THE CONTINUOUS SPECTRA OF HYDROGEN LIKE ATOMS

A THESIS

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INTRODUCTION:

As is well known, the Bohr-Sommerfeld quantum theory of atomic phenomena and structures provided, in itself, no explanation of the intensities of spectral lines or of the probabilities of transition between the stationary states. The theory of these problems had its origin in the additional postulate made by Bohr in 1918, which is called the Correspondence Principle.

The Correspondence Principle states that in the limit of large quantum numbers, or in the limit as h is made to approach 0, the intensities and polarization of the radiation emitted by a mechanical atomic system, when considered quantum mechanically, is to be the same as that which would be predicted for the same mechanical system by classical electrodynamics. It postulates, in addition, that this correspondence is approximately maintained even when the quantum numbers are not large.

Altho this principle has offered a very powerful method for the investigation of many atomic phenomena, it has suffered from two fundamental difficulties. The first may be explained as follows. Classically, the intensities of the radiation frequencies emitted by an electron moving in an orbit is determined by the amplitudes of the Fourier components into which the electric moment of the electron may be resolved. Quantum theoretically, radiation is emitted only as the result of a transition between two stationary states. The Correspondence Principle offers no unique way of deciding, in general, which is the state, final or initial, whose amplitudes are to determine the radiation, or a method of averaging the amplitudes of the two states, if that be the reasonable procedure. Indeed, for large quantum numbers it makes little difference which of the two states is chosen, or what averaging process is used, but, in principle, the ambiguity still persists even in these regions. Only when the amplitudes for both states, and those intermediate, are 0, is the unique prediction made that these transitions do not occur and that hence the intensity of the corresponding radiation is also 0.

The other difficulty lay in the ambiguity arising when the atomic system is degenerate, as is the case for the Kepler hydrogen problem. Here, as for a given energy state there is a multiplicity of equivalent orbits, the question must be answered as to which orbit of this manifold is to be resolved into Fourier components to determine the intensities of the radiation. The Correspondence Principle, as stated, does not supply the answer. However, this difficulty may be avoided, in some cases, if the degenerate system is considered as the limit of a perturbed system in which the degeneracy is removed.

It is one of the significant achievements of the Theory of Quantum Mechanics that it does remove these ambiguities characteristic of the Correspondence Principle, as stated by Bohr. And this simply consists in giving a precise definition of the electric moment to be associated with the electron, while computing from it by the classical electrodynamical formulae the radiation that is to be emitted.

In the language of the Wave Mechanics, this definition may be stated as follows: If the two states, defined by the quantum numbers n, m, have associated with them the normalized eigenfunctions ψ_n and ψ_m, the matrix element of the coordinate q for the transition between these states is given by:

(1) $$q_{nm} = \int q\psi_n\psi_m^* d\tau$$

where the integration is to be extended over the space for which the eigenfunctions were defined, which may be three dimensional or not, and where * designates the conjugate value, in case the ψ's are complex. The "moment" corresponding to this transition is then given by:

(1a) $$M_{nm} = q_{nm}e^{\frac{2\pi i}{h}(E_n-E_m)t}$$

where En, Em are the energies or eigenvalues corresponding to the states. And the electric moment which is to determine the radiation by the classical electrodynamical formulae is obtained by multiplying M_{nm} by e, the charge of the electron.

The precise definition (1) obviously removes the first difficulty, mentioned above, of the older quantum theory. And when the system is degenerate, under the assumption that the various components of the degenerate state act independently, or incoherently, the total intensity of the transition from E_n to E_m is given by summing the individual intensities for the possible transitions between the various pairs of components, each corresponding to an (n m) transition for the energy. Thus the second difficulty is resolved also.

When the Schrodinger wave equation for the atomic system permits a continuous as well as a discrete set of eigenvalues, as does the Kepler problem, the definitions (1), (1a) are still valid. In this case, one or both of the indices (n m) are no longer integral, but may assume a continuous range of values. When only one is non-integral, the matrix element q_{nm} corresponds to a transition between a discrete state and a continuous state, or between a quantized elliptic and an unquantized hyperbolic state, in the language of the old Bohr model. Such transitions give rise to continuous spectra, each of which begins at the limit of the discrete spectrum, the transitions of which have as a final state, for emission, the same as that of the particular continuous spectrum. This type of continuous spectrum is sometimes called the "affinity" spectrum of the atomic or molecular system.

When neither of the indices (n m) is integral, the transition is that between two hyperbolic unquantized states, and the spectrum is the general continuous spectrum with no definite limits. The interpretation, given here, of the origin of the continuous spectra was first proposed by Bohr $^{1)}$.

It must be stated that altho, formally, the definition (1) is maintained also for the continuous spectra, it may happen that the integral does not converge, thus making the definition meaningless. Hence, in general, the integrals (1) for continuous spectra are replaced by the expressions:

$$(1b) \qquad q_{Em} = \lim_{\Delta E \to 0} \frac{1}{\Delta E} \int q \psi_m \left[\int_E^{E+\Delta E} \psi(\eta)\, d\eta \right] d\tau \quad ,$$

where m is the discrete integar and E represents the eigenvalue of the continuous range. And if m is also non-integral, but corresponds to the continuously varying eigenvalue, (1) is always divergent and it must be replaced by:

$$(1c) \qquad q_{\varepsilon E} = \lim_{\substack{\Delta E \to 0 \\ \Delta \varepsilon \to 0}} \frac{1}{\Delta E \Delta \varepsilon} \int q \int_{\varepsilon}^{\varepsilon+\Delta\varepsilon} \psi(\eta)\, d\eta \int_E^{E+\Delta E} \psi(\xi)\, d\xi \; d\tau .$$

In almost all cases, however, the convergence of (1b) permits the change of the order of integration and removal of the limiting process; then (1b) becomes identical with (1). This actually occurs in the present problem. (cf. (5) below.)

STATEMENT OF THE PROBLEM.

Altho the definition (1a) is common to all the equivalent forms of the Quantum Mechanics, the definition of the matrices q_{nm} by (1) is that to be applied only in the wave mechanical treatment of the atomic problem. In the Matrix Mechanics, the q_{nm} are evaluated directly by algebraical processes from the matrix formulation of the problem. And in fact, Schrodinger 2) and Eckart 3) were led to the wave mechanical definition (1) by the requirement that their definition must be equivalent to that which would be implied by the postulates of the Matrix Mechanics.

However, these derivations by the Matrix Mechanics break down in case either or both of the indices (n m) refer to a continuous range of eigenvalues. The operator method of Born and Wiener 4) was then devised to take care of these cases; but, as yet, no problems of significance have been solved in this way. In general, too, the processes of analysis involved in the wave mechanical treatment of the quantum theory seem less abstruse, altho they are often quite complicated. Hence this method, and definition (1) will be adopted here.

The intensities of the line spectra of hydrogen have been calculated by the wave mechanics by Schrodinger 5), Epstein 6), Sugiura 7), and Kupper 8). The matrices for the continuous spectra have as yet not been satisfactorily treated, except as noted below.

As these continuous matrices are necessary for the treatment of other phenomena, as the photoelectric effect, rates of recombination, intensities of X rays, as well as for the study of the continuous spectra themselves, the present investigation for their evaluation was undertaken.

In particular, only the matrices corresponding to transitions between a discrete and continuous state in a hydrogen like atom are here evaluated. This problem has been generally treated by Oppenheimer 9), but his final results are not satisfactory for detailed discussion. And Sugiura 7) has given the matrices for the special cases where the discrete state is the lowest of the Lyman, Balmer and Paschen series of levels. The present analysis yields general formulae and such as are convenient for numerical computation.

Specifically then, the problem here investigated is the evaluation of the Schrodinger matrices for the affinity spectrum of hydrogen like atoms. This is an essentially analytical problem. And for completeness, the derivation of some results, as the normalization of the eigenfunctions and the integrals of the spherical harmonics, that have been previously given by others, will be derived here, too.

As given by Schrodinger, the wave equation for an unperturbed non-relativistic hydrogen like atom of atomic number Z, is :

$$(2) \qquad \nabla^2\psi + \frac{2\mu}{K^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0.$$

Here, ψ, is the amplitude function, μ, e, the mass and charge of the electron, $K = h/2\pi$, h is Planck's constant, r is the distance of the electron from the nucleus, taken as at rest, and E is the energy constant of the atomic system. When this equation is separated in the polar coordinates (r, θ, Φ), the solution is given by:

$$(3) \qquad \psi = P^m_{k-1}(\cos\theta)\,{\cos \atop \sin} m\Phi\,\chi(r)$$

where

$$(4) \qquad \frac{d^2\chi}{dr^2} + \frac{2}{r}\frac{d\chi}{dr} + \left(\frac{2\mu E}{K^2} + \frac{2\mu Ze^2}{K^2 r} - \frac{(k-1)k}{r^2}\right)\chi = 0.$$

In (3) and (4), $k \geqslant 1$, and is integral; $0 \leqslant m \leqslant k-1$, and m is integral also; $P^m_{k-1}(\cos\theta)$ is the associated spherical harmonic of degree k-1 and order m. Both $\cos m\Phi$ and $\sin m\Phi$ satisfy the Schrodinger conditions of peridiocity in Φ, and hence either may be used, excepting the case for which $m = 0$, when only the former is not trivial. Thus, it may already be noted that with the exception of this case the system has a two fold degeneracy with respect to the quantum number m.

Referring now to (1), the essential problem of this investigation is the evaluation of the matrix integrals:

$$(5) \qquad q(n, k,m;n',k',m') = \int q\psi(n,k,m)\psi^*(n',k',m')d\tau ,$$

where n, n' are parameters, defined exactly below, for the eigenvalues of E; q is a coordinate, either x, y, or z; $d\tau = r^2\sin\theta d\theta d\Phi dr$, and the integration is extended over the whole coordinate space.

PROPERTIES OF THE WAVE FUNCTIONS.

Before proceeding with the solution of the problem, just stated, it will be well to analyze some of the properties of the eigenfunctions $\chi(r)$, and also to obtain their asymptotic expansions. Thruout these considerations, the notation of Epstein 6) will be used.

Equation (4) was studied by Schrodinger in his first paper 10). To satisfy the requirements of single-valuedness, continuity and finiteness for ψ, and hence for $\chi(r)$, Schrodinger found the following to be true. Such solutions, $\chi(r)$, exist for all values of E for which $E > 0$. These values of E correspond to the hyperbolic orbits in the old Bohr model of the hydrogen like atom. And as all such E's are allowed, they are said to form a continuous spectrum of energy states.

If, however, the value of E corresponds to an elliptic orbit, i.e. if $E < 0$, solutions ψ, satisfying the requirements, exist only if E satisfies the relations:

$$(6) \qquad \frac{\mu e^2 Z}{K^2 \alpha} = -n \equiv -(s+k); \qquad \alpha^2 = -\frac{2\mu E}{K^2},$$

where n is a positive integar ≥ 1. (6), when rearranged, gives directly the Bohr expression for the energy of the stationary states of the hydrogen like atom. (6) also serves to define the parameter s, which is integral if n is integral. s corresponds to the radial quantum number, whereas k corresponds to the azimuthal quantum number of the older quantum theory. The series of integars n defines the discrete spectrum of energy states.

It is convenient to use the notation of (6) also for the case where $E > 0$. Then, α, and n are imaginary, and s is complex.

Schrodinger [10)] has given the explicit solutions of (3) as polynomials multiplied by exponentials, for the discrete eigènfunctions, and as contour integral expressions for the continuous eigenfunctions. For the present investigation it will be more convenient to use the general representations and method of Epstein [6)].

Thus, the dependent variable $\chi(r)$ is first changed to M(s,2k,r) by the substitution:

(7) $$\chi(r) = r^{k-1}e^{\alpha r}M(r).$$

M(r), then, satisfies the equation:

(7a) $$\frac{d^2M}{dr^2} + 2(\alpha + \frac{k}{r})\frac{dM}{dr} - \frac{2\alpha s}{r} M = 0,$$

using the notation of (6). The solution of this, satisfying the condition of finiteness, is directly seen to be:

(8) $$M(s,2k,r) = 1 + \frac{s}{1!2k}(2\alpha r) + \frac{s(s-1)(2\alpha r)^2}{2!2k(2k+1)} + \ldots.$$

This can be expressed as the following limiting form of a hypergeometric function:

(8a) $$M(s,2k,r) = \lim_{\substack{x\to 0;\,\beta\to\infty \\ \beta x = r}} F(-s,\beta,2k,-2\alpha x).$$

It may be noted, here, that if s is an integer, (8) reduces to a polynomial which is easily shown to make (7) equivalent to Schrodinger's expression for the discrete $\chi(r)$. Otherwise, (8) is an infinite series.

By means of (8a) a recurrence relation for the functions M may be readily obtained. For it may be easily verified that:

$$(b-c+1)zF(a,b,c,z) - (c-1)(1-z)F(a,b,c-1,z) + (c-1)F(a-1,b,c-1,z) = 0.$$

Proceeding to the limits as indicated in (8a), the relation follows:

$$(9) \qquad 2\alpha r M(s,2k,r) = (2k-1)\left[M(s+1,2k-1,r) - M(s,2k-1,r)\right] .$$

This formula will be of use later. It holds for the M's representing both the discrete and continuous eigenfunctions.

As noted above, for the continuous spectrum, α is imaginary and s is complex. The question then suggests itself as to the complex nature of the functions $\chi(r)$. It will now be shown that the $\chi(r)$ are real. It is first convenient to introduce the notation:

$$(6a) \qquad n \equiv i\lambda \equiv -\frac{t}{\alpha} ; \quad \alpha \equiv i\gamma ; \quad n' \equiv -\frac{t}{\alpha'} .$$

Now it is well known 11) that the hypergeometric functions F(a,b,c,z) can be represented by the definite integral:

$$F(a,b,c,z) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(c-a)} \int_0^1 t^{a-1}(1-t)^{c-a-1}(1-zt)^{-b}dt.$$

Applying this to (8a), and noting that $\lim_{w\to\infty}(1+x/w)^{-w} = e^{-x}$, $\chi(r)$ takes the form:

$$(10) \qquad \chi(r) = \frac{r^{k-1}\Gamma(2k)}{|\Gamma(k-n)|^2} \int_0^1 e^{-(2t-1)\alpha r} t^{k-n-1}(1-t)^{k+n-1}dt.$$

Making the change of variables: $t = (\gamma-y)/2\gamma$, $\chi(r)$ becomes:

$$(11) \qquad \chi(r) = \frac{r^{k-1}\Gamma(2k)}{|\Gamma(k-n)|^2(2\gamma)^{2k-1}} \int_{-\gamma}^{\gamma} (\gamma^2-y^2)^{k-1}\cos\left(ry + \lambda\log\frac{\gamma+y}{\gamma-y}\right) dy \quad ,$$

which is obviously a real expression.

The real character of $\chi(r)$ appears in a somewhat different way in the following derivation of its asymptotic expansion. If in (10) the integral from 0 to 1 is divided as:

$$\int_0^1 \Big[\quad \Big] dt = \int_0^{-i\infty} \Big[\quad \Big] dt - \int_1^{-i\infty} \Big[\quad \Big] dt ,$$

and if in the latter integral the change of variables w = 1-t is made, then:

$$(12) \; \chi(r) = \frac{r^{k-1}\Gamma(2k)}{|\Gamma(k-n)|^2}\left\{ \int_0^{-i\infty} e^{(1-2t)\alpha r} t^{k-n-1}(1-t)^{k+n-1}dt + \int_0^{i\infty} e^{(2t-1)\alpha r} t^{k+n-1}(1-t)^{k-n-1}dt \right\}.$$

As the expression within the brackets is the sum of two conjugates, this again shows that the $\chi(r)$ are real, altho (12) does not give the real part in the explicit form of (11).

The asymptotic expansion for $\chi(r)$ follows after expanding the term $(1-t)^{k+n-1}$ as:

$$(1-t)^{k+n-1} = \sum_{0}^{j}{}_{m} f_m t^m + R_j(t),$$

in which $\lim_{j\to\infty} R_j(t) = 0$, if $|t| < 1$, and similarly for $(1-t)^{k-n-1}$. As, here, $|t|$ is not always < 1, the series obtained by the formal expansion $\sum_{0}^{\infty}{}_{m} f_m t^m$ is divergent; still, it gives in Poincare's sense, the asymptotic expansion for $\chi(r)$ when substituted in the integrals of (12). This is now explicitly obtained by setting $t = -iy$ and noting that the resulting integrals are Gamma functions. The result is:

$$(13)\quad \chi(r) \sim \frac{\Gamma(2k)}{|\Gamma(k-n)|^2\, r}\left\{\frac{e^{\alpha r} r^n}{(2\lambda)^{k-n}} \sum_{0}^{\infty}{}_{m} f_m \frac{\Gamma(m+k-n)}{(2\alpha r)^m} + \text{complex conjugate}\right\}.$$

Leaving aside the terms in (13) for which $m > 0$, the asymptotic expansion for $\chi(r)$ may be written as:

$$(14)\qquad \chi(r) \sim \frac{2\Gamma(2k)}{r}(S\cos\delta - T\sin\delta), \text{ where:}$$

$$(14a)\qquad \delta = \gamma r + \lambda\log r;\quad S + iT = \frac{1}{\Gamma(k+n)\ (2\alpha)^{k-n}};\quad S^2 + T^2 = \frac{e^{-\pi\lambda}}{|\Gamma(k+n)|^2(2\gamma)^{2k}}.$$

It is interesting to note that the asymptotic expansion for $\chi(r)$ may also be obtained readily by beginning directly with the double loop contour integral expression, about (1,0) for the hypergeometric function. 11) This may then be expressed linearly in terms of the single loop contours about $t = 0$ and $t = 1$, respectively 11), for which the asymptotic expansions are already given by Schlesinger, page 220. The equations are the following:

$$\chi(r) = \frac{r^{k-1}e^{\alpha r}\Gamma(2k)}{|\Gamma(k-n)|^2}\int_{(1,0)} t^{k-n-1}(1-t)^{k+n-1}e^{-2\alpha rt}dt/(1-e^{-2\pi in})(1-e^{2\pi in})$$

$$= \frac{r^{k-1}e^{\alpha r}\Gamma(2k)}{|\Gamma(k-n)|^2(-1)^{k+n-1}}\Bigl[\int_{(1)} t^{k-n-1}(t-1)^{k+n-1}e^{-2\alpha rt}dt/(1-e^{2\pi in})$$

$$- \int_{(0)} t^{k-n-1}(t-1)^{k+n-1}e^{-2\alpha rt}dt/(1-e^{-2\pi in})\Bigr]$$

$$\sim \frac{r^{k-1}e^{\alpha r}\Gamma(2k)}{|\Gamma(k-n)|^2(-1)^{k+n-1}}\Bigl[(-1)^{k+n-1}\Gamma(k+n)e^{-2\alpha r}(-2\alpha r)^{-k-n}$$

$$- (-1)^{k-n-1}\Gamma(k-n)(-2\alpha r)^{n-k}(-1)^{k+n-1}\Bigr]$$

$$= \frac{\Gamma(2k)}{|\Gamma(k-n)|^2 r}\Bigl[\frac{e^{\alpha r}r^n\Gamma(k-n)}{(2\alpha)^{k-n}} + \text{complex conjugate}\Bigr],$$

which is the value found above in (13).

NORMALIZATION:

As mentioned above, in order for the integrals:

$$q(n,k,m;n',k',m') = \int q\psi(n,k,m)\psi^*(n',k',m')d\tau \tag{5}$$

to be physically interpretable as the equivalents of the quantum mechanical matrix amplitudes, the eigenfunctions of the integrand must be normalized eigenfunctions. This means that the functions ψ of (3) must be multiplied by such factors as will make

$$\int\psi(n,k,m)\psi(n',k',m')d\tau = \delta_{nn'}\delta_{kk'}\delta_{mm'} , \tag{15}$$

where $\delta_{ij} = \begin{matrix} 0 & i = j \\ 1 & i \neq j \end{matrix}$. In the usual manner, the requirement is made that the functions of r, θ, and Φ be normalized separately. This obviously satisfies the general condition (15). To effect the normalization, then, the integrals:

$$N_r^2(n,k) \equiv \int_0^\infty r^2\chi^2(n,k,r)dr \quad , \tag{15a}$$

$$N_\theta^2(k-1,m) \equiv \int_0^\pi \left\{P_{k-1}^m(\cos\theta)\right\}^2 \sin\theta d\theta, \tag{15b}$$

$$N_\Phi^2(m) \equiv \int_0^{2\pi} \begin{matrix}\cos\\ \sin\end{matrix} m\Phi \begin{matrix}\cos\\ \sin\end{matrix} m\Phi \, d\Phi \quad , \tag{15c}$$

are evaluated and the normalized eigenfunction is then written as:

$$\psi_{n,k,m} = \frac{\chi(n,k,r)P_{k-1}^m(\cos\theta)\begin{matrix}\cos\\ \sin\end{matrix} m\Phi}{N_r(n,k)\ N_\theta(k-1,m)\ N_\Phi(m)} . \tag{16}$$

In (15) and (15a) the conjugate notation has been omitted for as has been shown above the $\chi(r)$ are real.

Clearly, by the above definitions:

$$N_\Phi^2(m) \begin{matrix} = \pi, & m \neq 0 \\ = 2\pi, & m = 0 \end{matrix} . \tag{17}$$

$$N_\theta^2(k-1,m) = \frac{2(m+k-1)!}{(2k-1)(k-m-1)!} . \tag{18}$$

In the evaluation of $N_r(n,k)$ the case in which $\chi(r)$ refers to the discrete spectrum must be distinguished from that in which it refers to the continuous spectrum. In the former case, the evaluation has been carried thru by Epstein 6), among others, with the result that:

(19)
$$N_r^2(n',k) = \frac{2n'\overline{(2k-1)!}^2(n'-k)!}{(n'+k-1)!(-2\chi')^{2k+1}}$$

It may be noted that the quite different expressions given by others, as for example, by Sommerfeld in his Erganzungsband p. 77, is due to the different definition, with respect to the arbitrary constant coefficient, of the functions $\chi(r)$. When this is taken into account, the apparently different values of N_r are readily seen to be identical.

However, when the $\chi(r)$ refer to the continuous spectrum, for which n is imaginary, the normalization cannot be carried out directly. For from the asymptotic expansion (14) it is seen that for large values of r, $\chi(n,k,r)$ behaves as $1/r$, and hence the integral $\int_0^\infty r^2\chi^2(n,k,r)\,dr$ does not converge. The theory of the normalization under these circumstances has been worked out by Fues 12), and his method will be applied here.

Formally, the normalization and orthogonality conditions for a system of discrete and continuous eigenfunctions, as stated by Fues, and based on the researches of Weyl 13), are:

(20)
$$\int DU_kU_l\,dx = \delta_{kl} \quad ,$$

(20a)
$$\int DU_k\Delta_nF\,dx = 0 \quad ,$$

(20b)
$$\frac{1}{\Delta_nE}\int D\Delta_nF\Delta_mF\,dx = \delta_{nm} \; ,$$

where D represents the usual density factor, and x is a symbol for all the integration variables. Δ_nF, Δ_mF are "eigen differentials", defined by:

(21)
$$\Delta_nF \equiv \int_{\Delta_nE} U(E,x)\,dE \equiv \int_{\Delta_nE} \psi(E)u(E,x)\,dE \quad .$$

$U(E,x) \equiv \psi(E)u(E,x)$ is the normalized eigenfunction for the continuous range, and $\psi(E)$ is the normalizing factor equivalent to $1/N_r N_\theta N_\Phi$ of (16). U_k, U_l are the normalized eigenfunctions for the discrete range. $\Delta_n E$ is the n^{th} infinitesimal interval of the infinity into which the continuous range of eigenvalues is supposed to be divided. Here, the eigenvalues for two states will be denoted by the letters E, ε. As a whole, for the normalization of the continuous eigenfunctions the eigen differentials play the role of the eigenfunctions themselves.

In (20b) the order of integration may be changed for one of the $\Delta_n F$ (this obviously cannot be repeated for the second $\Delta_m F$, as the divergent integral will then be obtained); the result is that:

$$\frac{1}{\Delta_n E}\int_{\Delta_n \varepsilon}\left[\int D\psi(\varepsilon)u(\varepsilon,x)\int_{\Delta_m E}\psi(E)u(E,x)\,dE\,dx\right]d\varepsilon = \delta_{nm} \quad .$$

This, however, can be true for any arbitrary interval $\Delta_n E$ only if:

$$\int D\psi(\varepsilon)u(\varepsilon,x)\int_{\Delta}\psi(E)u(E,x)\,dE\,dx = \begin{matrix}0\\1\end{matrix} \quad , \tag{22}$$

as ε belongs or does not belong to the interval Δ .

An equivalent but much more useful form of the normalization condition is derived by Fues as follows: Let the original Sturm Liouiville equations for E and ε be:

$$L\left[U(E,x)\right] + DEU(E,x) = 0 \quad ,$$

$$L\left[U(\varepsilon,x)\right] + D\varepsilon U(\varepsilon,x) = 0 \quad ,$$

where L is the self-adjoint differential form: $L(y) = (Py')' - Qy$. If these are multiplied by $U(\varepsilon)$ and $-U(E)$, respectively, and added, the equation results:

$$U(\varepsilon,x)\left[PU'(E,x)\right]' - U(E,x)\left[PU'(\varepsilon,x)\right]' = (\varepsilon - E)DU(E,x)U(\varepsilon,x) \quad .$$

If this be now divided by $\varepsilon - E$, integrated with respect to E over the range Δ, and then with respect to x over the domain, the right hand side becomes the integral of (22) and the left side gives the equivalent condition, namely:

$$(23)\qquad \int dx \left\{ \int_{\Delta} \psi \frac{(E)\psi(\varepsilon)}{E-\varepsilon} \left[u(E,x)\{Pu'(\varepsilon,x)\}' - u(\varepsilon,x)\{Pu'(E,x)\}' \right] dE \right\} = \begin{matrix} 0 \\ 1 \end{matrix}$$

as ε lies or does not lie in Δ.

It should be noted that (23) gives the normalization of u(x) for the scale of eigenvalues, E. But by (4) and (6), the true eigenvalues of the $\chi(r)$ functions are $(-\alpha^2)$ rather than the energies E themselves. Hence if (23) be applied to the $\chi(r)$ functions with E, dE referring to the energies, and if the normalization is to be obtained for the scale of energy values, as is desirable for the physical interpretation of the problem, the integral of (23) should be given the value $\frac{d}{dE}(-\alpha^2) = \frac{2\mu}{K^2}$ instead of the value 1.

This may also be effected by making the change of variable in (4) as: $\rho = \sqrt{\frac{2\mu}{K^2}}\, r$, at the very beginning of the analysis. Then the energy E will appear thruout as the eigenvalue itself. However, in this case, the coordinate matrices must be integrals with respect to ρ, instead of r, and the dx in (23) will be $d\rho$ also. The normalization factors will appear to be quite different in the two cases, but the final matrices, which alone are of physical interest, will be fully equivalent. In fact, the above change of variable will simply replace in all the equations of the present analysis α by $\sqrt{-E}$; and it is not difficult to show from this that the final matrix amplitudes obtained by the two methods are actually equivalent.

Here, the first of the above methods will be applied; hence, (23) takes the form, for the $\chi(r)$ functions:

$$(23a)\qquad \begin{matrix} 0 \\ \frac{2\mu}{K^2} \end{matrix} = \lim_{r \to \rho} \int_{\Delta} \frac{\psi(E)\psi(\varepsilon)\, dE}{E-\varepsilon} \int_0^r \left[\chi(E,r)\{P\chi'(\varepsilon,r)\}' - \chi(\varepsilon,r)\{P\chi'(E,r)\}' \right] dr$$

$$= \lim_{r \to \rho} \int_{\Delta} \frac{\psi(E)\psi(\varepsilon)\, dE}{E-\varepsilon} \Big[P\{\chi(E,r)\chi'(\varepsilon,r) - \chi(\varepsilon,r)\chi'(E,r)\} \Big]_0^r .$$

As by (4), $P = r^2$ for the $\chi(r)$ functions, the integrand vanishes at $r = 0$; and as r may be taken arbitrarily large, the asymptotic expansion for $\chi(r)$ may be used at the upper limit.

Thus by (14), the value of the above bracket at the upper limit is:

$$
\begin{aligned}
4\overline{\Gamma(2k)}^{2}\Big[& \cos\delta(E)\cos\delta(\epsilon)\left\{T(E)S(\epsilon)\delta'(E) - T(\epsilon)S(E)\delta'(\epsilon)\right\} \\
& + \sin\delta(E)\sin\delta(\epsilon)\left\{T(E)S(\epsilon)\delta'(\epsilon) - T(\epsilon)S(E)\delta'(E)\right\} \\
& - \sin\left[\delta(E)+\delta(\epsilon)\right]\left\{T(E)T(\epsilon) - S(E)S(\epsilon)\right\}\left\{\frac{\delta'(E) - \delta'(\epsilon)}{2}\right\} \\
& + \sin\left[\delta(E)-\delta(\epsilon)\right]\left\{T(E)T(\epsilon) + S(E)S(\epsilon)\right\}\left\{\frac{\delta'(E) + \delta'(\epsilon)}{2}\right\}\Big] .
\end{aligned}
$$

By (14a), for large r, $\delta = \gamma r + \lambda \log r \sim \gamma r$; $\delta' = \gamma + \lambda/r \sim \gamma$; and by (6), $\gamma = -i\alpha \sim \sqrt{E}, \sqrt{\epsilon}$. Thus S, T, and it may be assumed also for the functions $\psi(E)$, $\psi(\epsilon)$, are slowly varying functions of E, ϵ, while if r is large δ varies rapidly with E, ϵ ; hence in the integration of (23a) with respect to E, the trigonometric functions oscillate very rapidly, so that unless $E \sim \epsilon$ the integration will give a value which vanishes as $r \to \infty$.

On the other hand, if $\epsilon \to E$ and $r \to \infty$, all the terms, except the last, in the above bracket remain finite when divided by $E-\epsilon$. Hence their integration over the infinitesimal non-vanishing range of E will actually vanish as $\epsilon \to E$. However, as to the last term, the result is different, for:

$$
\frac{\sin\left\{\delta(E)-\delta(\epsilon)\right\}}{E-\epsilon}\left\{T(E)T(\epsilon) + S(E)S(\epsilon)\right\}\left\{\frac{\delta'(E) + \delta'(\epsilon)}{2}\right\} \xrightarrow[\epsilon \to E]{} \frac{\mu r\left\{T^2(E)+S^2(E)\right\}}{K^2}
$$

Hence this term must be actually integrated. Therefore the normalization requirement reduces to:

$$
\frac{2\mu}{K^2} = 4\overline{\Gamma(2k)}^{2}\psi^2(E)\left\{T^2(E)+S^2(E)\right\}\gamma(E)\int_{\epsilon-\eta}^{\epsilon+\eta} \sin\left[r\sqrt{\frac{2\mu}{K^2}}(\sqrt{E}-\sqrt{\epsilon}) + \frac{tK}{\sqrt{2\mu}}\log r \cdot \left(\frac{1}{\sqrt{E}} - \frac{1}{\sqrt{\epsilon}}\right)\right] dE
$$

Setting: $x = \frac{r\sqrt{2\mu}}{K}(\sqrt{E} - \sqrt{\epsilon})$; $b = \frac{tK^2}{2\mu\sqrt{E\epsilon}} \frac{\log r}{r}$, then, as $\frac{\log r}{r} \to 0$ as $r \to \infty$, b is very small and may be considered as relatively constant, altho E does vary.

Also, $dE/(E-\zeta) \sim dx/x$; the limits, for $r \to \infty$, become $-\infty$ and $+\infty$, and the integral becomes: $\int_{-\infty}^{+\infty} \frac{\sin(x-bx)}{x} dx = \pi$, as $|b| < 1$, in the limit. Hence, finally, the normalization factor $\psi(E)$ is given by:

$$(24) \quad \frac{1}{N_r^2(n,k)} \equiv \psi^2(E) = \frac{2\mu}{4\pi K^2 \gamma(E)\{T^2(E)+S^2(E)\}\Gamma(2k)^2} = \frac{\mu e^{\pi\lambda}(2\gamma)^{2k-1}|\Gamma(k+n)|^2}{\pi K^2 \Gamma(2k)^2} .$$

It may be noted that (24) differs in two respects from the normalization factor (19) for the discrete spectrum, which may now be written as:

$$(24a) \quad \frac{1}{N_r^2(n',k)} \equiv \psi^2(E') = \frac{(2\alpha')^{2k+2}\Gamma(n'+k)}{4t\Gamma(n'-k+1)\Gamma(2k)^2} .$$

In the first place, (24a) refers to the intensity of a single line, ($\Delta n' = 1$), while (24), as remarked above, refers to the density of intensities in the energy scale $\Delta E = 1$. This involves the factor $\frac{dn}{dE} = \frac{-\mu t}{K^2\alpha^3}$, by (6) and (6a). Multiplying (24) by this factor and then rearranging it so as to have the form of (24a), it is found that the remaining ratio is $\frac{(-1)^k e^{\pi\lambda}}{2\sinh \pi\lambda} = \frac{(-1)^{-s}}{2 \sinh \pi\lambda}$. This factor is essentially due to the fact that the definitions of $\chi(r)$ by the series (8) involves a contour about (0,1) for the continuous eigenfunctions, while it involves simply a circuit about $t = 0$ for the discrete $\chi(r)$, (cf. (14a)). However, as $\lambda \to \infty$, i.e. as $E \to 0$, the above factor becomes 1, and then (24) and (24a) become formally identical, as they should at their common limit.

EVALUATION OF THE MATRIX INTEGRALS.

It follows directly from the definition of the Schrodinger matrices (5), that all the matrix elements involve the evaluation of an integral of the form:

$$(25)\qquad X(n,k;n',k') = \int_0^\infty r^3 \chi(n,k,r)\chi(n',k',r)dr \, .$$

Epstein 6), among others, has evaluated these integrals for the case where n and n' are integars, i.e. for matrix elements corresponding to transitions between two discrete states. His method consisted essentially in the following: the evaluation of the above integral is first reduced to the evaluation of the integrals:

$$(26)\qquad R(s,s') = \int_0^\infty r\chi(s,k,\alpha,r)\chi(s',k,\alpha',r)dr,$$

where s, s' are given by (6). A differential equation was then deduced which R(s,s') satisfied, and this was explicitly solved. The same method has been used by Epstein 14) to compute the intensities of the components of the Stark effect patterns for hydrogen like atoms.

However, for the case when one of the functions $\chi(r)$ in (25) refers to a continuous state, the evaluation of the integrals X have been given by Oppenheimer 9), but not in a satisfactory form, and by Sugiura 7) for particular values of the discrete parameters. In the following, these integrals will be computed for general values of the discrete and continuous parameters, and they will be expressed in a form useful for numerical computation and discussion.

As here, too, only the evaluation of the integrals (26) is carried thru directly, the reduction of (25) to the integrals (26) will be given for completeness, altho it is outlined in Epstein's paper.

Because of the selection rules, which will be given below, the only transitions normally permissible are those which have the values of k differ by 1. Thus the only integrals that need be considered, are:

$$X(n,k\pm 1,\lambda;n',k,\lambda') = \int_0^\infty r^3\chi(\lambda,k\pm 1,r)\chi(\lambda',k,r)\,dr.$$

Applying (7) and (9) twice to the integrand, it follows that:

$$X(n,k+1,\lambda;\ n',k,\lambda') = \int_0^\infty r^3 e^{(\lambda+\lambda')r} r^k M(s,2k+2,r)r^{k-1}M(s',2k,r)\,dr$$

$$= \frac{2k(2k+1)}{4\lambda^2}\int_0^\infty r^2\,\chi(s+2,k,r) - 2\chi(s+1,k,r) + \chi(s,k,r)\}\chi(s',k,r)\,dr.$$

If now (4) be multiplied by $r^2\chi(\lambda',r)$ and if from it is subtracted the corresponding equation for $\chi(\lambda',r)$, multiplied by $r^2\chi(\lambda,r)$, and the result integrated with respect to r from 0 to ∞, the relation follows, that:

$$(27)\qquad (\lambda^2-\lambda'^2)\int_0^\infty r^2\chi(s,\lambda,k,r)\chi(s',\lambda',k,r)\,dr + 2\{(s+k)\lambda - (s'+k)\lambda'\}R(s,s',k) = 0,$$

where R(s,s') is given by (26), and the notation of (6) is introduced. Applying this to the above and noting that by (6) and (6a) $s+k+1 = \frac{-t}{\lambda}$; $s'+k = \frac{-t}{\lambda'}$, the reduction formula desired is obtained:

$$(28)\qquad X(n,k+1,\lambda;n',k,\lambda') = \frac{2k(2k+1)}{2\lambda(\lambda'^2-\lambda^2)}\left\{R(s+2,s',k) - R(s,s',k)\right\}.$$

It should be noted that the s, s' occuring on the right side are related to the n, n' of the left, by the relations: s = n-k-1; and n' = s'+k. Thus the problem is reduced essentially to the evaluation of the integrals R(s,s'). In this evaluation, and thereafter, for definiteness, the primed letters will refer to the discrete and unprimed to the continuous states.

By the definition of the Bessel functions, the following equation may be set up:

$$(29)\qquad \int_C J_{2k-1}(2\sqrt{2\bar{\lambda}yrt})\,t^{-k-\bar{s}-1/2}e^{-yt}\,dt = \sum_m \frac{(-1)^m(2\bar{\lambda}yr)^{(2k+2m-1)/2}}{\Gamma(m+1)\Gamma(2k+m)}\int_C t^{-\bar{s}+m-1}e^{-yt}\,dt.$$

Here, C is the Hankel contour for the Gamma function 15), if $\overline{s} = s$ is complex. If $\overline{s} = s'$ and is real and integral, C is a circuit about the pole $t = 0$. Then, for the first case, (29) becomes:

$$\int_C J_{2k-1}(2\sqrt{2\alpha yrt})\,t^{-k-s-1/2}e^{-yt}dt = 2i(-1)^{s+1}y^{s+k-1/2}(2\alpha r)^{k-1/2}\sin\pi s \sum_m \frac{(-2\alpha r)^m\Gamma(m-s)}{\Gamma(m+1)\Gamma(2k+m)}.$$

For the second case, (29) takes the form:

$$\int_C J_{2k-1}(2\sqrt{2\alpha' yrt})\,t^{-k-s'-1/2}e^{-yt}dt = (-1)^{s'}2\pi i(2\alpha' r)^{k-1/2}y^{s'+k-1/2} \sum_m \frac{(2\alpha' r)^m}{\Gamma(m+1)\Gamma(2k+m)(s'-m)!}\ .$$

Now by (7) and (8), the $\chi(r)$ may be expressed for the two cases as:

$$(30)\quad \chi(s,\alpha,r) = \frac{r^{k-1}e^{\alpha r}\Gamma(2k)}{\Gamma(-s)}\sum_m \frac{(-2\alpha r)^m\Gamma(m-s)}{\Gamma(m+1)\Gamma(2k+m)},\quad \text{and}$$

$$(30a)\quad \chi(s',\alpha',r) = r^{k-1}e^{\alpha' r}\Gamma(2k)s'!\sum_m \frac{(2\alpha' r)^m}{\Gamma(m+1)\Gamma(2k+m)(s'-m)!}\ .$$

Hence, it follows that for either case:

$$(31)\quad \chi(\overline{s},\overline{\alpha},r) = \frac{e^{(\overline{\alpha}r-\pi i\overline{s})}\Gamma(1+\overline{s})\Gamma(2k)r^{-\frac{1}{2}}}{2\pi i(2\overline{\alpha})^{k-\frac{1}{2}}y^{\overline{s}+k-1/2}}\int_C J_{2k-1}(2\sqrt{2\overline{\alpha}yrt})\,t^{-k-\overline{s}-1/2}e^{-yt}dt.$$

In these expressions the parameter y must have a positive real part; otherwise it drops out of the result and is arbitrary.

Now from the theory of Bessel functions 16), it may be proved that:

$$(32)\quad \int_0^\infty J_p(2\sqrt{ar})J_p(2\sqrt{br})e^{-cr}dr = c^{-1}\exp\left\{-\frac{a+b}{c} - \frac{p\pi i}{2}\right\} J_p\left(\frac{2i\sqrt{ab}}{c}\right)\ .$$

In this expression the real part of $c > 0$. So substituting for the $\chi(r)$ in (26) the expressions of (31), interchanging the order of integration -- permissible because of the convergence of the resulting integrals and of the original one-- so as to integrate with respect to r first, then with the aid of (32), the result is:

$$R(s,s') = \frac{\Gamma(1+s)\Gamma(1+s')\Gamma(2k)^2 e^{-\pi i(s+s'+k-1/2)}}{4\pi^2(\alpha+\alpha')(4\alpha\alpha')^{k-1/2}y^{s+s'+2k-1}} \int_C t^{-s-k-1/2} e^{-yt + 2\alpha yt/(\alpha+\alpha')} dt$$

$$\int_C v^{-s'-k-1/2} e^{-yv + 2\alpha' yv/(\alpha+\alpha')} J_{2k-1}\left(\frac{-4iy\sqrt{\alpha\alpha' tv}}{\alpha+\alpha'}\right) dv.$$

Setting: $u = \frac{\alpha-\alpha'}{\alpha+\alpha'}$, and carrying out the integration with respect to v according to the formulae deduced from (29), $R(s,s')$ takes the form:

$$R(s,s') = \frac{\Gamma(1+s)\Gamma(1+s')\Gamma(2k)^2 e^{-\pi i(s+k-1)}}{2\pi(\alpha+\alpha')(4\alpha\alpha')^{k-1/2}y^{s+s'+2k-1}} \left\{\frac{e^{3\pi i}y(1-u^2)}{u}\right\}^{k-1/2} (uy)^{s'+k-1/2}$$

$$\sum_m \frac{\left\{e^{3\pi i}y(1-u^2)\right\}^m}{u^m\Gamma(m+1)\Gamma(2k+m)(s'-m)!} \int_C t^{-s+m-1} e^{uyt} dt.$$

To ensure the convergence of the integrals in this last expression for $R(s,s')$, the imaginary part of y has to be so chosen so that the real part of uy is less than 0; this is clearly permissible, for thus far only the real part of y has been restricted. If the y is so chosen, the above integrals are essentially Gamma functions. When they are evaluated and the result reduced, the summation turns out to be a hypergeometric function, and the final value of $R(s,s')$ becomes:

(33) $$R(s,s',k) = \frac{(-1)^{-s}\Gamma(2k)u^{s+s'}}{(\alpha+\alpha')^{2k}} F(-s,-s',2k,1-1/u^2) .$$

As s' is real positive and integral, the hypergeometric function can be transformed so that 15):

(33a) $$R(s,s',k) = \frac{(-1)^{-s}\Gamma(2k)^2\Gamma(2k+s+s')u^{s+s'}}{\Gamma(2k+s)\Gamma(2k+s')(\alpha+\alpha')^{2k}} F\left(-s,-s',-s-s'-2k+1,\frac{1}{u^2}\right).$$

In the special case when the parameter s is also real, this expression becomes identical with the value derived by Epstein 6) for this case.

With the aid of (28) the explicit expression for the integrals X may now be given; it is:

(34) $$X(n,k+1,\alpha;n',k,\alpha') = \frac{\Gamma(2k+2)(-1)^{-s}u^{s+s'}}{2\alpha(\alpha^2-\alpha'^2)(\alpha+\alpha')^{2k}}\left\{F\left(-s,-s',2k,1-\frac{1}{u^2}\right) - u^2F(-s-2,-s',2k,z)\right\}.$$

where $z = 1 - \frac{1}{u^2}$

COMPLETE EXPRESSIONS FOR THE SCHRODINGER MATRICES.

In the notation of (16) the complete Schrodinger matrices may be written as:

$$(35)\quad q(n,k,m;n',k',m') = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \frac{q r^2 \chi(n,k,r)\chi(n',k',r) P_{k-1}^{m}(\cos\theta)P_{k'-1}^{m'}(\cos\theta)\sin\theta}{N_r(n,k)N_r(n',k')\, N_\theta(k-1,m)N_\theta(k'-1,m')} \frac{\genfrac{}{}{0pt}{}{\cos}{\sin} m\Phi \genfrac{}{}{0pt}{}{\cos}{\sin} m'\Phi \; dr\,d\theta\,d\Phi}{N_\Phi(m)N_\Phi(m')} \quad .$$

It is now convenient to introduce the following notation:

$$(36)\quad J(m,k-1;m',k'-1) = \int_0^{\pi} \frac{P_{k-1}^{m}(\cos\theta)P_{k'-1}^{m'}(\cos\theta)\cos\theta\sin\theta\,d\theta}{N_\theta(k-1,m)N_\theta(k'-1,m')} \quad .$$

$$(36a)\quad K(m,k-1;m',k'-1) = \int_0^{\pi} \frac{P_{k-1}^{m}(\cos\theta)P_{k'-1}^{m'}(\cos\theta)\sin^2\theta\,d\theta}{N_\theta(k-1,m)N_\theta(k'-1,m')} \quad .$$

$$(36b)\quad L(m,m') = \int_0^{2\pi} \frac{\genfrac{}{}{0pt}{}{\cos}{\sin} m\Phi \genfrac{}{}{0pt}{}{\cos}{\sin} m'\Phi\, d\Phi}{N_\Phi(m)N_\Phi(m')} \quad .$$

$$(36c)\quad \left.\begin{matrix} M(m,m') \\ N(m,m') \end{matrix}\right\} = \int_0^{2\pi} \frac{\genfrac{}{}{0pt}{}{\cos}{\sin} m\Phi \genfrac{}{}{0pt}{}{\cos}{\sin} m'\Phi \left\{\begin{matrix}\cos \\ \sin\end{matrix}\right. \Phi \; d\Phi}{N_\Phi(m)N_\Phi(m')} \quad .$$

Thus in terms of these integrals the matrices may be written as:

$$(37)\quad q = z = r\cos\theta : \quad z(n,k,m;n',k',m') = I(n,k;n',k')J(m,k-1;m',k'-1)L(m,m'),$$

$$(38)\quad q = \genfrac{}{}{0pt}{}{x}{y} = \genfrac{}{}{0pt}{}{r\sin\theta\cos\Phi}{r\sin\theta\sin\Phi} : \genfrac{}{}{0pt}{}{x}{y}(n,k,m;n',k',m') = I(n,k;n',k')K(m,k-1;m',k'-1)\genfrac{}{}{0pt}{}{M(m,m')}{N(m,m')},$$

where the $I(n,k;n',k')$ are defined by:

$$(37a)\quad I(n,k;n',k') = \psi(\alpha,k)\psi(\alpha',k')X(n,k,\alpha;n',k',\alpha').$$

Tho the integrals (36) have been evaluated by others, their values will be derived here, too, for completeness.

It is to be noted, first, that the ambiguity in the functions of Φ in (35) and in the integrals (36b), (36c) is simply the analytical expression for the fact that the hydrogen like atom is inherently degenerate. Furthermore, this degeneracy associated with the quantum number m is not essentially removed by such perturbations as occur in the Stark effect, till the second order perturbations are considered, as is seen from the analysis of the Stark effect theory, (cf. Epstein[14), for example).

This degeneracy with respect to Φ may also be expressed, as has been done by others, by writing $e^{im\Phi}$ for the Φ function in (16) and permitting m to assume negative as well as positive values.

Recalling (17), and the definition (36b), it follows directly that:

$$L(m,m') = \delta_{mm'} \tag{39}$$

It should be noted, however, that for $m = m' \neq 0$, the transition indicated in (35) may occur in two ways, i.e. as $\cos m\Phi \rightarrow \cos m'\Phi$, or $\sin m\Phi \rightarrow \sin m'\Phi$, and hence it must be counted twice in computing the intensities. For $m = m' = 0$, it is clear that only one such transition is possible.

Similarly, it may be easily seen from their definitions that:

$$\left.\begin{matrix} M(m,m') \\ N(m,m') \end{matrix}\right\} \neq 0, \text{ only when } \quad m \pm m' = 1. \tag{40}$$

When m, m' do satisfy the above relation, the following analysis may be made as to their particular values:

$$\begin{matrix} m = 0;\ m' = 1; \\ m = 1;\ m' = 0; \end{matrix} \left\{\begin{matrix} M(m,m') \\ N(m,m') \end{matrix}\right\} = 1/2, \text{ with only one transition;}$$

$$m-m' = +1; \begin{cases} M(m,m') = 1/2, \text{ with two equivalent transitions;} \\ N(m,m') = \pm 1/2, \text{ each with a single transition;} \end{cases} \tag{40a}$$

$$m-m' = -1; \begin{cases} M(m,m') = 1/2, \text{ with two equivalent transitions;} \\ N(m,m') = \mp 1/2, \text{ each with a single transition.} \end{cases}$$

Taking into account the degeneracy of the states for which neither m, m' are 0, with their different values for M(m,m'), N(m,m'), it follows directly that when the M(m,m') and N(m,m') are squared and summed over the possible combinations for (m,m'), each such combination will contribute 1/2 whether one of the m's is 0 or not. And by (39), $I^2(m,m')$ will contribute 2 for all $m = m' \neq 0$, and 0 for $m = m' = 0$.

The values of the integrals (36a) may be derived quite simply in the following way. From (38) and (40) it is seen that the only integrals of interest are those for which $|m \pm m'| = 1$. For this case, using the notation: $w = \cos\theta$, and the well known orthogonality properties and recurrence relations for the P_r^m, it follows that:

$$\int_0^\pi P_n^m(\cos\theta)P_r^{m+1}(\cos\theta)\sin^2\theta d\theta = \int_{-1}^{+1}\sqrt{1-w^2}P_n^m(w)P_r^{m+1}(w)dw = \int_{-1}^{+1}P_r^{m+1}(w)(\sqrt{1-w^2})^{m+1}\frac{d^m}{dw^m}P_n(w)dw$$

$$= \int_{-1}^{+1}P_r^{m+1}(w)(\sqrt{1-w^2})^{m+1}\frac{d^m}{dw^m}\left\{\frac{1}{2n+1}\left\{\frac{dP_{n+1}}{dw}(w) - \frac{dP_{n-1}}{dw}(w)\right\}\right] dw$$

$$(41) \qquad = \frac{1}{2n+1}\int_{-1}^{+1}P_r^{m+1}(w)\left[P_{n+1}^{m+1}(w) - P_{n-1}^{m+1}(w)\right]dw \quad = 0, \text{ if } |r-n| \neq 1,$$

$$(41a) \qquad \begin{aligned} &= \frac{2}{(2n+1)(2n+3)}\frac{(n+m+2)!}{(n-m)!}, \qquad \text{if } r = n+1, \\ &= \frac{-2}{(2n-1)(2n+1)}\frac{(n+m)!}{(n-m-2)!}, \qquad \text{if } r = n-1. \end{aligned}$$

Similarly, because of (37) and (39) only the integrals (36) need be considered for which m = m'. They may be evaluated as follows:

$$\int_{-1}^{+1}P_k^m(w)P_r^m(w)wdw = -\int_{-1}^{+1}\frac{w^2}{2}\frac{d}{dw}(P_k^m(w)P_r^m(w))dw = \frac{1}{2}\int_{-1}^{+1}(1-w^2)(P_k'^m P_r^m + P_k^m P_r'^m)dw.$$

Using the recurrence relation: $(1-w^2)P_r'^m = \sqrt{(1-w^2)}\,P_r^{m+1} - mwP_r^m$, the above reduces to:

$$(42)\quad \int_{-1}^{+1} P_r^m(w)P_k^m(w)\,w\,dw = \frac{1}{2(m+1)}\int_{-1}^{+1}\sqrt{(1-w^2)}\left\{P_r^m(w)P_k^{m+1}(w) + P_k^m(w)P_r^{m+1}(w)\right\}dw,$$

to which, now, (41a) may be applied.

Thus, by means of (18), (41a), and (42), the values of K and J may be tabulated as follows:

$$(43)\qquad J(m,k-1;m,k'-1) = \begin{array}{ll} \sqrt{\dfrac{(k-1)^2 - m^2}{4(k-1)^2 - 1}} & k' = k-1. \\ \sqrt{\dfrac{k^2 - m^2}{4k^2 - 1}} & k' = k+1. \end{array}$$

$$(44)\qquad K(m,k-1;m',k'-1) \begin{array}{lll} = & \sqrt{\dfrac{(m+k-1)(m+k-2)}{4(k-1)^2 - 1}} & m' = m-1;\ k' = k-1. \\ = & -\sqrt{\dfrac{(k-m+1)(k-m)}{4k^2 - 1}} & m' = m-1;\ k' = k+1. \\ = & -\sqrt{\dfrac{(k-m-1)(k-m-2)}{4(k-1)^2 - 1}} & m' = m+1;\ k' = k-1. \\ = & \sqrt{\dfrac{(m+k+1)(m+k)}{4k^2 - 1}} & m' = m+1;\ k' = k+1. \end{array}$$

The selection rules may now be written down. By (39) and (40), those for m are:

$$(45)\qquad q = z:\ \ \Delta m = 0; \qquad q = \overset{x}{\underset{y}{:}}\ \ \Delta m = \pm 1.$$

By (43) and (44), the selection rule for k follows. It is that:

(46) $\Delta k = \pm 1$, in order that the matrices do not vanish.

Now the actual intensities associated with transitions between the states (n,k,m) and (n',k',m') are proportional to the squares of the matrix elements of (37) and (38). Thus they may be expressed as:

$$I_z(n,k,m;n',k',m') = C\left|z(n,k,m;n',k',m')\right|^2$$

$$I_{\substack{x\\y}}(n,k,m;n',k',m') = C\left|\substack{x\\y}(n,k,m;n',k',m')\right|^2,$$

where C is an appropriate constant.

However, when neglecting the relativity effect, the energy of the unperturbed hydrogen like atom depends only on n or n'. Hence to obtain the intensity of transitions for a given energy change, the squared matrix elements must be summed over all the (m,m') and (k,k') permissible for the given (n,n'). This means that the intensities must be written as:

$$I_q(n,n') = C \sum_{m,k} q^2(n,k,m;n',k',m') \quad . \tag{47}$$

In this summation it must be observed that the (n,k,m) and (n',k',m') obey the inequalities: $n' \geq k' \geq m'+1$; $k \geq m+1$. Carrying thru the summation in this way, and recalling (37), (39), and (43), there result the equations:

$$\begin{aligned}
I_z(n,n') &= C \sum_{m,k} I^2(n,k;n',k') J^2(m,k-1;m',k'-1) L^2(m,m') \\
&= C \sum_{m,k} I^2(n,k;n',k') J^2(m,k-1;m,k'-1) \\
&= C \sum_k \Bigg[\frac{I^2(n,k;n',k+1)}{4k^2-1} \Big\{ 2 \overset{k-1}{\underset{1}{\sum_m}} (k^2-m^2) + k^2 \Big\} \\
&\qquad + \frac{I^2(n,k;n',k-1)}{4(k-1)^2-1} \Big\{ 2 \overset{k-2}{\underset{1}{\sum_m}} \big((k-1)^2 - m^2\big) + (k-1)^2 \Big\} \Bigg]
\end{aligned}$$

$$= \frac{C}{3} \sum_k \Big[kI^2(n,k;n',k+1) + (k-1)I^2(n,k;n',k-1) \Big] \quad . \tag{48}$$

And similarly:

$$\begin{aligned}
I_{\substack{x\\y}}(n,n') &= \frac{C}{2} \sum_{m,k} I^2(n,k;n',k') K^2(m,k-1;m',k'-1) \\
&= \frac{C}{2} \sum_k \Bigg[\frac{I^2(n,k;n',k-1)}{4(k-1)^2-1} \Big\{ \overset{k-1}{\underset{1}{\sum_m}} (m+k-1)(m+k-2) + \overset{k-3}{\underset{0}{\sum_m}} (k-m-1)(k-m-2) \Big\} \\
&\qquad + \frac{I^2(n,k;n',k+1)}{4k^2-1} \Big\{ \overset{k-1}{\underset{1}{\sum_m}} (k-m+1)(k-m) + \overset{k-1}{\underset{0}{\sum_m}} (k+m-1)(k+m) \Big\} \Bigg]
\end{aligned}$$

$$= \frac{C}{3} \sum_k \Big[kI^2(n,k;n',k+1) + (k-1)I^2(n,k;n',k-1) \Big] = I_z(n,n') \tag{49}$$

It is thus seen that the values of I corresponding to the three coordinates x,y,z are all equal, so that to get the total intensity any of them may be evaluated and the result multiplied by three. It finally remains to give the explicit expressions for the functions $I(n,k;n',k')$.

By (37a) and (34), the required expression is:

$$(50)\quad I(n,k+1;n',k) = \frac{\psi(\alpha,k+1)\psi(\alpha',k)\Gamma(2k+2)(-1)^{-s}u^{s+s'}}{2\alpha(\alpha^2-\alpha'^2)(\alpha+\alpha')^{2k}}\Big\{F(-s,-s',2k,1-\frac{1}{u^2})$$

$$- u^2F(-s-2,-s',2k,1-\frac{1}{u^2})\Big\} .$$

And as noted before, in this equation: $s+k+1 = n$; $s'+k = n'$.

With the same method by which (28) was derived, a relation between X and R can be derived in which $k' = k+1$; this leads to:

$$(51)\quad I(n,k;n',k+1) = \frac{\psi(\alpha,k)\psi(\alpha',k+1)\Gamma(2k+2)(-1)^{-s}u^{s+s'}}{2\alpha'(\alpha'^2-\alpha^2)(\alpha+\alpha')^{2k}}\Big\{F(-s,-s',2k,1-\frac{1}{u^2})$$

$$- u^2F(-s,-s'-2,2k,1-\frac{1}{u^2})\Big\} .$$

And here, $s+k = n$; $s'+k+1 = n'$.

By (50) and (51) the values to be put into (49) may be computed without difficulty. Here, the cases will be given in which the discrete level is either the Lyman or Balmer state. These are obtained by letting the s' in (50) and (51) be 0 or 1. The appropriate expressions will now be derived, no restriction on n' being made at the present.

$s' = 0$: $I(n,k+1,n',k)$: $k = n'-s' = n'$; $s = n-k-1 = n-n'-1 = i\lambda-n'-1$.

Putting in these values and (24) and (19) into (50), the result is:

$$I(n,k+1;n',k) = \frac{\sqrt{\mu}\,|\Gamma(n'+n+1)|(-4\alpha'\gamma)^{n'+1/2}e^{\pi\lambda/2}(-1)^{-n+n'+1}u^{n-n'-1}}{2\alpha(\alpha^2-\alpha'^2)K\sqrt{\pi\Gamma(2n'+1)}(\alpha+\alpha')^{2n'}}(1-u^2)$$

$$(52)\qquad = \frac{-\sqrt{\mu}\,2^{2n'+3/2}n'^{n'+2}e^{-2\lambda\tan^{-1}n'/\lambda}\lambda^{n'+3}e^{\pi\lambda/2}\sqrt{\prod_{0}^{n'}(\lambda^2+r^2)}}{Kt^2\sqrt{\Gamma(2n')\sinh\pi\lambda}(\lambda^2+n^2)^{n'+2}} .$$

In the last transformation use has been made of the relations:

$-u = e^{2i\tan^{-1}n'/\lambda}$; and: $|\Gamma(i\lambda)| = \sqrt{\pi/\lambda\sinh\pi\lambda}$ (cf. $^{15)}$).

$s' = 0$: $I(n,k;n',k+1)$: $k = n'-s'-1 = n'-1$; $s = n-k = n-n'+1$.

Hence, by (51):

$$I(n,k;n',k+1) = \frac{+2\alpha'\sqrt{\mu}\,|\Gamma(n'-1+n)|\,\Gamma(2n')(-4\alpha'\gamma)^{n'-3/2}(-1)^{-n+n'+1}u^{n-n'+1}e^{\pi\lambda/2}}{K(\alpha'^2-\alpha^2)(\alpha+\alpha')^{2n'-2}\sqrt{\pi\Gamma(2n'+1)\Gamma(2n'-2)}}$$

$$\left\{F(-s,-s',2k,1-\frac{1}{u^2}) - u^2F(-s,-s'-2,2k,1-\frac{1}{u^2})\right\} .$$

The bracket expression may be written as:

$$\frac{1}{2k(2k+1)}\left\{(u-\frac{1}{u})^2\left\{s(1-s)-n(2k+1)\right\} + n(2k+1)(\frac{1}{u^2}-u^2)\right\} = \frac{4t^4(n^2-n'^2)}{(\alpha^2-\alpha'^2)^2(2n'-1)(n'-1)n^2n'^3} .$$

Putting in this value and reducing, I(n,k;n',k+1) takes the form:

$$(53)\quad I(n,k;n',k+1) = \frac{-\sqrt{\mu}\,2^{2n'+1/2}\lambda^{n'+3}n'^{n'+1}e^{\pi\lambda/2}e^{-2\lambda\tan^{-1}n'/\lambda}\sqrt{\prod_0^{n'-2}(\lambda^2+r^2)}}{Kt^2\sqrt{\Gamma(2n')\sinh\pi\lambda'}\,(\lambda^2+n'^2)^{n'+1}} .$$

$s' = 1$; $I(n,k+1;n',k)$: $k = n'-1$; $s = n-k-1 = n-n'$.

$$I(n,k+1;n',k) = \frac{\sqrt{\mu}\,|\Gamma(n'+n)|\,(-4\alpha'\gamma)^{n'-1/2}\sqrt{2(2n'-2)!}\,e^{\pi\lambda/2}(-1)^{-n+n'}u^{n-n'+1}}{K(2n'-3)!\sqrt{\pi n'}\,4\alpha(\alpha^2-\alpha'^2)(\alpha+\alpha')^{2n'-2}}$$

$$\left\{F(-s,-s',2k,1-\frac{1}{u^2}) - u^2F(-s-2,-s',2k,1-\frac{1}{u^2})\right\} .$$

In this case, the bracket may be written as:

$$\frac{1}{2k}\left\{n(u-\frac{1}{u})^2 + (k+1)(u^2-\frac{1}{u^2})\right\} = \frac{8t^4(n^2-n'^2)}{2k(\lambda^2-\lambda'^2)^2n'^2n^3} .$$

This gives for I(n,k+1;n',k):

$$(54)\quad I(n,k+1;n',k) = \frac{-\sqrt{\mu}\,2^{2n'+1/2}n'^{n'+2}\lambda^{n'+2}e^{\pi\lambda/2}e^{-2\lambda\tan^{-1}n'/\lambda}\sqrt{\prod_0^{n'-2}(\lambda^2+r^2)}}{Kt^2\sqrt{\Gamma(2n'-1)\sinh\pi\lambda'}\,(\lambda^2+n'^2)^{n'+1}} .$$

$s' = 1$; $I(n,k;n',k+1)$: $k = n'-2$; $s = n-n'+2$.

$$I(n,k;n',k+1) = \frac{2^{3/2}\alpha'\sqrt{\mu}\,|\Gamma(n'+n-2)|\,(-4\alpha'\gamma)^{n'-5/2}\sqrt{(2n'-2)!}\,(-1)^{-n+n'}u^{n-n'+3}e^{\pi\lambda/2}}{K\Gamma(2n'-4)\sqrt{4n'\pi}\,(\alpha'^2-\alpha^2)(\alpha+\alpha')^{2n'-4}}$$

$$\left\{F(-s,-s',2k,1-\frac{1}{u^2}) - u^2F(-s,-s'-2,2k,1-\frac{1}{u^2})\right\} .$$

Again, the bracket may be reduced to:

$$\frac{1}{2k(2k+1)(2k+2)u}\Big\{-n(3k^2+6k+n^2+2)(u-\frac{1}{u})^3 -(k+1)(k^2+3n^2+2k)(u+\frac{1}{u})^3 -4n(2k^2+3k+1)(u-\frac{1}{u})$$

$$+4(k+1)(k^2+3n^2+2k)(u+\frac{1}{u})\Big\} = \frac{16t^6(n'^2-n^2)(n'^3-n'^2-n'n^2-3n^2)}{(\lambda^2-\lambda'^2)^3un'^5n^4(2n'-4)(2n'-3)(2n'-2)}$$

It now follows that:

$$(55)\quad I(n,k;n',k+1) = \frac{-2^{2n'-1/2}\sqrt{\mu}\,n'^{n'}\lambda^{n'+2}e^{\pi\lambda/2}e^{-2\lambda\tan^{-1}n'/\lambda}(n'^3-n'^2+n'\lambda^2+3\lambda^2)\sqrt{\prod_0^{n'-3}(\lambda^2+r^2)}}{Kt^2\sqrt{\Gamma(2n'-1)\sinh\pi\lambda'}\,(n'^2+\lambda^2)^{n'+1}} .$$

APPLICATION TO THE LYMAN AND BALMER SPECTRA:

These formulae, valid for all n', will now be applied to the Lyman and Balmer continuous spectra, for which n' = 1 and 2, respectively.

As $n' \geq k' \geq m'+1$; $k' \geq 1$, it follows that for the Lyman spectrum $n' = 1$, $k' = 1$, $s' = 0$, for the discrete term and $k = k'+1 = 2$ for the continuous state, so that (52) is to be applied in this case. (49) reduces to the second term, and the total intensity becomes, introducing $\beta = 1/\lambda$,

$$(56)\quad I_L = CkI^2(n,2;1,1) = \frac{C2^8\mu e^{-\frac{4}{\beta}\tan^{-1}\beta}}{K^2t^4(1+\beta^2)^5(1-e^{-2\pi/\beta})} \,.$$

On the other hand, for the Balmer spectrum, n' = 2. Hence there are the possibilities for the discrete state: $s' = 0$, $K' = 2$, $k = 3, 1$; and $s' = 1$, $k' = 1$, $k = 2$. Thus, by (49) the intensity of the spectrum is given by:

$$I_B = C\left[I^2(n,1;2,2) + 2I^2(n,3;2,2) + I^2(n,2;2,1)\right] .$$

Applying now (52), (53) and (54), this becomes:

$$(57)\quad I_B = \frac{C\;2^{15}\;e^{-\frac{4}{\beta}\tan^{-1}2\beta}}{K^2t^4(1+4\beta^2)^7(1-e^{-2\pi/\beta})}(15 + 32\beta^2 + 16\beta^4).$$

It may be noted that by the definitions (6) and (6a):

$$(58)\quad \beta^2 = \frac{1}{\lambda^2} = \frac{E}{Rh};\quad R = \frac{2\pi^2\mu e^4Z^2}{h^3} = \text{Rydberg's no:}\ t = \frac{Z}{a};\ a = h^2/4\pi^2\mu e^2 = \text{radius}$$

of first Bohr circle, for hydrogen. As E is simply the positive energy of the electron in the continuous state, the total energy with respect to the normal state is E+Rh.

To determine the constant C, it is simply noted that by the classical electrodynamics, the average rate of emission of energy by an oscillator is:

$$(59)\qquad -\frac{\overline{dE}}{dt} = \frac{2(2\pi\nu)^4}{3c^3}\,\overline{P^2}\,,$$

where $\overline{P^2}$ is the average square of the electric moment of the oscillator. And if x is the amplitude of the motion, then, clearly, $\overline{P^2} = e^2x^2/2$. However, as a Fourier component in the classical resolution of the motion is related to the quantum mechanical elementary oscillations as:

$$A \cos 2\pi\nu t\tau = A_{nm} e^{2\pi i\nu_{mn}t} + A_{mn} e^{2\pi i\nu_{nm}t} ,$$

it follows that the amplitudes are related as $A_\nu^2/2 = 2A_{nm}A_{mn}$. But in the product $A_{mn}A_{nm}$ both the (n m) transition and its inverse are included; hence for a single process the quantum mechanical equivalent of $x^2/2$ will be simply $e^8|x_{nm}|^2$. It follows, then, that for spontaneous emission C will have the value:

$$C = \frac{32\pi^4 e^2 \nu^4}{3c^3} . \tag{59a}$$

The average number of elementary processes per second, which for spontaneous emission is the first of Einstein's coefficients, is given by dividing CI^2 by h , so that:

$$A_{n\rightarrow n'} = \frac{CI^2}{h} = \frac{32\pi^4 e^2 \nu_0^3 I^2(n;n')}{3c^3 h}. \tag{60}$$

It should be mentioned that the e in (58), (59a) and (60) refers to the charge of the electron.

Fron an experimental point of view, it is almost impossible to observe rates of spontaneous emission as such, because of the fact that in any practical experimental arrangement the observed emitted intensities depend, perhaps primarily, upon the conditions of excitation, temperature and other perturbing effects, whereas the Einstein coefficient refers to an intrinsic property of the atom that is emitting the radiation.

The intensities of absorption, on the other hand, may, in principle, be more easily analyzed experimentally. For, certainly for the absorption processes beginning in the normal state, no external excitation conditions are necessary to make the absorption possible. But unfortunately, in this case, too, experimental studies are hardly more than possible, since hydrogen exists normally in the molecular state and either high temperatures or external excitation are necessary for its dissociation into atoms, to which alone the present theory of atomic continuous affinity spectra is applicable. And in fact, no quantitative data has as yet been obtained on the absorption intensities for the affinity spectra of hydrogen. Stark 17) has observed them in canal ray studies, and Yu 18) in photographs of stellar spectra. But these are not suited for any close comparison with the deductions that may be made from the theoretical formulae derived in this investigation.

Nevertheless, it is of interest to at least give explicitly some of the features which the theory does predict, altho they will not be analyzed from an experimental point of view, at present. For this purpose, Einstein's absorption coefficient willbe computed. As is well known, it is related to the coefficient of spontaneous emission by the relation: $B_{n'\rightarrow n} = \frac{c^3}{8\pi h\nu^3} A_{n\rightarrow n'}$. This gives for the coefficient of absorption per atom:

$$(61)\qquad \alpha_\nu = \frac{Bh}{c} = \frac{4\pi^3\nu e^2 I^2(n,n')}{3hc} \quad .$$

It is convenient, in making physical interpretations to consider α_ν as a function of ν/ν_0, where ν_0 is the limiting frequency of the corresponding discrete spectrum. Thus for the Lyman spectrum, $\nu_0 = R$; and for the Balmer spectrum, $\nu_0 = R/4$, on the other hand, refers to the frequency that would be emitted or absorbed in a transition corresponding to the continuous spectrum. Hence for the Lyman continuous spectrum, $\nu = \frac{E+Rh}{h}$; $\nu/\nu_0 = 1+\beta^2$; and for the Balmer continuous spectrum, $\nu = \frac{E+Rh/4}{h}$; while $\nu/\nu_0 = 1+4\beta^2$; since E represents only the positive energy of the electron in the continuous state.

By (56), (58) and (61), the value of for the Lyman spectrum is:

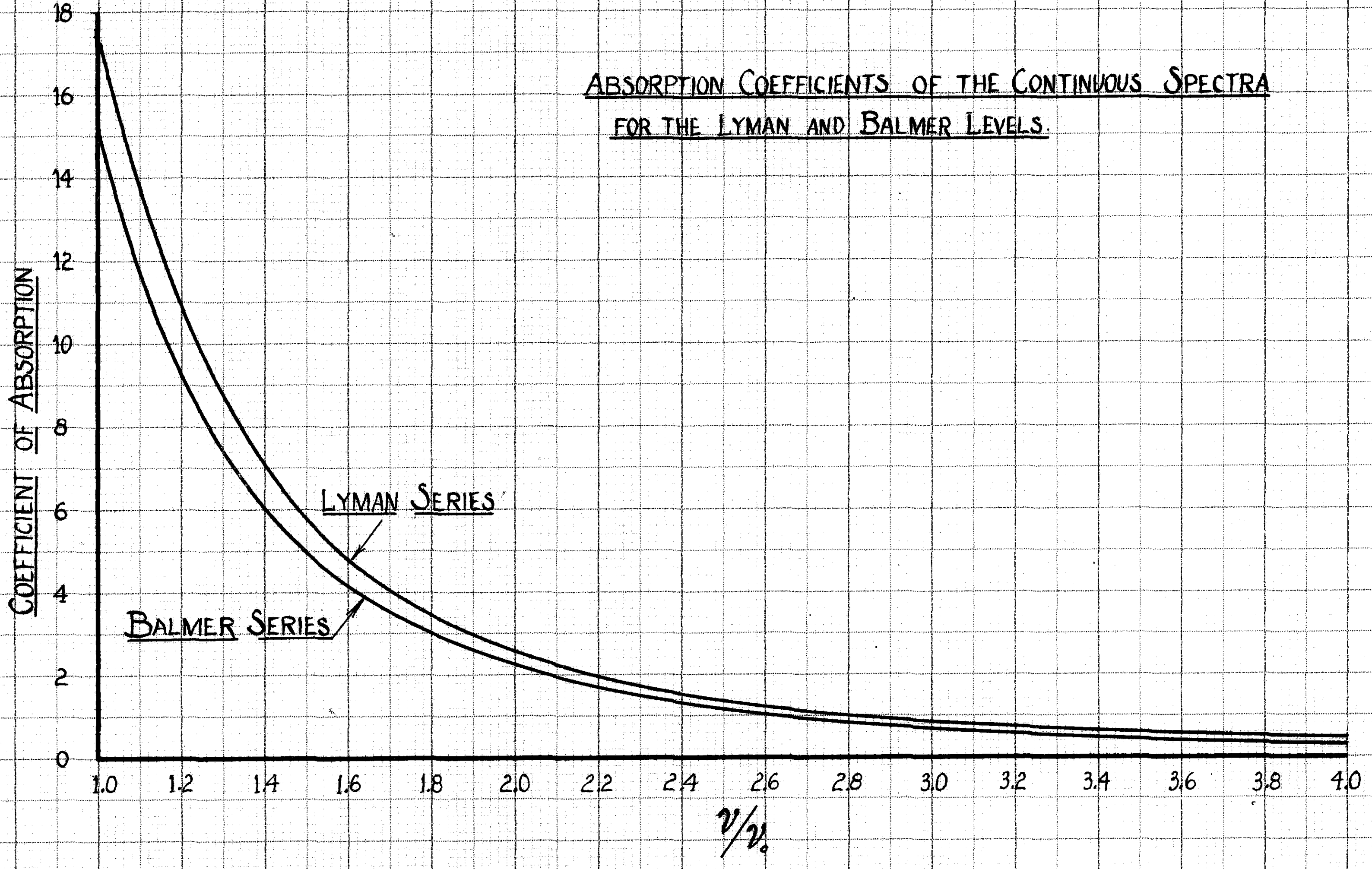
$$(62)\quad \alpha_{\nu_L} = \frac{\mu\pi^3 2^{16} e^2 R\, e^{-4\sqrt{\frac{\nu_0}{\nu-\nu_0}}\tan^{-1}\sqrt{\frac{\nu-\nu_0}{\nu}}}}{3K^2t^4ch(\nu/\nu_0)^4(1-e^{-2\pi\sqrt{\frac{\nu_0}{\nu-\nu_0}}})},$$

and for the Balmer spectrum:

$$(63)\quad \alpha_{\nu_B} = \frac{\mu\pi^3 2^{15} e^2 R\, e^{-4\sqrt{\frac{\nu_0}{\nu-\nu_0}}\tan^{-1}\sqrt{\frac{\nu-\nu_0}{\nu}}}}{3K^2t^4ch(\nu/\nu_0)^6(1-e^{-4\pi\sqrt{\frac{\nu_0}{\nu-\nu_0}}})}\cdot(\nu/\nu_0+2)(\nu/\nu_0+4)$$

In the curves on the next page α_{ν_L} and α_{ν_B} are plotted against the ν/ν_0 for the two spectra; in both cases the α_ν are divided by the common factor: $c' \equiv \frac{\pi^3 2^{15} e^2 R}{9K^2t^4ch}$; furthermore, the scales are in the ratio of 10 to 1; i.e., for example, at $\nu/\nu_0 = 1$, the actural values are $\alpha_{\nu_L}/c' = 1.717\ 10^{-3}$, while $\alpha_{\nu_B}/c' = 15.096\ 10^{-3}$. From these curves it is seen that in the scale of equivalent ν/ν_0 the probability of absorption from the Balmer level is approximately nine times that of absorption from a Lyman level; also, this ratio is roughly maintained thruout the range of the curve.

It is of interest to note the behavior of the absorption at the series limits. It is easily verified from the above formulae for α_{ν_L} and α_{ν_B} that, at least for the Lyman and Balmer spectra, the curves approach the axis: $\nu/\nu_0 = 1$, not with an infinite slope but with a definite non-vanishing angle. In general, at the series limits, $E \to 0$, so that $\lambda \to 0$, and $u \to -1$. As was noted before, (cf. (33a)), when s is also real and integral, the general expression for R(s,s') and hence for X reduces to the form valid for the discrete spectra. It was also shown, (cf. (24a)), that as $E \to 0$, the normalization factors for the discrete and continuous ranges become formally identical, when referred to the same scale. Hence the values of I and for the series limit from the discrete side will also be obtained by letting $\lambda \to 0$, $E \to 0$, $u \to -1$, tho to be exact, they would approach it discontinuously up to the very limit. Thus, it is obvious that



ABSORPTION COEFFICIENTS OF THE CONTINUOUS SPECTRA
FOR THE LYMAN AND BALMER LEVELS.

the limit as approached from the continuous range is equal to that obtained when it is approached from the discrete side, so that there is therefore a continuous transition at these limits which represent ionization of the atom by the absorption of radiation.

Formulae for the limiting values of I(n,k+1;n',k) and I(n,k;n',k+1), easy to apply for s' small, may be derived without difficulty for general values of n'. The method is as follows:

By (24) and (6a): $\lim\limits_{\alpha\to 0}\psi(\alpha,k+1) = \dfrac{(2t)^{k+1/2}\sqrt{2\mu}}{K\Gamma(2k+2)}$;

also: $\lim\limits_{\alpha\to 0}(-u)^{s+s'} = e^{-2n'}$; and by (33)

$$\lim_{\alpha\to 0}\frac{1}{\alpha}\Big[R(s,s',k) - R(s+2,s',k)\Big] = \frac{(-1)^{-n'+k}e^{-2n'}\Gamma(2k)}{\alpha'^{2k}}\Bigg[\lim_{\alpha\to 0}\frac{(1-u^2)}{\alpha}$$
$$+\sum_{r=1}^{n'-k}\frac{1}{r!}\left(\frac{-4}{\alpha'}\right)^r\prod_{m=0}^{r-1}\frac{(s'-m)}{(2k+m)}\lim_{\alpha\to 0}\alpha^{r-1}\left\{\prod_{m=0}^{r-1}\left(\frac{-t}{\alpha}-k-m-1\right)-\prod_{m=0}^{r-1}\left(\frac{-t}{\alpha}-k-m+1\right)\right\}\Bigg] .$$

Now $\lim\limits_{\alpha\to 0}\dfrac{(1-u^2)}{\alpha} = 4/\alpha'$; and:

$$\lim_{\alpha\to 0}\lambda^{r-1}\left\{\prod_{m=0}^{r-1}\left(\frac{-t}{\alpha}-k-m-1\right)-\prod_{m=0}^{r-1}\left(\frac{-t}{\alpha}-k-m+1\right)\right\} = (-t)^{r-1}\left[\sum_{m=0}^{r-1}(-k-m-1)-\sum_{m=0}^{r-1}(-k-m+1)\right]$$

$= (-2r)(-t)^{r-1}$. Hence, finally:

$$(64)\quad \lim I(n,k;n',k+1) = \frac{(-1)^{k-n'+1}e^{-2n'}n'^{k+2}2^{2k+2}}{t^2\,(2k)\,K}\mu\sqrt{\frac{\Gamma(n'+k)}{\Gamma(n'-k+1)}}$$
$$\left[1 + 2\sum_{r=0}^{n'-k-1}\frac{(-4n')^r}{r!}\prod_{0}^{r}\frac{(n'-k-m)}{(2k+m)}\right] .$$

When s' = 0, the summation is to be omitted.

In an exactly similar manner it may be shown that:

$$(65)\quad \lim I(n,k;n',k+1) = \frac{(-1)^k 2^k\sqrt{\mu}}{(2k)t^2K}\sqrt{\frac{\Gamma(k+n'-1)}{\Gamma(n'-k)}}\,n'^{k+1}e^{-2n'}$$
$$\left[\sum_{r=1}^{n'-k-1}\frac{(-1)^r}{r!}(4n')^r\prod_{0}^{r-1}\frac{(n'-k-1-m)}{(2k+m)} - \sum_{r=1}^{n'-k+1}\frac{(-1)^r}{r!}(4n')^r\prod_{0}^{r-1}\frac{(n'-k+1-m)}{(2k+m)}\right] .$$

Here, when s' = 0, the first summation is to be omitted.

The variation of the absorption coefficients with the atomic number Z can be obtained from (62) and (63), for the Lyman and Balmer spectra. By (58), $R \sim Z^2$, while $t = Z/a$. Hence for short wavelengths, large ν, $\alpha_{\nu_L} \sim Z^5$; and $\alpha_{\nu_B} \sim Z^5$, also. At the series limits, on the otherhand, as $\nu \rightarrow \nu_0$, the variation of the absorption coefficients with Z is quite different; in fact, $\alpha_{\nu_L} \sim 1/Z^2$ and $\alpha_{\nu_B} \sim 1/Z^2$, at the series limits.

The variation of the absorption coefficients with the wave length may also be easily obtained from (62) and (63). Thus it is seen directly that for large ν, both of the coefficients, for both series, vary as $1/\nu^{7/2}$ or as $\lambda^{7/2}$. On the other hand, at the series limits, both α_{ν_L} and α_{ν_B} vary as $1/\nu^4$ or as λ^4. For intermediate ranges of ν, the variation of the absorption coefficients can,at least approximately, be obtained without any difficulty from the formulae as given.

The experimental data for the absorption spectra of X rays is not at all as meagre as that for the affinity spectra of hydrogen itself. Still, it would take a rather careful analysis of the data and of the validity of the approximation involved in applying the above formulae to X rays, before any such test of the formulae and theory would be of significance. As this is a problem in itself, it will not be attempted here, and the formulae will not be further analyzed for possible predictions or explanations of experimental phenomena.

However, it may be mentioned, in conclusion, that the formulae derived in the present investigation have applicability not only to questions of atomic spectra, but also to problems such as electron capture and photoelectric emission. It is essentially a matter of physical interpretation of the formulae already derived, to apply them to these other problems.

This research was carried out under the direction of Dr. Paul S. Epstein. It is a pleasure to acknowledge his continued assistance and encouragement; in fact, the general method of the evaluation of the matrix integrals was developed by him. Without his aid this investigation could not have been carried to completion.

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SUMMARY:

This investigation consists of a theoretical study, by the Wave Mechanics, of the intensities of the affinity spectra of hydrogen like atoms.

The main properties of the eigenfunctions for the continuous range of eigenvalues are investigated. They are shown to be real, and their asymptotic expansions are derived. The theory of the normalization of continuous eigenfunctions is applied, and their normalization factors are obtained.

The integrals for the coordinate matrices corresponding to transitions from the continuous states to the discrete levels are then evaluated. It, then, is shown that the squares of the complete Schrodinger matrices for the three coordinates x, y, and z, are equal, their common value being derived.

The general formulae are applied to the special cases of the continuous spectra associated with the Lyman and Balmer discrete levels. The absorption coefficients of these spectra, as a function of the frequency, are deduced and plotted. It is found that for equivalent ratios of the absorbed frequency to the critical ionization frequency of the discrete level, the probability of absorption from the Balmer level is approximately nine times that from the Lyman level.

The values of the matrices, for any discrete state, are given for the long wave length limit of the continuous spectra. Finally, the variation with wave length and atomic number of the absorption coefficients for both the long and short wave length limits of the Lyman and Balmer continuous spectra are briefly discussed.