NOTE ON THE WIDTH OF SPECTRAL LINES DUE TO COLLISIONS AND QUANTUM THEORY

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1. According to the classical wave theory collisions among molecules of a luminous gas produce a spectral width of the lines emitted by the gas. The width discussed here is due to the fact that the Fourier analysis of a wave train involves a band of frequencies in the neighborhood of the main frequency of the wave train. It is the purpose of this note to point out that according to the quantum theory a broadening of the lines is to be expected for the same reason and that the amounts of the broadening in the classical and in the quantum theories are nearly equal.

The existence of the broadening effect is a direct consequence of a principle due to Bohr according to which systems which are not strictly multiply periodic do not admit of sharp quantization.

The magnitude of the effect can be estimated by imagining collisions of a simplified nature. Thus if the collisions should be exactly periodic and all of exactly the same kind e.g., such as to reverse the phase of the motion the problem reduces itself to the type considered by Ehrenfest and the writer. It is obvious from the treatment there given that a width of the spectral line is introduced. Since probabilities of transitions correspond to intensities of various harmonics in the motion the classical spectral width is also the spectral width to be expected on the quantum theory provided the motion considered in the classical theory is a properly chosen mean between the initial and final energy levels.

Actual collisions are not periodic nor are they all of the same nature. Their effect can be approximated, however, by introducing a number of types of collisions each of a definite period and nature. As before there is a correspondence between the classical and the quantum theories.

It may be postulated that in the limit as the number of periods introduced becomes infinite the result is still applicable.

2. Intrinsic Width of Spectral Lines.—Let a hydrogen atom be entirely isolated and let radiation be the only means of disturbing it. The only part of the radiation which can seriously affect the atom is the part having frequencies in the neighborhood of the emission and absorption frequencies. To simplify matters let us consider with Einstein only one of the frequencies \( \nu \) which corresponds to the emission line caused by the fall of the atom from the high energy level \( m \) to the low energy level \( n \).

Let the volume density in the frequency range \( \nu \rightarrow \nu + dv \) be \( \rho(\nu)dv \).
Let $\rho(\nu)$ decrease indefinitely. We want to know whether in the limit of $\rho = 0$ the line $\nu$ has a finite or infinitely small width. It seems proper to call this spectral width the intrinsic width of a line.

Unless further reasoning is adduced it appears necessary to differentiate between the intrinsic width of an emission line and the width of the same line when considered in absorption. It is probable, however, that the two are equal.

In fact they must be equal if a single atom of the kind considered is to remain in equilibrium when put into black body radiation. For if this atom should absorb one combination of frequencies and emit a different one it would in the course of time change the distribution of energy among frequencies by decreasing the energy density in the range which it absorbs and increasing it in the range into which it emits.

Let us consider the emission width. According to Einstein, i. c., if $\rho = 0$ there is a finite probability that atoms should fall from $m$ to $n$ in a finite time. Thus there is a quasiperiodic modulation of the motion of the electron. The times in the state $n$ are lengthened indefinitely as $\rho$ decreases. The times in the state $m$ maintain a finite length. Thus before the transitions $m \rightarrow n$ there has been a disturbance in the internal state of the atom owing to the transitions $n \rightarrow m$ which may be conceived of as influencing the strictness of the quantum rules on account of the violation of the periodicity of the atom. If this view is correct, i.e., if it is correct to regard the immediately preceding history as an indication of the spectral width we should expect the emission lines to have a finite intrinsic spectral width and the absorption lines, corresponding to transitions $n \rightarrow m$ preceded by extremely long quiet intervals, to have a vanishingly small intrinsic spectral width.

If, on the other hand, the average state is an indication for both then we are concerned with the Fourier Analysis of a motion the essence of which is a homogeneous wave train to which an intermittent wave of the nature considered by Lorentz has been added. In the limit the width of the spectral lines would become infinitely small.

The writer sees no possibility of deciding which of the above points of view is the correct one if any. It seems to him, however, that the intrinsic spectral width of a line considered in the manner of Sommerfeld and Heisenberg or Green as following from the Correspondence Principle may be thought of also directly in terms of quantum theory by analogy with the cases of the first section of this note. From this point of view the time $\tau$ of Compton is fundamental and is thought of as impairing the strictness of quantum rules in a manner analogous to collisions.

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CHANGE IN WAVE-LENGTH BY SCATTERING

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In a recent paper A. H. Compton has shown that there is strong evidence of a change in frequency of X-rays and γ-rays when scattered by paraffin, graphite, or aluminium. More recently Compton has shown that theoretically the change in wave-length should be

$$\Delta \lambda = \frac{2h}{mc} \sin^2 \frac{\theta}{2}$$

where \(h\) is Planck’s constant, \(c\) the velocity of light, \(m\) the mass of an electron, and \(\theta\) the angle between the primary beam and the scattered radiation.