997.641A) and that difference as known from the other pairs containing it. The difference cannot be accurately found from the pair at 871.396 and 865.435 inasmuch as the first line is really double. Twenty new lines have been classified. These locate fourteen new terms. The complete list of classified lines and the complete term table are listed in Tables IX and X, respectively. Using the conversion factor 1.2336×10^{-4} for changing cm^{-1} to electron volts the ionization potential is 69.698 ± 0.003 volts.

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The Correction of Continuous Spectra for the Finite Resolution of the Spectrometer

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The relation between the theoretical intensity function of a continuous spectrum and the intensity measured with an ionization chamber (or counter) and a spectrometer, is discussed. It is shown that while the problem of correcting the observed intensity for the finite resolution of the spectrometer does not always have a mathematically unique solution, the requirement that the theoretical intensity have a smooth graph is sufficient to make the solution practically unique. On this basis, an approximate solution of the problem is given, which involves the first and second differences of a set of equally spaced measurements. A second method of solution is discussed which involves the scansion of a template of the measured intensity wave-length curve by a photoelectric cell connected to a recording galvanometer. This method has practical disadvantages but illustrates several theorems derived analytically in the earlier part of the paper.

INTRODUCTION

THE problem of correcting the measurements of a continuous spectrum for the effect of the finite resolution of the spectrometer has apparently received little attention. It is known that if $I(\lambda)$ is the intensity measured with an ionization chamber or counter, and $\rho(\lambda)$ is the theoretical intensity, the two functions are connected by an equation of the form

$$I(\lambda)=\int_{-a(\lambda)}^{+a(\lambda)}\rho(\lambda+\xi)K(\lambda,\xi)d\xi. \tag{1}$$

The functions a and K are positive and have been determined for various types of instruments, but the general nature of the relation thus established between I and ρ has not been investigated. Eq. (1) has usually been approximated by

$$I(\lambda)=\alpha(\lambda)\rho(\lambda), \tag{2}$$

where

$$\alpha(\lambda)=\int_{-a(\lambda)}^{+a(\lambda)}K(\lambda,\xi)d\xi, \tag{3}$$

but there are cases in which this is not a sufficient approximation, e.g., some of the measurements of continuous beta-ray spectra made for the purpose of determining the mass of the neutrino.[1]

The validity of this approximation is readily estimated as follows: let $\rho_+(\lambda)$ and $\rho_-(\lambda)$ be the largest and smallest values, respectively, of $\rho(\lambda+\xi)$ for $|\xi|\leqslant a(\lambda)$. Then it follows from the positiveness of K that

$$\alpha\rho_-\leqslant I\leqslant\alpha\rho_+. \tag{4}$$

[1] W. J. Henderson, Proc. Camb. Phil. Soc. **31**, 285 (1935); E. M. Lyman, Phys. Rev. **51**, 5 (1937).

This inequality can be given a graphical interpretation: through any point P of the I, λ curve, draw a straight line parallel to the λ axis, which extends a distance $a(\lambda)$ to either side of P. Then the graph of $\alpha(\lambda)\rho(\lambda)$ will intersect this line. If the point P traces the I, λ curve, the ends of the line will trace two other curves. It cannot be proven rigorously that the graph of $\alpha\rho$ will lie between these two curves at all points, but it will be seen below that it is safe to assume that this will be the case if the spectrum is a continuous one. The two limits thus obtained for $\alpha\rho$ may differ by more than the experimental error in the measurements of I; if this is the case, then Eq. (2) is usually not a sufficiently good approximation. It is ordinarily difficult to diminish the difference between the two limits, since this depends on the spectrum and on the resolving power of the spectrometer. The error in the measurement of I on the other hand, can be decreased with comparative ease; it may therefore be desirable to work under conditions that invalidate Eq. (2), and to devise more elaborate methods of calculating ρ from I.

General Theory of Eq. (1)

If Eq. (1) is considered as an equation for determining ρ in terms of I, a number of general theorems concerning its solutions may be proven. It is easily seen that its solution is not unique unless certain data analogous to boundary conditions are available. To see this, it may be noted that if f is the difference of two solutions of Eq. (1), then it must satisfy the homogeneous equation

$$0=\int_{-a(\lambda)}^{+a(\lambda)} f(\lambda+\xi)K(\lambda,\ \xi)d\xi, \qquad (5)$$

and conversely, if f is a solution of this equation, and I_1 a solution of Eq. (1), then $I_2=I_1+f$ will be another solution of the latter. Of course, it might be that Eq. (5) has no solution other than $f\equiv 0$, but this does not seem likely. As an example, let a and K be constants; then any periodic function of λ, of period $2a$, whose integral over one complete period vanishes, will be a solution of Eq. (5). This illustration seems to be typical of the general case that arises in practise.

The characteristics of the practical case are (a) that $K(\lambda, \xi)\geq 0$ and has only a finite number of roots when $|\xi|\leq a(\lambda)$, i.e., it does not vanish identically over any whole interval of ξ; (b) that both $\lambda-a(\lambda)$ and $\lambda+a(\lambda)$ are monotonically increasing functions of λ.

For convenience, let the interval on the λ axis from $\lambda-a(\lambda)$ to $\lambda+a(\lambda)$ be called the r interval at λ. It then follows from (a) that any solution of Eq. (5) must change sign at least once in any r interval, or else be zero throughout that interval. Confining attention to regular solutions, it follows from this and (b) that if such a solution is zero throughout one r interval, it is zero everywhere. For, suppose that f is a solution of Eq. (5) that vanishes throughout the r interval at λ_0 but is not zero in the interval from $\lambda_0+a(\lambda_0)$ to $\lambda_1>\lambda_0+a(\lambda_0)$. It will then be possible to choose λ_1 so that f does not change sign in the last mentioned interval. Because of (b), there will then be an r interval ending at λ_1 in which f neither changes sign nor is everywhere zero. This possibility has already been excluded, hence the supposition is false.

These results have several consequences for the solutions of Eq. (1): thus the graphs of any two of its solutions will intersect at least once in every r interval. Therefore there is, practically speaking, at most one solution that has a smooth graph. More precisely, if two solutions differ by an appreciable amount at even one point, at most one of them can have a smooth graph. This remark justifies the trial-and-error method of solution used by Henderson.[1]

However, the requirement that ρ have a smooth graph does not determine the solution with mathematical uniqueness. In order to accomplish this, it is necessary that the values of ρ be specified throughout one complete r interval. This specification thus plays much the same role in the theory of Eq. (1) as do the initial values in the theory of differential equations. However, this datum is not always available, unless the spectrum has a limit, beyond which the function ρ vanishes identically. In this case, the precise location of the limit need not be known (theoretically) in order to find the solution required.

There are several special examples of Eq. (1) for which the general solution can be obtained. The calculations that would be required for their application to practical problems would be very laborious and the effects of experimental error

would be cumulative. Furthermore, it would ordinarily be necessary to have recourse to the method of trial and error in order to find the correct initial conditions (or spectrum limit) and this would multiply the labor. Consequently the general solution will not be very useful, even when found, and it seems preferable to develop systematic approximate methods for finding a smooth solution.

Approximate Determination of a Smooth Solution

The remaining considerations of this paper will be based on the assumption that a and K are both independant of λ, so that Eq. (1) becomes

$$I(\lambda)=\int_{-a}^{+a}\rho(\lambda+\xi)K(\xi)d\xi. \tag{1.1}$$

Then α, defined by Eq. (3) is a constant, and it may be supposed that the units of ρ and I have been so chosen that its value is unity. The following definitions will also be useful:

$$\eta=\int_{-a}^{+a}\xi K(\xi)d\xi,$$
$$\zeta^2=\tfrac{1}{2}\int_{-a}^{a}(\xi-\eta)^2K(\xi)d\xi; \tag{6}$$

both $|\eta|$ and ζ are less than a. If the function K is symmetric, η will be zero. The quantity ζ may be called the half-width of K. It will be supposed that measurements have been made at equally spaced intervals of $\lambda: \lambda_n=\lambda_0+nb$, $I(\lambda_n)=I_n$, etc.

It is next necessary to formulate the requirement that ρ have a smooth graph in such a manner that it can be utilized analytically. It is characteristic of a smooth curve that it can be approximated by parabolas over relatively long intervals; hence it may be required that if

$$\rho(\lambda+x)=\rho(\lambda)+x\rho'(\lambda)+\tfrac{1}{2}x^2\rho''(\lambda)+R(\lambda, x), \tag{7}$$

then $|R(\lambda, x)|<\epsilon$ whenever $|x|\leqslant a+b$, (8)

where ϵ is a negligible quantity. It is always questionable whether, for a given I, there is a solution that satisfies this requirement. If there is such a solution, then the graph of I must be approximable by a parabola in any interval of length $2b$, with an error less than ϵ. It is very likely that this will also be a sufficient condition for all spectra that can properly be classed as continuous with respect to the resolving power of the spectrometer. In fact, this might well be adopted as a criterion for this relation,[2] with the additional proviso that $b>a$ (see below), and that ϵ be the experimental error in the measurements of I.

The Eq. (7) may be used, with $\lambda=\lambda_n$, to calculate I_{n+1}, I_n and I_{n-1}:

$$\begin{aligned} I_{n+1}&=\rho_n+(\eta+b)\rho_n'+\tfrac{1}{2}[(\eta+b)^2+2\zeta^2]\rho_n'',\\ I_n&=\rho_n+\eta\rho_n'+\tfrac{1}{2}[\eta^2+2\zeta^2]\rho_n'',\\ I_{n-1}&=\rho_n+(\eta-b)\rho_n'+\tfrac{1}{2}[(\eta-b)^2+2\zeta^2]\rho_n''. \end{aligned} \tag{9}$$

These equations are approximate, but the error is in each case less than ϵ. They may be solved for ρ_n:

$$\rho_n=I_n-(\eta/2b)\Delta_2I_n+[(\eta^2-2\zeta^2)/2b^2]\Delta^2I_n, \tag{10}$$

in which the abbreviations

$$\begin{aligned} \Delta_2I_n&=I_{n+1}-I_{n-1},\\ \Delta^2I_n&=I_{n+1}-2I_n+I_{n-1}, \end{aligned} \tag{11}$$

have been used. The magnitude of the error in ρ_n is readily estimated: it is certainly less than

$$(1+a/b+4a^2/b^2)\epsilon.$$

If $b\gg a$ then the error will approach ϵ, but it must be recalled that b cannot be indefinitely increased without affecting the validity of Eq. (8). In any event, the errors of the calculation are not cumulative, since the result for ρ_n does not depend on the result for ρ_{n-1}.

A Photoelectric Method of Approximate Solution

The foregoing method of approximate solution leaves little to be desired in the way of computational simplicity. The method to be discussed in this section is not as simple, and the solutions obtained by it are subject to cumulative errors. It is presented rather as an instructive mathematical curiosity than as a feasible alternative to the previous method.

[2] It should be noted that this criterion can always be fulfilled for any spectrum if the measurements are sufficiently inaccurate. Conversely, if the measurements are extremely accurate, it becomes an exceedingly stringent criterion. From this point of view, it may be regarded as determining the desirable accuracy of the measurements for a given spectrum and spectrometer.

In Eq. (7), replace λ by $\lambda-x$, and x by $x+\xi$, and then substitute into Eq. (1.1). The result will be

$$I(\lambda)=\rho(\lambda-x)+(x+\eta)\rho'(\lambda-x)+\tfrac{1}{2}[(x+\eta)^2+2\zeta^2]\rho''(\lambda-x), \quad (12)$$

with an error that is less than ϵ provided that $x<b$. Next suppose that an opaque template of the I, λ curve is scanned by a photoelectric cell connected to a recording galvanometer. The ordinate of the trace, G, will be a function of λ that satisfies the equation

$$I(\lambda)=G(\lambda)+AG'(\lambda)+BG''(\lambda), \quad (13)$$

where A and B are constants and the unit of G has been conveniently chosen.

Eqs. (12) and (13) suggest that one inquire whether matters can be so arranged that

$$A=(x+\eta), \quad B=\tfrac{1}{2}[(x+\eta)^2+2\zeta^2]. \quad (14)$$

The disposable parameters are

the period of the galvanometer: $T=2\pi/\omega$ sec.;
its damping constant: p sec.$^{-1}$;
the speed with which the template is scanned: s (units of λ)/sec.;
the constant: x (units of λ).

The quantities η and ζ are to be considered as fixed, and of the four disposable parameters, s and x are the most readily varied. In terms of these quantities, the Eq. (14) becomes

$$\begin{aligned}(x+\eta)&=2ps/(\omega^2+p^2),\\ \tfrac{1}{2}(x+\eta)^2+\zeta^2&=s^2/(\omega^2+p^2),\end{aligned} \quad (14.1)$$

whose solutions for x and s are

$$\begin{aligned}x&=-\eta\pm 2p\zeta/(\omega^2-p^2)^{\frac{1}{2}},\\ s&=\pm\zeta(\omega^2+p^2)/(\omega^2-p^2)^{\frac{1}{2}},\end{aligned} \quad (15)$$

the undetermined sign being the same in both equations.

In order that x and s shall both be real, it is necessary that $\omega>p$; in other words, the galvanometer must be under-damped, even though p need not be zero. It can also be seen that $sT>2\pi\zeta$: during the period of one free oscillation of the galvanometer, an interval of the I, λ curve must be scanned that is greater than the half-width of K. These two requirements may be contrasted with the characteristics of an ordinary microphotometer, whose galvanometer is critically damped ($\omega=0$) and whose scanning speed is normally such that $sT\ll\zeta$. It is thus quite obvious that if the requirements of Eq. (15) were imposed on a microphotometer intended for use in registering line spectra, the results obtained with it would not be very sensible. This finds its mathematical explanation in the fact that the graph of a line spectrum will not satisfy the smoothness criterion unless ϵ is given a very large value, greater than the experimental error in the measurements. The method is thus restricted to continuous spectra.

Supposing that Eq. (15) is satisfied, it still does not follow that $G(\lambda)$ and $\rho(\lambda-x)$ are identical. The galvanometer trace will depend, not only on $I(\lambda)$ but also on the initial conditions of the galvanometer motion. Common sense indicates that the galvanometer should be at rest when the scansion begins: there should be no "galvanometer wiggles" in the trace. This conclusion is justified by a more detailed examination of the mathematics. It can easily be shown from Eq. (15) that the trace of a free vibration of the galvanometer is not a smooth curve unless its amplitude is considerably less than ϵ. This remark serves to establish a convenient standard for the estimation of smoothness. The further theorem, that if both $G(\lambda)$ and $\rho(\lambda-x)$ have smooth graphs their difference is less than ϵ, cannot be proven with complete rigor, since Eq. (12) is only approximate. Ignoring this source of error, the theorem is valid. However, this source of error may very easily be important, since it may result in systematically cumulative differences between the calculated and theoretical ρ functions. Consequently the method is not to be recommended for actual use, and is of interest largely because of the close analogy between the "galvanometer wiggles" and the solutions of the homogeneous integral equation, Eq. (5).