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ON THE CONTINUOUS SPECTRUM OF THE HYDROGEN ATOM

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The purpose of the present paper is to obtain expressions for the intensities in the continuous spectrum of atomic hydrogen suitable for numerical calculations. This purpose is accomplished by means of a new integral representation for the wave function in this special case. As examples of application, we calculate the absorption spectra of hydrogen beyond the limits of the Balmer and of the Lyman series as well as certain limiting values of the absorption.

1. *Introductory.*—The knowledge of the continuous part of atomic matrices is necessary for the theoretical treatment of many phenomena such as photoelectric effect, rates of recombination, intensity of x-rays and others. But even for the simplest case of hydrogen-like atoms, expressions suitable for numerical calculations have not yet been given. The general problem of normalization in the continuous range has been elucidated by Fues,[1] and a treatment of hydrogen-like atoms was undertaken by Oppenheimer.[2] The expressions he gives are, however, too complicated to be of much use numerically. The purpose of the present

communication is to supply this want for transitions from continuous (hyperbolic) stationary states into discrete (elliptic) ones. Only one or two illustrative applications of the formulas will be made in section 5 to show their advantages for numerical purposes, while the main physical discussion is reserved for a later publication.

The quantization of hyperbolic orbits was developed on the basis of Bohr's theory by one of the present writers, especially with a view to explaining photoelectric phenomena. After a first spurious attempt,[3] it was shown[4] by him that in these states (positive energy, $E > 0$) the azimutal quantic numbers are discrete integers, while the radial quantic number, and consequently the energy may assume any positive value.
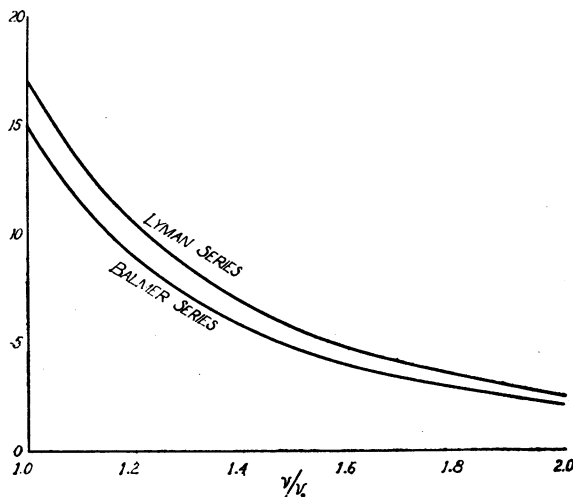

FIGURE 1

These conclusions have been strikingly confirmed by Schroedinger's wave dynamics.[5]

The representation of wave functions which has been given by one of us in a previous paper[6] is valid also for the continuous or hyperbolic range

$$\mathbf{X}(r) = r^{k-1} e^{\alpha r} \left[1 + \frac{s}{1 \cdot 2k} 2\alpha r + \frac{s(s-1)}{2! 2k(2k+1)} (2\alpha r)^2 + \ldots \right]. \quad (1)$$

As in that paper, l denotes the total, $k - 1$ the azimutal quantic number, $s = l - k$. The parameter α is given by $\alpha = -\mu e^2 Z/K^2 l$, and is connected with the energy by the relation $E = -K^2\alpha^2/2\mu$.[7] It follows that α is real if $E < 0$ (elliptic orbits) and imaginary if $E > 0$ (hyperbolic orbits).

The elements of the atomic matrix essentially depend on the integral

$$X = \int_0^\infty r^3 \chi_1(\alpha r) \chi_2(\alpha' r) dr, \quad (2)$$

where $\chi_1(\alpha r)$ and $\chi_2(\alpha' r)$ refer to the initial and to the final states of the atom.

2. *Properties of Wave Functions in the Continuous Range.*—For hyperbolic states the parameter l is imaginary as well as $\alpha(l = i\lambda, \alpha = i \mid \alpha \mid$, λ and $\mid \alpha \mid$ being real and positive). The question arises, therefore, whether the function $\chi(r)$ is complex. It was shown (loc. cit.) that our series (1) is a limiting case of the hypergeometric series

$$\chi = r^{k-1} \exp(\alpha r) \lim_{x = r/\beta, \beta = \infty} F(-s_1, \beta_1, 2k_1, -2\alpha x). \qquad (3)$$

Making use of the expression of hypergeometric functions by a definite integral and going to the limit $\beta = \infty$, we obtain[8]

$$\chi(r) = r^{k-1} \frac{\Pi(2k-1)}{\Pi(k-l-1)\,\Pi(k+l-1)}$$
$$\int_0^1 e^{-(2t-1)\alpha r} \, t^{k-l-1} (1-t)^{k+l-1} \, dt. \qquad (4)$$

As $k \geqslant 1$, this integral is convergent. Substituting the new integration variable $t' = (1 - t)$, we obtain a new form of the integral which differs from (4) only by l and α being replaced by $-l$ and $-\alpha$, respectively, i.e., it is the complex conjugate of expression (4). The function $\chi(r)$ is, therefore, equal to its own complex conjugate and this shows that it is real.

From (4) we easily obtain the asymptotic expressions for large values of r. We can divide the path 0 to 1 into two parts: (a) from 0 to $-i\infty$, (b) from $-i\infty$ to 1. We see, at once, that the factor with $(1 - t)$ can be omitted as negligible and that the two integrals become gamma functions:

$$\chi(r) = \frac{(2k-1)!}{r} \left\{ \frac{r^l}{\Pi(k+l-1)} \frac{e^{\alpha r}}{(2\alpha)^{k-l}} + \text{conj. comp.} \right\}, \qquad (5)$$

or

$$\left\{ \begin{array}{l} \chi(r) = (2k-1)! \, (T \cos \delta + S \sin \delta)/r, \, \delta = \mid \alpha \mid r - \lambda \log r, \\[2mm] \qquad T^2 + S^2 = \dfrac{4e^{-\Pi\lambda}}{\Pi(k+l-1)\,\Pi(k-l-1)} \dfrac{1}{\mid 2\alpha \mid^{2k}}. \end{array} \right. \qquad (6)$$

3. *Evaluation of the Integrals.*—It was shown (loc. cit.) that the integral (2) can be reduced to the simpler one

$$R(s, s') = \int_0^\infty r\chi(s, k, \alpha)\chi(s', k, \alpha')dr. \qquad (7)$$

We shall generalize the problem and are going to compute this expression for any values of α and α'. For the applications, we can specialize it

again by assigning to these parameters their above dependence on l and l'. For the case of real and integral $l_1 l'$, we derived a differential equation for function (7) and gave its explicit expression (loc. cit.). Though the same differential equation remains true in the general case, there arise certain doubts as to which of its integrals satisfies the physical requirements of the problem. We prefer, therefore, to evaluate (7) by a different method. This method is based on the following representations of our χ-functions by a definite integral

$$\begin{cases} \chi(s,\alpha,r) = \dfrac{(2k-1)!}{2\pi i} \Pi(s) \exp\left[\alpha r - (s+1)\Pi i\right] y^{-l+1/2} (2\alpha)^{-k+1/2} r^{-1/2}. \\[2mm] \qquad \cdot \displaystyle\int J_{2k-1}(2\sqrt{2\alpha y r t}) t^{-l-1/2} e^{-yt} dt. \end{cases} \tag{8}$$

The path of integration is a complex loop coming from $+\infty$ along the real axis, making a positive circuit round the point $t = 0$ and going back to $+\infty$. In the case, when $l - k$ is integral, the singularity in the point $t = 0$ is a pole and our loop degenerates into a circuit round this pole. This formula is easily obtained by using the power expansion of Bessel functions and noticing that the integral in each term of the expanded expression is a gamma function. The parameter y must have a positive real part; apart from this, it drops out of the result and is arbitrary. However, it is valuable because by a suitable choice of its imaginary part, we can secure the convergence of the following operations.

We substitute (8) for both factors in the integrand (7) and apply the following relation from the theory of Bessel functions[10,11]

$$\int_0^\infty J_p(2\sqrt{ar}) J_p(2\sqrt{br}) e^{-cr} dr = \frac{1}{c} \exp\left(-\frac{a+b}{c} - \frac{p\pi i}{2}\right) J_p(2i\sqrt{ab}/c). \tag{9}$$

The conditions of convergence permit us to carry out the integration with respect to r first. One of the remaining integrations is exactly of the type (8). Using this formula, we obtain an expansion with an Euler integral in each term which we replace by a gamma function. The result is a hypergeometric series

$$\begin{cases} R(s_1 s') = (-1)^s \dfrac{(2k-1)! \, u^{s+s'}}{(\alpha + \alpha')^{2k}} F\left(-s, -s', 2k, 1 - \dfrac{1}{u^2}\right), \\[2mm] \qquad u = (\alpha - \alpha')/(\alpha + \alpha') = (l' - l)/(l' + l). \end{cases} \tag{10}$$

s' being real, positive, and integral, this can be also written as)

$$R(s,s') = (-1)^s \dfrac{(2k-1)! \, (2k-1)! \, \Pi(l+l'-1)}{\Pi(l+k-1) \, \Pi(l'+k-1)} \cdot \dfrac{u^{s+s'}}{(\alpha+\alpha')^{2k}}. \tag{11}$$

$$F\left(-s, -s', -l-l'+1, \dfrac{1}{u^2}\right).$$

In the special case, where the parameter l is also real this expression becomes identical with equation (21), loc. cit.

The relation existing between $R(s,s')$ and integral (2) can be derived from previously established equations (loc. cit.) as

$$\overline{X}(l,\, k\, +\, 1,\, \alpha;\, l',\, k,\, \alpha') \,=\, \frac{2k(2k\,+\,1)}{8\alpha^2\alpha'u}\,(1\,-\,u^2)\,[R(s,s')\,-\,R(s\,+\,2,\,s')].$$

$$(12)$$

Unlike the preceding equations, this formula does not apply to the general case of arbitrary α and α': the constants are specialized $\alpha = -\,\mu e^2 Z/lK^2$, $\alpha' = \mu e^2 Z/l'K^2$, moreover, $s = l - k - 1$, $s = l' - k$. An analogous equation obtains in the case when k refers to the hyperbolic state and $k + 1$ to the elliptic.

4. *Normalization.*—Our expressions become divergent in the case $l = l'$, $\alpha = \alpha'$, so that it is inconvenient to apply them for the purpose of normalizing our functions. The theory of normalization for the continuous range has been worked out by Fues.[1] According to him, the normalizing conditions for our case can be stated as follows:

$$\lim{}_{r\,\rightarrow\,\infty} \int_\Delta \frac{\varphi(\alpha)\varphi(\alpha')}{\alpha'^2\,-\,\alpha^2}\left[r^2\left\{\chi(\alpha')\,\frac{d\chi(\alpha)}{dr}\,-\,\chi(\alpha)\,\frac{d\chi(\alpha')}{dr}\right\}\right]_0^r\,d\alpha'^2\,=\,\frac{2\mu}{K^2}.$$

He shows further that the bracket expression can be replaced by $(S^2 + T^2)$. $\sin(\delta_{\alpha'} - \delta_\alpha)d\delta/dr$. According to (6) this leads to the expressions

$$\varphi^2(\alpha)\,=\,\frac{\mu}{\pi K^2}\,e^{\pi\lambda}\,\mid 2\alpha\mid^{2k-1}\,\frac{\Pi(k\,+\,l\,-\,1)\,\Pi(k\,-\,l\,-\,1)}{(2k\,-\,1)!\,(2k\,-\,1)!}.\quad(13)$$

This is the normalization factor for the continuous range. It differs in two respects from our previous expression for discrete states

$$\varphi^2(\alpha'_{,}k)\,=\,\frac{\mid 2\alpha'\mid^{2k+1}\Pi(k\,+\,l'\,-\,1)}{2l'\Pi(l'\,-\,k)(2k\,-\,1)!\,(2k\,-\,1)!}.\quad(14)$$

In the first place, expression (14) refers to the intensity of a single line ($\Delta l' = 1$), while (3) refers to the density of intensities in the energy scale ($\Delta E = 1$). This involves the factor $dl/dE = \mu/K^2\alpha^2$. The remaining ratio can be brought into the form $(-1)^k e^{\pi\lambda}/2 \sin h\pi\lambda$. Mathematically speaking, this is due to the definition of our χ-functions by series (1) which for the continuous range is equivalent to integral (4) taken from 0 to infinity, while for the discrete functions the path of integration is a circuit round the origin. It is interesting to note that for large values of λ this factor becomes one, so that the two expressions, referred to the same scale, become formally identical.

5. *Final Expression. Examples.*—To obtain the square of a matrix

element corresponding to the transition from l, $k + 1$ to l', k, we have to form the product $I = e^2k\varphi^2(\alpha, k + 1)\varphi^2(\alpha', k)\overline{X}^2$. Our formulas (12) (13), (14) give

$$
\left\{
\begin{aligned}
I &= -\frac{K^6 k(k + l' - 1)!\,\lambda^4}{32\mu^3 e^6 Z^4 s'!\,\sin. h\Pi\lambda} \cdot \frac{\overset{k}{\underset{x=1}{\Pi}}\,(x^2 + \lambda^2)}{(2k - 1)!\,(2k - 1)!}\exp(\pi\lambda - 4\lambda\operatorname{arctn} l'/\lambda). \\
&\qquad \cdot [4l'\lambda/(\lambda^2 + l'^2)]^{2k+2}\Phi^2, \qquad\qquad (15) \\
\Phi &= u^{s'-1}\left[F\left(-s, -s', 2k, 1 - \frac{1}{u^2}\right) - u^2 F\left(-s-2, -s', 2k, 1 - \frac{1}{u^2}\right)\right].
\end{aligned}
\right.
$$

It should be noticed that $l'/\lambda = \sqrt{-E/E'}$, $l'\lambda/\lambda^2 + l'^2) = \sqrt{-EE'}/(E - E')$. Our final expression is convenient for numerical computations: If s' is small, the hypergeometric functions are reduced to few terms. If s' is even moderately large, they can be evaluated by the method of the steepest descent which was invented by Riemann precisely for the discussion of hypergeometric functions.

As an example of application, we give the curves for the continuous absorption spectrum beyond the limits of the *Lyman* and of the *Balmer* series (Fig. 1). We denote the limit of the series by ν_0 and plot the co-efficient of absorption per atom $\alpha_\nu = (2\pi)^3\nu I/6c$ against the ratio ν/ν_0. The scale is arbitrary and for the Balmer series ten times as large as for the Lyman series.

Another example are the limiting values of the absorption for the series limit $\nu/\nu_0 = 1$. It is easy to see from our formulas that this limiting value is the same as in the unresolved part of the line spectrum near the limit. The decrease of absorption is steep on the continuous side. Our limiting value applies, therefore, to either side of the series limit. In the case $s' = 0$, $k = l'$ we have: $\alpha_{\nu_0} = 4\pi^{1/2}K^3 l'^{5/2}(e/2)^{-2l'}/3\mu^2 e^2 Z^2 c$.[13] In the case, $l' \gg k$, on the other hand: $\alpha_{\nu_0} = 1{,}04 \cdot 2^4 K^3 l'^{7/3}/\mu^2 e^2 Z^2 c$. The probabilities of spontaneous transition differ from these expressions by a factor $\mathrm{const.}/l'^4$. Hence, in spite of the infinite number of quantic states, the expression for the total probability of capture of an electron is convergent. As appears from Temple's work,[9] it is of advantage to use in the treatment of problems involving capture of electrons parabolical coördinates. But we should like to point out that our expressions (10), (13), (14) are directly applicable, also, in the case of parabolical coördinates. They need only a change of notations to represent the functions, denoted by one of us[10] by the letters M and N, and determining the matrices in this case. We propose to calculate the rates of recombination by this method in a later publication.

[1] E. Fues, *Ann. Physik*, **80,** 367 (1926). See also J. R. Oppenheimer, *Phys. Rev.*, **31,** 66 (1928).

[2] J. R. Oppenheimer, *Z. Phys.*, **41**, 268 (1927).

[3] P. S. Epstein, *Ann. Phys.*, **50**, 815 (1916).

[4] P. S. Epstein, *Proceedings Amsterdam*, **23**, 1194 (1921).

[5] E. Schroedinger, *Ann. Phys.*, **79**, 367 (1926).

[6] P. S. Epstein, *Proc. Nat. Acad. Sci.*, **12**, 629 (1926).   We shall refer to this paper as loc. cit.

[7] μ, e mass and charge of electron, Z atomic number, $K = h/2\pi$.

[8] This integral is a linear combination of Schroedinger's two integrals, V_1 and V_2.

[9] G. Temple, *Proc. Roy. Soc.*, **121**, 673 (1928).

[10] P. S. Epstein, *Phys. Rev.*, **28**, 69 (1921).   I seize this opportunity for stating that, owing to an oversight, a factor 2 is missing in that paper in the intensity expressions of all those components for which I am indebted to Mr. Slack for drawing my attention to this omission.

[11] This formula is due to Sonin (*Math. Ann.*, **16**, 40, 1880).   See, also, N. Nielsen, *Cylinderfunktionen*, p. 184.   Leipzig, 1904.

[12] C. F. Gauss, *Werke*, Vol. III, p. 213.   Goettingen, 1876.

[13] In this formula the first letter e represents the basis of natural logarithms, the second the charge of the electron.

ON A FLUORESCENCE SPECTRUM OF OXYGEN

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The spectrum of the light from a mercury arc scattered by oxygen at atmospheric pressure and photographed with a quartz spectrograph shows, besides the Raman lines which have been reported by the writer in other notes,[1] a series of doublets, extending from the ultra-violet limit of the spectrum on the plate down to the visible region.   This appears as a fluorescence spectrum excited by the resonance line λ1849 of mercury, which is strongly absorbed in O_2.

As it seems that this fluorescence of oxygen had never been noticed before, probably because of its extreme weakness, exposures of 50 to 80 hours being needed to bring it out, and, as on the other hand, I have been able to determine its relationship with the known O_2 bands, I will give a brief account of the results obtained.

A large Hilger quartz spectrograph was used.   Wave-lengths were measured by comparison with an iron arc spectrum to an accuracy ranging from ± 0.3 Å in the visible to ± 0.1 in the far ultra-violet.

Before giving the observed wave-lengths of the lines, it is better to explain the general structure of this spectrum.

From Ossenbrüggen's work,[2] we know very well the structure of the Schumann-Runge band system of O_2, a $^3S \longrightarrow {}^3S$ transition, according to