

* Advance Note from a Report to the Carnegie Inst., of Washington, D. C.

¹ With more sensitive apparatus, I have since obtained similar acoustic pressures, with clear quill tubes free from pinholes.

² Carnegie Publications, Washington, No. 310, 1921, § 24, et seq.

³ These PROCEEDINGS, 11, 1925, p. 582, for instance.

TRANSITION PROBABILITIES AND PRINCIPAL QUANTUM NUMBERS

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On first consideration it would appear that a simple means of confirming or correcting an assignment of quantum numbers to the terms of a spectrum is afforded by a comparison of transition probabilities calculated on the basis of the correspondence principle with values obtained experimentally from the intensities of the lines, their dispersion or similar properties. Any such information as to the principal quantum numbers in series spectra would be particularly valuable, for the assignment of these numbers as proposed by Bohr involves a consideration of the arrangement of electron orbits in the atom and its relation to the periodic properties of the elements. However, on closer examination it appears that if the calculation is made on the basis of the ordinary conception of the correspondence principle the transition probabilities in series spectra will be to a first approximation independent of the principal quantum numbers assigned to the terms, in spite of the fact that the order of the corresponding harmonic is determined by the change in these numbers during a transition. This approximate independence follows as a result of the general assumptions as to the nature of the motion of the series electron which have been used for an interpretation of the main features of series spectra. It is true that with an exact knowledge of the motion of the series electron a dependence of the transition probabilities on the principal quantum numbers would result, but from such a detailed knowledge it would be possible to determine the quantum numbers directly.

Thus from the standpoint of the quantum theory in the form on which calculations have so far been based it does not appear that the discussion of transition probabilities affords a practical method for checking the principal quantum numbers. In particular the author is unable to agree with the tentative conclusions drawn by W. Kuhn¹ from his measurements of the magnetic rotation of the plane of polarization in thallium vapor as to

the necessity of modifying Bohr's original assignment of principal quantum numbers in this element.

The reasons for the above statements will appear more clearly if we consider the way in which it is possible to estimate the corresponding amplitudes, from which the transition probabilities may be calculated. A formal method of making such an estimate, following as closely as possible the theories of Bohr and Kramers, has been outlined in two papers by the author.^{2,3} There it was considered that to a first approximation the motion of the series electron is a central motion and hence doubly periodic, with frequency ω for the radial motion and σ for the superposed rotation. The Fourier series representing such a motion contains frequencies $|\tau\omega + \sigma|$ and $|\tau\omega - \sigma|$ where τ is the order of the harmonic, and in rectangular coordinates it may be written

$$x + iy = \sum_{-\infty}^{+\infty} C_{\tau} e^{2\pi i(\tau\omega + \sigma)t}.$$

As to the amplitudes C_{τ} it has been shown that to within an approximation which is essentially that with which the energies may be represented by a formula of the Rydberg type they are given by the expression

$$C_{\tau} = \frac{a}{\pi} \sin \rho \pi \sum_{-\infty}^{+\infty} b_m J_m(\rho\epsilon). \quad (1)$$

The approximation applies to orbits which may be thought of as composed of outer segments in which the motion is nearly Keplerian joined by inner segments in which the deviations from Keplerian motion may be large, but which are traversed in a time which is short compared to the period of the radial motion. In equation (1) a and ϵ are, respectively, the semi-major axis and eccentricity of the Keplerian ellipses of which the outer segments form a part, while b_m is an algebraic factor involving only ϵ and ρ , and J_m is a Bessel function of order m . The order τ of the harmonic enters only through ρ which has been introduced as an abbreviation for the quantity $\tau + \sigma/\omega$ and may be thought of as an "effective order" of the harmonic. Since, then

$$\rho = \tau + \sigma/\omega. \quad (2)$$

it is readily seen that we may write for the frequency $\omega_0 = \tau\omega \pm \sigma$ of any harmonic,

$$\omega_0 = \rho\omega.$$

For the purpose of calculating the transition probabilities one considers the spontaneous radiation from a given stationary state as equivalent to that of a set of classical oscillators with electric moments

$$eA_k \cos 2\pi\nu_k t$$

where the ν_k are the frequencies associated by the quantum relation with the possible transitions to states of lower energy, and A_k is connected with Einstein's probability coefficient by the equation,

$$A'_{i, h\nu_k} = \frac{32\pi^4 e^2}{3c^3} \nu_k^4 A_k^2.$$

Since ν_k may be represented as an appropriate mean value of a "corresponding" frequency $|\tau\omega \pm \sigma|$ in the motion of the series electron namely that for which $\Delta n = \tau$, $\Delta k = \pm 1$, where n and k are the principal and subordinate quantum numbers, it may be assumed that A_k can also be represented as some average value of the amplitude C_τ of this corresponding harmonic. In many cases this mean value is probably given with sufficient accuracy by Eq. (1) with substitution of mean values of the parameters a and ϵ and of the effective order ρ .

Reasonable mean values of these quantities may be found in terms of the energies or term values of the stationary states involved, or what amounts to the same thing, in terms of their effective quantum numbers as defined by the equation

$$E = -Th = -\frac{Rh}{n^{*2}} \quad (3)$$

where E is the energy of the series electron, T the term value and R the Rydberg constant. We may, for instance, use as the effective mean value \bar{n}^* the simple arithmetical mean of n^* in the stationary states and similarly for \bar{k} , in which case \bar{a} and $\bar{\epsilon}$ are given by the well-known relations

$$\bar{a} = \frac{e^2}{2Rh} \bar{n}^{*2}, \quad \bar{\epsilon} = \sqrt{1 - \frac{\bar{k}^2}{\bar{n}^{*2}}}.$$

To obtain the mean value $\bar{\rho}$ we must estimate the mean value of σ/ω , and it appears possible to do this formally in terms of n^* , by means of the relation which exists between the frequencies in a multiply periodic motion and the quantum numbers. In fact, as previously shown, the ratio σ/ω is equal to the negative of the derivative of the "quantum defect" q with respect to k , i.e., $\sigma/\omega = -\frac{dq}{dk}$ where q is defined by the equation

$$E = -\frac{Rh}{(n-q)^2}. \quad (4)$$

As Bohr has shown⁴ the quantum defect, q , is, on the basis of just the assumptions used in deriving (1), independent of n and a function of k alone, and the general approximate validity of (4), which is the Rydberg formula, is strong evidence for the correctness of these assumptions. For an aver-

age of $\frac{dq}{dk}$ it seems reasonable to take $\frac{\Delta q}{\Delta k}$ where Δ denotes the finite difference between initial and final states, and by virtue of the fact that k changes always by one unit we have

$$\overline{\sigma/\omega} = -\Delta q. \quad (5)$$

By comparison of (3) and (4) we see that $n^* = n - q$ and from (2) and (5) it follows that we may write

$$\bar{\rho} = \tau + \sigma/\omega = \Delta n - \Delta q = \Delta n^*.$$

The quantities \bar{a} , $\bar{\epsilon}$ and $\bar{\rho}$ and hence A_k are thus given in terms of the energies in the stationary states alone and the transition probabilities as calculated in this way will not be altered by changing arbitrarily the principal quantum numbers of the terms. This may perhaps be more simply demonstrated by noting that if any quantum number is changed by a given number of units σ/ω and τ will be changed by the same number of units but in opposite senses, so that $\bar{\rho}$ remains unaltered.

Besides showing clearly that the transition probabilities may be calculated approximately from the term values alone, the procedure outlined above is very convenient for the numerical calculation of the corresponding amplitudes. On the other hand no strict justification can be given for the use of the method of averaging employed, although some support for it may be found in the fact that if it is used for a calculation of the frequencies (by means of the relation $\nu = \bar{\omega}_0 = \bar{\rho} \bar{\omega} = \Delta n^* \frac{2R}{n^*3}$) an approximate agreement with the experimental frequencies is obtained.

The considerations of this note have been based entirely on what may already be called the "classical" form of the quantum theory. The recent reformulation of the theory due to Heisenberg⁵ and Born and Jordan⁶ permits a more direct calculation of the transition probabilities, although as yet the calculation cannot be carried through for the central motions here considered. Since, however, there is approximate agreement between the results of the two theories in many cases, one may hazard the guess that in the newer form of the theory the quantity analogous to $\tau + \sigma/\omega$ will appear as a whole, not separable into τ and σ/ω and will determine the transition probabilities, giving the same type of independence of the principal quantum numbers as deduced here from the older form of the theory.

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¹ W. Kuhn, *Naturwissenschaften*, **13**, 724 (1925).

² F. C. Hoyt, *Physic Rev.*, **25**, 174 (1925).

³ F. C. Hoyt, *Physic Rev.*, **26**, 749 (1925).

⁴ See M. Born, "Vorlesungen über Atommechanik," Berlin, 1925, p. 184.

⁵ W. Heisenberg, *Zeit. Physik*, **33**, 879 (1925).

⁶ M. Born and P. Jordan, *Ibid.*, **35**, 858 (1925).

ABSORPTION AND RESONANCE RADIATION IN EXCITED HELIUM AND THE STRUCTURE OF THE 3889 LINE

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In a recent issue of *Nature*¹ a brief letter was published on the results of some experiments on the optical properties of excited helium. A detailed account of the experimental work and plates representing the results obtained are being sent to the *Philosophical Magazine* for publication. The following is a summary of those results, with the addition of some discussion of their significance.

The method used differed from the usual photometric method in that the light, after passing through the absorbing column, was resolved by means of an echelon grating and examined for a weakening of the central portion of the line, which would be affected by the absorption. It was found possible to completely reverse several lines of the helium spectrum by an absorbing column 80 cm. in length. The lines reversed included not only the principal series of both the singlet and doublet systems, but also the diffuse subordinate series of both systems, not, however, the lines of the sharp subordinate series. Table 1 gives a list of the lines which were reversed.

TABLE 1
HELIUM LINES REVERSED BY ABSORPTION IN A COLUMN OF EXCITED HELIUM OF LENGTH 80 CM. PRESSURE OF GAS 4.0 MM.

WAVE-LENGTH	LINE	WAVE-LENGTH	LINE
3889 Å	$1\sigma-2\pi$	5016 Å	1S-2P
3187	$1\sigma-3\pi$	3964	1S-3P
5876	$1\pi-2\delta$	3614	1S-4P
4471	$1\pi-3\delta$	6678	1P-2D
4026	$1\pi-4\delta$	4922	1P-3D
3819	$1\pi-5\delta$		

In agreement with the results of other observers, it was found that the presence of small amounts of hydrogen in the discharge greatly reduced