Mean Absorption and Equivalent Absorption Coefficient of a Band Spectrum

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The note deals with the absorption of a band in which the lines have the dispersion form; the effect of the overlapping of neighboring lines upon the absorption is taken into account. The analytical problem can be solved for a periodic pattern of lines with equal intensity S, width 2α and distance d from each other. Simple expressions are derived for the limiting cases of small α/d (formula (8)) and large α/d. In the latter case the transmission by a layer of thickness x is given by

$$I=I_0e^{-(Sx/d)\tanh(2\pi\alpha/d)}.$$

It appears that this formula gives a fairly good mean approximation even for small values of α/d, while the true transmission in this case is not exponential. It is shown that in problems of radiative transfer and radiative equilibria this approximate formula for the transmission can be used; *i.e.* the factor of x in the above exponent may be substituted in the equations of transfer as equivalent of a mean absorption coefficient.

THE theory of the absorption of spectral lines has been the object of extensive investigations.[1] The theory of infra-red band lines especially was developed by Dennison[2] and a comparison of the experimental and theoretical absorption of such bands has been carried out by Matheson.[3] It has also been directly proved in various cases[3,4] that these lines have the dispersion form required by the theory of collision broadening. In these investigations it was assumed that the effect of the overlapping of neighboring lines is negligible, or the absorbing layers were chosen so thin that this condition was practically fulfilled. We want here to develop an elementary theory of the effects produced by the overlapping of lines in the absorption by layers of considerable thickness. This includes as a limiting case the transition from line absorption into continuous absorption when the line distance becomes smaller than the line width. Although the model considered here is somewhat too simplified to be directly applicable to the absorption of real band spectra, we are able to draw some interesting conclusions from it. The main difficulty of band spectra absorption lies in the fact that the *mean* absorption is not, in general, of the exponential type, $I=I_0e^{-kx}$. (As frequently expressed in the older literature, the absorption does not follow Beer's law.) This introduces many mathematical complications, especially in problems of radiative energy transfer and radiative equilibria. Band spectra play a great role in terrestrial and stellar radiation transfer; for instance the radiative heat transfer in the earth's atmosphere takes place within two water bands and a CO_2 band. In this connection it seemed of particular interest to investigate the possibility of replacing the rapidly oscillating absorption coefficient of a band by a mean coefficient which only depends upon the much slower variation of the total line intensity from line to line. For numerous radiative transfer problems this yields a good approximation, as we shall see.

We shall confine our calculations to the case of lines which have the familiar dispersion form, as for instance that produced by collision broadening. The absorption coefficient for the individual line as function of the frequency has then the form

$$k(\nu)=\frac{S\alpha/\pi}{(\nu-\nu_0)^2+\alpha^2}, \tag{1}$$

where 2α is the width and S the total line intensity $\int kd\nu$. The amount of radiation, say Q, absorbed in a layer of optical thickness x is given by

$$Q=I_0\int_{-\infty}^{+\infty}(1-e^{-k(\nu)x})d\nu,$$

where I_0 is the incident intensity. Now if x is very small, Q will of course be proportional to the total line intensity S. As soon as x becomes

[1] Ladenburg and Reiche, Ann. d. Physik **42**, 181 (1913); a comprehensive treatment in Max Born's treatise *Optik*.
[2] D. M. Dennison, Phys. Rev. **31**, 503 (1928).
[3] L. A. Matheson, Phys. Rev. **40**, 813 (1932).
[4] H. Becker, Zeits. f. Physik **59**, 601 (1929).

somewhat larger, the absorption will be complete in the core of the line while the amount of radiation absorbed in the wings still increases with increasing x. It can be shown that in this case a good approximation is obtained by neglecting α^2 in the denominator of (1). The integration can then readily be carried out and yields the result

$$Q=2(S\alpha x)^{\frac{1}{2}}I_0, \tag{2}$$

the absorption being proportional to the square root of the line intensity and the optical thickness. The formula must obviously be valid in a band spectrum provided the line width is small compared to the distance of successive lines and provided the fraction of radiation absorbed is small compared to unity so that the overlapping of the lines is negligible. Formula (2) has been verified experimentally in numerous instances.

We proceed now to the general case for which the width is not small compared to the line distance. In order to have a problem that is accessible to analytical treatment we shall consider an infinite sequence of lines, all having the same intensity S and a constant distance d from each other. Then the absorption coefficient is

$$k(\nu)=\sum_{n=-\infty}^{n=+\infty}\frac{S\alpha/\pi}{(\nu-nd)^2+\alpha^2}. \tag{3}$$

To evaluate the sum we note that (3) is an analytic function of ν which has single poles at the points $\nu=nd\pm i\alpha$. It is well known that under certain restrictions an analytic function $f(z)$ which has only single poles can be expanded in a sum of rational fractions corresponding to these poles[5] (Mittag-Leffler's theorem). If a_1, $a_2\cdots$ are the poles and b_1, $b_2\cdots$ the corresponding residues we have

$$f(z)=f(0)+\sum b_n\left(\frac{1}{z-a_n}+\frac{1}{a_n}\right).$$

By virtue of this theorem (3) may be written

$$k=(iS/2d)[\cot(\tau+i\beta)-\cot(\tau-i\beta)]$$

where

$$\tau=\pi\nu/d,\quad \beta=\pi\alpha/d. \tag{4}$$

[5] Whittaker-Watson, ch.7.4.

We may write instead of this

$$k=\frac{S}{2d}\cdot\frac{\sinh 2\beta}{\sin(\tau+i\beta)\sin(\tau-i\beta)}$$

$$=\frac{S}{d}\frac{\sinh 2\beta}{\cosh 2\beta-\cos 2\tau}. \tag{5}$$

If we introduce the mean fractional transmission $T=I/I_0$, we have

$$T=\frac{1}{\pi}\int_0^{\pi}e^{-k(\tau)x}d\tau. \tag{6}$$

Before evaluating (6) for the general case we shall consider the limits of small and of large β.

1. Small β

Here we have from (5)

$$kx=S\beta x/d\sin^2\tau=C/\sin^2\tau. \tag{7}$$

Substituting into (6) and introducing $1/\sin^2\tau=y$ as integration variable we get

$$T=\frac{1}{\pi}\int_1^{\infty}e^{-Cy}\frac{dy}{y(y-1)^{\frac{1}{2}}}.$$

It follows that

$$-\frac{dT}{dC}=\frac{1}{\pi}\int_1^{\infty}e^{-Cy}\frac{dy}{(y-1)^{\frac{1}{2}}}=\frac{e^{-C}}{\pi}\int_0^{\infty}\frac{e^{-Cz}}{Z^{\frac{1}{2}}}dz=\frac{e^{-C}}{(\pi C)^{\frac{1}{2}}}.$$

Integrating with respect to C we find

$$T=-\frac{1}{\pi^{\frac{1}{2}}}\int^{C}e^{-C}\frac{dC}{C^{\frac{1}{2}}}=\frac{2}{\pi^{\frac{1}{2}}}\int_{C^{\frac{1}{2}}}e^{-u^2}du.$$

The upper limit of the last integral has to be chosen so that $T=1$ for $C=0$, which shows that the limit is $+\infty$. If therefore ϕ designates as usual the probability integral, we have by (4) and (7)

$$T=1-\phi((\pi S\alpha x)^{\frac{1}{2}}/d). \tag{8}$$

For small values of x this becomes equivalent to formula (2).

2. Large β

In this case we have from the second expression (5)

$$k=(S/d)\tanh 2\beta\cdot(1+\cos 2\tau/\cosh 2\beta).$$

Substituting in (6) we obtain

$$T=\frac{1}{2\pi}e^{-(Sx/d)\tanh 2\beta}$$

$$\times\int_0^{2\pi} e^{-(Sx/d)\cdot\tanh 2\beta\cdot\cos 2\tau/\cosh 2\beta}d(2\tau)$$

$$=e^{-(Sx/d)\tanh 2\beta}J_0(i(Sx/d)\tanh 2\beta/\cosh 2\beta)$$

J_0 is the Bessel function of order zero and its argument is purely imaginary. Now $J_0(0)=1$ and the function increases at first extremely slowly with increasing imaginary argument, e.g. $J_0(1)=1.27$. The argument of the Bessel function is smaller than the argument of the exponential by a factor $1/\cosh 2\beta$. Furthermore the exponential decreases more rapidly with increasing argument than the Bessel function increases. The degree of approximation remains therefore almost unaffected by putting the Bessel function equal to unity throughout and writing

$$T=e^{-(Sx/d)\tanh(2\pi\alpha/d)}. \tag{9}$$

According to the derivation (9) is valid for large values of α/d. It appears however that it yields a fair degree of approximation for all other values of α/d. If for instance we make α/d small we have

$$T=e^{-2\pi S\alpha x/d^2}. \tag{10}$$

In order to compare this with formula (8) which is the correct expression for small α/d the functions e^{-2x} and $1-\phi(\sqrt{x})$ have been plotted together in Fig. 1. For thin layers where the square root formula (2) for the absorption is valid, (10) would of course be a poor approximation. It is seen however that for values of T which are not too close to unity or to zero the two curves do not differ largely from each other. Since this is true for small values of α/d, it will hold *a fortiori* for intermediate values of this quantity.

3. The intermediate case

In order to reduce (6) to a more convenient form in the general case, we introduce a new integration variable u by $k=Su/d$. From (5) we have then

$$T=\frac{1}{2\pi}\oint\frac{e^{-Sxu/d}\cdot du}{u(2u\coth 2\beta-u^2-1)^{\frac{1}{2}}},$$

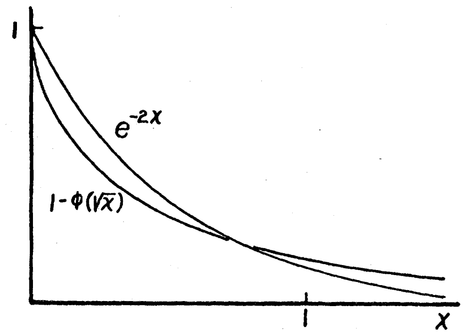

FIG. 1.

where the path of integration may conveniently be taken as a closed loop encircling the two singularities which arise from the zeros of the root ($u=\tanh\beta$ and $u=\coth\beta$, respectively). We introduce the abbreviation $A=Sx/d$. Differentiating with respect to A and introducing a variable v by $u=(v+\cosh 2\beta)/\sinh 2\beta$ we have

$$-\frac{dT}{dA}=\frac{1}{\pi}e^{-A\coth 2\beta}\int_{-1}^{+1}\frac{e^{-Av/\sinh 2\beta}}{(1-v^2)^{\frac{1}{2}}}dv$$

$$=e^{-A\coth 2\beta}J_0\left(\frac{iA}{\sinh 2\beta}\right)$$

by a well-known integral representation of the Bessel functions. Integrating the last equation with respect to A we obtain finally

$$T=\int_{Sx/d}^{\infty}e^{-A\coth 2\beta}J_0\left(\frac{iA}{\sinh 2\beta}\right)dA, \tag{11}$$

where the upper limit is again chosen so that $T=1$ for $x=\infty$. There seems to be no means of reducing (11) further in terms of elementary functions. The Bessel function can be replaced by its power series for small values of its argument and by its asymptotic expansion for large values of the argument; in both cases with two or three terms a good approximation is obtained.

Application

If the above formulae are to be applied to the absorption of band spectra, it must be remembered that the intensity of successive band lines decreases in most cases rather rapidly toward the edge of a band. This decrease is exponential and is therefore much faster than the decrease of intensity in the wings of an individual line. The strong lines in the center of a band will therefore give rise to a continuous background at the edges of the band and with sufficient thickness of the absorbing layer the background may become comparable in intensity and may even become much stronger than the outer band lines themselves.[6]

We can now apply the above calculations to the problem of radiative transfer. The fundamental equation of transfer is

$$dI/dx = -kI + E, \tag{12}$$

where x is the optical thickness and E is the emissive power of the substance. The equation expresses the obvious fact that the change in intensity I of a beam when passing through an infinitesimal slab is equal to the emission minus the absorption of the slab. I, E, k will in general be functions of the thickness x, of the frequency ν and of the direction of the beam. It is obviously not permissible to carry out an average with respect to ν for each individual quantity in (12). If nevertheless we want to simplify the problem by calculating from the outset with an average value of k which is only slowly variable with frequency, we must determine the degree of approximation of such a procedure. A natural definition of an average absorption coefficient may be obtained in the following way. To each value of the absorption coefficient there corresponds a mean free path of the light which is obviously proportional to k^{-1}. We may define an equivalent mean absorption coefficient, say k', by the condition that the mean free path averaged over a spectral interval be equal to the mean free path resulting from the equivalent absorption coefficient k'. Thus

$$(k')^{-1} = [k^{-1}]_{\mathrm{Av}} \tag{13}$$

and substituting the expression (5) for k

$$k' = (S/d) \tanh (2\pi\alpha/d).$$

This is precisely the absorption coefficient as derived above in the approximation formula (9).

The introduction of a mean free path has a good sense under physical conditions where the radiation will undergo a large number of absorption and emission processes before leaving the medium in which (12) is valid. The medium is then very *opaque*. If the opacity is high, the left hand side of (12) is small compared to each of the two terms on the right hand side. The solution of (12) can be found by a perturbation method;[7] the first terms are:

$$I = \frac{E}{k} - \frac{1}{k}\frac{d}{dx}\left(\frac{E}{k}\right) + \cdots. \tag{14}$$

Now, by Kirchhoff's law, E/k is nothing but the black-body radiation and it varies therefore only slowly with frequency. If (14) is averaged over a small frequency interval which however may contain several spectral lines, the equivalent mean absorption coefficient is just given by (13) provided E/k is kept constant in the averaging. The introduction of the equivalent absorption coefficient as defined above is therefore justified if the transmitting medium is sufficiently opaque.

[6] An example given by W. M. Elsasser, Phys. Rev. **53**, 768 (1938).

[7] E. A. Milne, *Handbuch der Astrophysik*, vol. 3, ch.2c.