 0.484	+ 0.482
0.1	17.30	- 0.069	- 0.069	2.1	2.26		
0.2	14.20	0.170	0.169	2.2	2.23	0.561	0.555
0.3	11.78	0.238	0.237	2.3	2.20		
0.4	9.80	0.265	0.264	2.4	2.18	0.625	0.615
0.5	7.90	0.261	0.260	2.5	2.16		
0.6	6.60	0.235	0.234	2.6	2.15	0.676	0.661
0.7	5.60	0.196	0.194	2.7	2.14		
0.8	5.00	0.148	0.146	2.8	2.13	0.714	0.691
0.9	4.50	0.095	0.092	2.9	2.12		
1.0	4.00	- 0.039	- 0.036	3.0	2.11	0.737	0.707
1.1	3.50	+ 0.019	+ 0.021	3.1	2.10		
1.2	3.20	0.076	0.079	3.2	2.09	0.747	0.709
1.3	3.00	0.133	0.136	3.3	2.08		
1.4	2.80	0.189	0.192	3.4	2.07	0.744	0.697
1.5	2.70	0.244	0.246	3.5	2.06		
1.6	2.60	0.297	0.298	3.6	2.05	0.729	0.672
1.7	2.50	0.347	0.348	3.7	2.035		
1.8	2.40	0.395	0.396	3.8	2.02	0.702	0.634
1.9	2.35	0.441	0.440	3.9	2.01		
2.0	2.30	+ 0.484	+ 0.482	4.0	2.00	+ 0.664	+ 0.586

$r$	$l = 0$ $E = 0$	$l = 0$ $E = +0.05$	$l = 1$ $E = 0$	$l = 1$ $E = +0.05$	$l = 2$ $E = 0$	$l = 2$ $E = +0.05$
0.0	0.000	0.000	0.000	0.000	0.000	0.000
0.5	-0.270	-0.270	-0.261	-0.260	+0.014	+0.015
1.0	-0.014	-0.012	-0.039	-0.036	0.057	0.063
1.5	+0.324	+0.327	+0.244	+0.246	0.128	0.143
2.0	0.528	0.526	0.484	0.482	0.228	0.252
2.5	0.582	0.570			0.347	0.379
3.0	0.512	0.484	0.737	0.707	0.474	0.510
3.5	0.351	0.308			0.596	0.631
4.0	+0.138	+0.082	0.664	0.586	0.705	0.728
4.5	-0.092	-0.156	0.532	0.427	0.791	0.794
5.0	0.313	0.375	0.356	0.228	0.848	0.820
5.5	0.503	0.553	+0.154	+0.011	0.872	0.804
6.0	0.648	0.674	-0.056	-0.206	0.859	0.744
6.5	0.739	0.731	0.260	0.403	0.811	0.645
7.0	0.774	0.723	0.445	0.567	0.730	0.511
7.5	0.754	0.655	0.600	0.688	0.619	0.350
8.0	0.683	0.535	0.720	0.760	0.483	+0.170
8.5	0.571	0.375	0.798	0.780	0.328	-0.018
9.0	0.424	-0.189	0.834	0.748	+0.161	0.205
9.5	0.254	+0.010	0.828	0.670	-0.012	0.382
10.0	-0.071	0.209	0.782	0.552	0.185	0.541
10.5	+0.116	0.395	0.700	0.402	0.351	0.674
11.0	0.297	0.557	0.587	0.229	0.506	0.776
11.5	0.465	0.687	0.450	-0.044	0.643	0.843
12.0	0.613	0.779	0.295	+0.144	0.760	0.872
12.5	0.736	0.829	-0.129	0.323	0.854	0.864
13.0	0.829	0.836	+0.042	0.487	0.922	0.818
13.5	0.890	0.800	0.212	0.627	0.962	0.738
14.0	0.919	0.724	0.374	0.736	0.975	0.628
14.5	0.915	0.614	0.524	0.812	0.960	0.492
15.0	0.879	0.475	0.656	0.852	0.919	0.336
15.5	0.814	0.314	0.768	0.853	0.854	-0.168
16.0	0.723	+0.140	0.856	0.818	0.767	+0.007
16.5	0.610	-0.041	0.919	0.748		0.182
17.0	0.478	0.220	0.955	0.646	0.537	0.350
17.5	0.332	0.390	0.965	0.519		0.505
18.0	0.176	0.544	0.948	0.370	-0.255	0.642
18.5	+0.015	0.676	0.906	0.206		0.756
19.0	-0.146	0.782	0.840	+0.034	+0.050	0.844
19.5	0.303	0.857	0.753	-0.140		0.902
20.0	-0.452	-0.900	+0.648	-0.310	+0.352	+0.930

$r$	$l = 0$ $E = 0$	$l = 0$ $E =$ $+ 0.05$	$l = 1$ $E = 0$	$l = 1$ $E =$ $+ 0.05$	$l = 2$ $E = 0$	$l = 2$ $E =$ $+ 0.05$
20.....	-0.452	-0.900	+0.648	-0.310	+0.352	+0.930
21.....	0.714	0.885	0.393	0.610	0.623	0.892
22.....	0.908	0.742	+0.102	0.829	0.845	0.738
23.....	1.021	0.496	-0.200	0.936	1.000	0.490
24.....	1.046	-0.183	0.486	0.922	1.080	+0.181
25.....	0.984	+0.154	0.735	0.791	1.082	-0.150
26.....	0.844	0.472	0.929	0.561	1.009	0.464
27.....	0.639	0.731	1.054	-0.263	0.867	0.723
28.....	0.387	0.900	1.106	+0.066	0.668	0.900
29.....	-0.107	0.961	1.082	0.387	0.426	0.975
30.....	+0.180	0.909	-0.987	+0.663	+0.159	0.942
32.....	0.701	+0.508			-0.389	-0.584
34.....	1.052	-0.114			0.851	+0.016
36.....	1.160	0.690			1.134	0.610
38.....	1.015	0.985			1.191	0.967
40.....	0.659	0.890			1.020	0.955
42.....	+0.173	-0.449			0.663	0.587
44.....	-0.346	+0.162			-0.190	+0.037
46.....	0.804	0.714			+0.316	-0.582
48.....	1.124	1.007			0.771	0.963
50.....	-1.260	+0.942			+1.108	-1.011

