THE HARMONIC ANALYSIS OF ELECTRON ORBITS

By Frank C. Hoyt

Abstract

Harmonic analysis of penetrating electron orbits in the Bohr atom has been effected on the assumption that the outer segments of such orbits may be considered as parts of Keplerian ellipses and that the penetrating part of the orbit, which is traversed in a time short compared with the period of the Keplerian motion, may be represented arbitrarily as a continuation of the exterior motion. If the Fourier series is written in the form $x+iy=\Sigma(-\infty \text{ to } +\infty)C_\tau e^{2\pi i(\tau\omega+\sigma)t}$, the formula for the amplitudes is

$$C_\tau=(a/2\pi)\sqrt{\sin^2(2\pi\sigma/\omega)+(\cos(2\pi\sigma/\omega)-1)^2}\ \ \Sigma'(-\infty \text{ to } +\infty)b_m J_m(\rho\epsilon)$$

$$\text{with } b_m=\frac{(1+\epsilon^2)(\rho-m)+\epsilon'}{(\rho-m)^2-1}-\frac{\epsilon\epsilon'+\frac{1}{2}\epsilon(\rho-m)}{(\rho-m)^4-4}-\frac{(3/2)\epsilon}{\rho-m}$$

where a = major axis of the outer segment; σ/ω = ratio of frequency of precession to the frequency of Keplerian motion $=2\pi$ times angular separation of outer segments; $\rho=\tau+\sigma/\omega$; ϵ is the eccentricity of outer segment; $\epsilon'=\sqrt{1-\epsilon^2}$. The J's are Bessel functions of the first kind. Tables are given of the values of C_τ for $\epsilon=.3, .6, .866, 1$, and $\sigma/\omega=0, 1/4, 1/2, 3/4, 1$. The error involved in the method may be large for high order harmonics or small values of ϵ. In the case of some orbits of sodium (3_1, 3_2, 4_2, and 5_2) the calculated values of the main coefficients agree fairly well with values obtained by Thomas from spectroscopic data by the method of Fues. Applications of this analysis to intensity relations in spectra will be made in a later paper.

1. Introduction. Description of Electron Orbits

According to the modern quantum theory of radiation the resolution of the motion of an electron within an atom into its harmonic components is of fundamental importance in determining the character of the radiation accompanying a transition between two stationary states. Thus it is possible by means of Bohr's correspondence principle[1] to draw conclusions in many cases as regards the intensity and polarization of spectral lines from a knowledge of the amplitudes in such an harmonic representation, although attempts to deduce a general quantitative relation between the probability of transition occuring in Einstein's theory of heat radiation and the properties of the electron motion have so far been unsuccessful.[2] The present paper will be concerned with the problem of the harmonic representation of a certain class of electron orbits of great importance in the theory of series spectra, and in a later paper it is hoped to give a discussion of possible applications to intensity relations.

[1] N. Bohr, Zeits. f. Phys. **13**, 142 (1923)

[2] See F. C. Hoyt (Phil. Mag. **46**, 135, 1923; **47**, 826, 1924) for a brief discussion of the correspondence principle, with references to the literature. See also Buchwald "Das Korrespondenzprinzip" Braunchweig, 1923.

For a detailed account of the theory of series spectra in relation to atomic structure the reader must be referred to the original articles of Bohr,[3] but it may be well to recall here some of the main features. According to the theory, the emission of series spectra is the result of the rebinding process occurring after the removal of one or more of the electrons belonging to the group of most loosely bound electron orbits in the neutral atom. Thus we have to consider transitions between stationary orbits in which one electron is, for at least a large part of its path, at a much greater distance from the atomic nucleus than the orbits of the more strongly bound electrons. This electron will be referred to as the "series electron," while the rest of the system, consisting of the nucleus and the orbits of the other electrons, will be referred to as the "atomic residue."

The orbits of series electrons may be divided into two essentially different classes, depending on whether the electron during its entire path moves in the outer region or whether it penetrates for a part of its path into the inner region in which the orbits of the other electrons lie. In the first case the orbits have been called by Bohr "orbits of the first kind," or non-penetrating orbits and in the second case "orbits of the second kind," or penetrating orbits.

In an orbit of the first kind the electron will, to a first approximation, move in a Keplerian ellipse on which is superposed a slow uniform rotation in the plane of the orbit. This follows at once from the fact that at great distances the field of the atomic residue may be considered as due to a point charge of $N-N_i$ units, where N is the atomic number and N_i the number of electrons in the atomic residue. At lesser distances the small deviations from an inverse square force are such as to preserve the central symmetry and will thus produce a uniform precession. Such an orbit is represented diagrammatically by curve I in Fig. 1, where the shaded circle represents the region occupied by the orbits of the inner electrons. For the sake of simplicity the slow precession which may occur is not shown.

The stationary states of such orbits may then be fixed by means of the well known theory for atoms containing only one electron, and the energy E and major axis a are given to a first approximation by the relations

$$E=-Rh(N-N_i)^2/n^2 \tag{1}$$

$$a=\frac{e^2}{2Rh}\,\frac{n^2}{N-N_i} \tag{2}$$

[3] N. Bohr, "The Theory of Spectra and Atomic Constitution," Camb. Univ. Press (1922); and Ann. der Phys. **51**, 228 (1923)

where R is the Rydberg constant, and n the principal quantum number. The existence of such orbits in an atom will then be shown in the spectrum by the occurrence of terms T represented approximately by the formula

$$T = Rh(N - N_i)^2(1/n^2) \ . \tag{3}$$

The exact description of orbits of the second kind in which the electron penetrates at intervals into the inner region is, on the other hand, a matter of greater difficulty in the present state of the quantum theory as it involves the question of the finer interaction of electrons within the atom. In most cases, however, the greater part of the orbit will be described at a considerable distance from the nucleus where the field is approximately that of a point charge, and it is only during the penetration into the inner region that large deviations from Keplerian motion will occur. Thus to a first approximation the orbit may be thought of as made up of a series of outer segments which are parts of Keplerian ellipses, joined by inner segments in which the deviation from Keplerian motion may be considerable. If we assume, as Bohr has done, that there is no interchange of energy between the electron and the atomic residue during the penetration, the outer segments will all be parts of ellipses having the same energy and the same major axis, and if we further assume that the field is always a central field, as suggested by the symmetry of the atomic structure, these ellipses will all have the same shape and be spaced at equal angles in the orbital plane.[4] An orbit of this kind is shown by curve II in Fig. 1. It is of great importance to note that the *time* spent by the electron in the inner region is in general very short in comparison with the time spent in the outer region, as the motion is very much more rapid in the interior.

The stationary states of orbits of the second kind may be fixed by means of the general theory for central orbits[5], which leads to a classification by means of the symbol n_k, where n is the principal quantum number and k the subordinate quantum number. As is well known, k determines the total angular momentum about the nucleus, while n determines the magnitude of the radial quantum integral according to the relation

$$\int m(dr/dt)^2 dt = (n - k)h \tag{5}$$

where dr/dt is the radial velocity and the integral is to be taken over a complete cycle of the radial motion. The energy and major axis of the Keplerian ellipse of which the outer segment forms a part will differ

[4] See N. Bohr, "The Effect of Electric and Magnetic Fields on Spectral Lines," The Seventh Guthrie Lecture, The Physical Society of London (1923)

[5] N. Bohr, Ann. der Phys. **51**, 244 (1923)

greatly from those of a hydrogen-type orbit with the same principal quantum number, as the contribution of the inner segment to the radial quantum integral, Eq. (5), is very large due to the increased velocity near the nucleus. These quantities are, however, conveniently represented in terms of an effective quantum number n* by means of the relations

$$E = -Rh(N-N_i)^2/n^{*2} = E_0(N-N_i)^2/n^{*2} \tag{6}$$

$$a = \frac{e^2}{2Rh}\,\frac{n^{*2}}{N-N_i} = a_0\,\frac{n^{*2}}{N-N_i} \tag{7}$$

where E_0 and a_0 are respectively the energy and major axis of a one-quantum orbit in hydrogen. The eccentricity of the outer segment is then given by the relation

$$\epsilon^2 = 1 - k^2/n^{*2}\,. \tag{8}$$

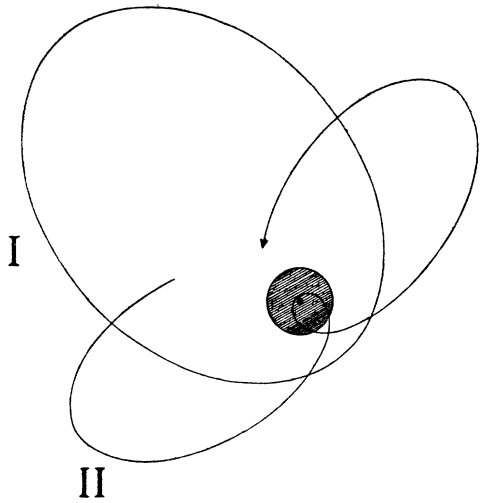

Fig. 1. I. Orbit of the first kind, or non-penetrating orbit.
II. Orbit of the second kind, or penetrating orbit.

The convenience of these relations lies in the fact that, since the work required to remove the electron is given by the value of the spectral term T divided by h, the effective quantum number may be found directly from spectroscopic data by means of the relation

$$n^* = (N-N_i)\sqrt{R/T}\,. \tag{9}$$

It has further been shown by Bohr[6] from the general principles of the quantum theory, that the energy of orbits of the second kind depends on the quantum integers in such a way that their existence in the atom ac-

[6] N. Bohr, loc. cit.[4], p. 298

counts for the occurrence of spectral terms given to a first approximation by the formula

$$T=\frac{Rh}{(n-a)^2}\ (N-N_i)^2 \tag{10}$$

where a is a constant depending only on k and not on n. This is the well known Rydberg formula.

2. Harmonic analysis of the Electron Orbits

For the purpose of exhibiting the relation demanded by the correspondence principle between the s-fold periodic motion of an electron and the properties of the radiation accompanying transition between stationary states it is necessary to express the displacements of the electron, referred to three mutually perpendicular axes, in Fourier series of the form

$$\xi=\sum_{\tau_1=-\infty}^{\tau_1=+\infty}\ .\ .\ \sum_{\tau_s=-\infty}^{\tau_s=+\infty} C_\tau \cos[2\pi(\tau_1\omega_1+\ .\ .\ .\ .\ \tau_s\omega_s)t+\gamma\tau_1\ .\ .\ \tau_s] \tag{11}$$

where τ's are integers, $\omega_1\ .\ .\ .\ \omega_s$ are the frequencies of the motion and the γ's are phase constants. The amplitudes C_τ depend only on the so called uniformization variables, and as Kramers[7] has shown it is possible to obtain integrals expressing these coefficients when the equations of motion can be solved by separation of the variables. It will be necessary here, however, to consider only the simpler case of central motion.

As is well known, any central motion (in general doubly periodic) may be represented as the superposition of a uniform rotation on a simply periodic motion,[8] in which case the displacements referred to rectangular coordinates in the plane of the orbit may be expressed in the following way. Let the periodic motion be represented as a sum of circular vibrations in the form

$$\xi+i\eta=\sum_{-\infty}^{+\infty} C_\tau e^{2\pi i\tau\omega t} \tag{12}$$

where ξ and η are rectangular coordinates and ω the frequency. Then the Fourier series for the doubly periodic central motion is directly obtained by superposing on this a uniform rotation of angular velocity $2\pi\sigma$, so that if x and y are the rectangular coordinates of a general central motion we have

$$x+iy=(\xi+i\eta)e^{2\pi i\sigma t}=\sum_{-\infty}^{+\infty} C_\tau e^{2\pi i(\tau\omega+\sigma)t} \tag{13}$$

[7] H. A. Kramers, Kgl. Danske Vidensk. Selsk. Skrifter **8**, III, 287 (1919)

[8] N. Bohr, The Quantum Theory of Line Spectra, Kgl. Danske Vidensk. Selsk. Skrifter **8**, IV, p. 33.

where
$$C_\tau = \frac{1}{2\pi}\int_0^{1/\omega} (\xi + i\eta) e^{-2\pi i \tau \omega t} dt \,, \tag{14}$$

which may be readily seen to correspond to the usual integral expression for a Fourier coefficient if it is remembered that C_τ may be a complex quantity. It must be born in mind in considering the applications of the correspondence principle, that the properties of the radiation accompanying a transition between two stationary states for which $n=n'$, $k=k'$ and $n=n''$, $k=k''$ respectively, are dependent on the frequency and amplitude of the corresponding harmonic in Eq. (13) for which $n'-n''=\tau$ and $k-k'' = \pm 1$, that is to the harmonic with frequency $|\tau\omega \pm \sigma|$. That the expression (13) contains terms with frequencies $\tau\omega+\sigma$ and $\tau\omega-\sigma$ follows from the fact that both positive and negative values of τ occur in Eq. (12). Thus we will understand by C_τ the amplitude of the harmonic with frequency $|\tau\omega+\sigma|$ and by $C_{-\tau}$ the amplitude of the harmonic with frequency $|\tau\omega-\sigma|$.

We shall now consider the harmonic representations of orbits of both the first and second kind, assuming as a first approximation at least that we have to do in both cases with a central motion. In each case we shall obtain an expression in the form of Eq. (13) for a simply periodic motion and then superpose on it a uniform rotation.

For orbits of the first kind, in so far as they may be considered as Keplerian ellipses on which is superposed a uniform rotation of frequency σ, the coefficients in Eq. (13) can be found by carrying out the integration in Eq. (14), as shown by Kramers[9] (ξ and η being in this case the rectangular coordinates of a Keplerian ellipse) and are given by the expression,
$$C_\tau = -(a/2\tau)\{(1+\epsilon')\, J_{\tau-1}(\tau\epsilon) - (1-\epsilon')\, J_{\tau+1}(\tau\epsilon)\} \tag{15}$$

where a is the semi major axis of the ellipse, ϵ the eccentricity and $\epsilon' = \sqrt{1-\epsilon^2}$. The J's are Bessel functions of the first kind. These are then the values of the amplitude in Eq. (13) obtained by the superposition of a uniform rotation σ.

In considering orbits of the second kind we encounter at once the difficulty of describing the motion in the interior of the atom. Remembering, however, that the *time* spent in this region, where the electron moves very rapidly, is an extremely small fraction of the time required to traverse an orbital loop, at least when ϵ is not far from one, it is reasonable to suppose that only the higher harmonics will depend to any considerable extent on the exact nature of this motion, as the contribution of the inner

[9] See Buchwald, Das Korrespondenzprinzip, p. 46.

segment to the time integral in Eq. (14) will be very small. We may thus represent this inner motion in a more or less arbitrary way, and this is most conveniently done by taking the motion in the interior as far as possible as a completion of the Keplerian motion of the outer segment. For the purpose of the analysis we shall then replace the true motion by a series of complete Keplerian ellipses, having the proper angular separation $2\pi\sigma/\omega$, ω being the number of outer segments traversed per unit time and σ the number of revolutions per second of the major axis. In order to do this it is necessary, however, to introduce a discontinuity, in that the electron must be thought of as passing instantaneously from the perihelion of one ellipse to that of the next. Such a motion is shown in

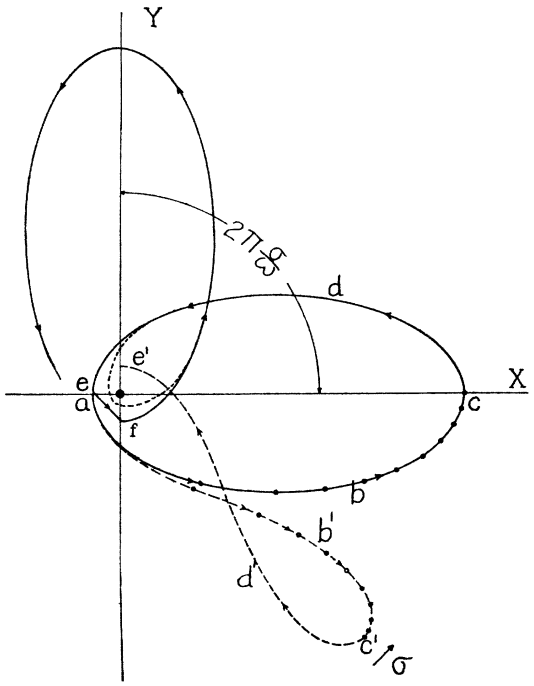

Fig. 2. Analysis of a penetrating orbit into a periodic orbit and a uniform rotation. ω = frequency in the periodic orbit; σ = frequency of rotation; $\epsilon = .866$; $\sigma/\omega = \frac{1}{4}$.

Fig. 2 for the case where $\sigma/\omega = 1/4$. The electron, starting from a, traverses the first complete ellipse *abcde* and then passes instantaneously from e to f, as shown by the heavy line, whereas in the true motion the path is more as indicated by the dotted line. The electron then traverses the second ellipse, and so on. The angular separation is of course 90°.

We now proceed to represent this substituted motion as the superposition of a uniform rotation on a periodic motion, in order to obtain an

expression in the form of Eq. (13). We see at once that this periodic orbit must be such that after the rotation has gone on for a time $1/\omega$ with angular velocity $2\pi\sigma$ in the positive direction it will give the first complete ellipse, as *abcde* in Fig. 2. This orbit may be found graphically, as it is of course the ellipse rotated in the negative direction for a time $1/\omega$, and and is shown by the dotted curve $ab'c'd'e'$. The small circles divide the the first ellipse into ten equal time intervals and correspond to those on the dotted curve. The orbit thus obtained is not closed but it is readily seen that if it be closed by an instantaneous path, so that e' coincides with a at time $t=1/\omega$ the periodic orbit obtained is the desired one, since a uniform rotation imposed on it will give the second ellipse from time $1/\omega$ to $2/\omega$, and so on for the consecutive ellipses, which will also have the angular separation.

It is now possible to obtain a Fourier series for this periodic orbit. In fact, if we represent the Keplerian motion rotated backwards for a time $1/\omega$ by such a series with fundamental period $1/\omega$ it will automatically give us a closed periodic orbit. Let x', y' be the rectangu'ar coordinates referred to axes as shown. Then if $t=0$ at the perihelion a, the parametric equations for the motion in the first ellipse are

$$x'+iy'=a(\cos u-\epsilon+i\epsilon'\sin u)\ ; \tag{16a}$$

$$2\pi\omega t=u-\epsilon\sin u\ , \tag{16b}$$

u being the eccentric anomaly. Then if ξ and η are the rectangular coordinates of the periodic motion desired, we have

$$\xi+i\eta=(x'+iy')e^{-2\pi i\sigma t} \tag{17}$$

or from Eq. (16)

$$\xi+i\eta=a(\cos u-\epsilon+i\epsilon'\sin u)e^{-2\pi i\sigma t}\ .$$

The coefficients of the Fourier expansion of $\xi+i\eta$ in the form of Eq. (12), are then given by

$$C_\tau=\frac{1}{2\pi}\int_0^{1/\omega} a\,(\cos u-\epsilon+i\epsilon'\sin u)e^{-2\pi i\sigma t}e^{-2\pi i\tau\omega t}dt \tag{18}$$

and these are also the values of the C's in the expression corresponding to Eq. (13) for the doubly periodic motion consisting of complete ellipses.

We have now to evaluate the integral in Eq. (18). Changing the variable of integration from t to u gives by means of Eq. (16b)

$$C_\tau=\frac{1}{2\pi}\int_0^{2\pi} a[\cos u-\epsilon+i\epsilon'\sin u]\,[1-\epsilon\cos u]\times e^{-i(\sigma/\omega)\,(u-\epsilon\sin u)}\,e^{-i\tau(u-\epsilon\sin u)}du\ . \tag{19}$$

The product of the two expressions in brackets may be written in the form

$$A_{-2}e^{-2iu}+A_{-1}e^{-iu}+A_0+A_1e^{iu}+A_2e^{2iu}=\sum_{-2}^{+2}A_ne^{in}\ ,$$

where

$$A_{-2}=-\tfrac{1}{4}\epsilon(1-\epsilon')\ ;\quad A_2=-\tfrac{1}{4}\epsilon(1+\epsilon')\ ;\quad A_{-1}=\tfrac{1}{2}(1+\epsilon^2-\epsilon')\ ;$$
$$A_1=\tfrac{1}{2}(1+\epsilon^2+\epsilon')\ ;\quad A_0=-(3/2)\epsilon\ .$$

Then with the abbreviation $\rho=\tau+\sigma/\omega$, Eq. (19) may be written in the form

$$C_\tau=\sum_{-2}^{+2}A_n\frac{a}{2\pi}\int_0^{2\pi}e^{-i(\rho-n)u}\,e^{i\rho\epsilon\sin u}\,du\ . \tag{20}$$

The evaluation of the integral

$$K\equiv(1/2\pi)\int_0^{2\pi}e^{-i(\rho-n)u}\,e^{i\rho\epsilon\sin u}\,du \tag{21}$$

does not lead to a simple Bessel function except in the case where $\rho-n$ is an integer, as in a periodic Keplerian motion. We can, however, obtain an expression for K as a convergent series containing Bessel functions in the following way. If we expand $e^{i\rho\epsilon\sin u}$ in a Fourier series of the form $\Sigma_{-\infty}^{+\infty}a_me^{imu}$ the coefficients a_m are given by the integral

$$a_m=(1/2\pi)\int_0^{2\pi}e^{i\rho\epsilon\sin u}\,e^{-imu}\,du$$

which is a well known expression for $J_m(\rho\epsilon)$. Thus

$$e^{i\rho\epsilon\sin u}=\sum_{-\infty}^{+\infty}J_m(\rho\epsilon)\,e^{imu}\ ,$$

and substitution in Eq. (21) gives

$$K=(1/2\pi)\int_0^{2\pi}\sum_{-\infty}^{+\infty}J_m(\rho\epsilon)e^{-i(\rho-m-n)u}du\ ;$$

or, on carrying out the integration,

$$K=(i/2\pi)\ [e^{-2\pi i(\rho-m-n)}-1]\sum_{-\infty}^{+\infty}\ J_m(\rho\epsilon)/(\rho-m-n)\ .$$

Substituting this value of K in Eq. (20) and reducing the finite summation with respect to n to an algebraic factor, gives as the final expression for the *absolute value* of the complex coefficient occurring in Eq. (13)

$$C_\tau=(a/2\pi)\sqrt{\sin^2(2\pi\sigma/\omega)+[\cos(2\pi\sigma/\omega)-1]^2}\ \sum_{-\infty}^{+\infty}\ b_mJ_m(\rho\epsilon)$$

where $$b_m=\frac{(1+\epsilon^2)(\rho-m)+\epsilon'}{(\rho-m)^2-1}-\frac{\epsilon\epsilon'+\frac{1}{2}\epsilon(\rho-m)}{(\rho-m)^4-4}-\frac{(3/2)\epsilon}{\rho-m}. \tag{22}$$

For $\sigma/\omega=0$ it may be shown that this reduces to Eq. (15) for the coefficients in a simple Keplerian ellipse, so that Eq. (22) is a general expression for orbits of either the first or second kind. In taking the absolute value of C_r we have neglected only the phase constants, which are of no importance in considering applications of the correspondence principle.

3. Calculations and Discussion of Results

The calculation of numerical values from Eq. (22) is a rather laborious process, although the convergence is very rapid for the lower harmonics, yet attempts to obtain a simpler series have not been successful. The amplitude of a given harmonic is a function of both σ/ω and ϵ, and values have been computed in a large number of cases. The results are

TABLE I

Values of C_r/a computed from Eq. (22) for various values of σ/ω

		Values of σ/ω				
	ϵ	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1
C_0/a	.300	−.450	−.706	−.925	−1.025	−.955
	.600	−.900	−1.084	−1.146	−1.052	−.812
	.866	−1.299	−1.363	−1.241	−.961	−.594
	1.000	−1.500	−1.394	−1.106	−.716	−.325
C_1/a	.300	.955	.733	.460	.096	−.140
	.600	.812	.494	.134	−.090	−.208
	.866	.594	.231	−.048	−.194	−.206
	1.000	.325	.025	−.145	−.175	−.112
C_2/a	.600	.209	.225	.133	.006	−.091
	.866	.206	.124	.009	−.076	−.122
	1.000	.112	.017	−.059	−.083	−.059
C_3/a	.600	.091	.126	.096	.016	−.044
	.866	.122	.080	.021	−.038	−.067
	1.000	.059	.011	−.032	−.049	−.037
C_4/a	.600	.044	.080	.071	.027	−.023
	.866	.067	.057	.021	−.021	−.046
	1.000	.037	.007	−.021	−.033	−.026
C_{-1}/a	.300	.012	.010	.070	.192	.450
	.600	.052	.172	.393	.646	.900
	.866	.139	.417	.753	1.071	1.299
	1.000	.325	.716	1.106	1.394	1.500
C_{-2}/a	.600	.010	.022	.030	.013	−.052
	.866	.039	.091	.105	.036	−.139
	1.000	.112	.175	.145	−.025	−.352
C_{-3}/a	.600	.003	.001	−.0003	−.004	−.010
	.866	.017	.039	.041	.013	−.039
	1.000	.059	.083	.059	−.016	−.112
C_{-4}/a	.600	.001	−.004	−.006	−.0004	−.0032
	.866	.009	.021	.021	.007	−.017
	1.000	.037	.049	.032	−.012	−.059

recorded in Table I. It is most convenient to have the amplitudes represented as a function of the eccentricity for discrete values of σ/ω, and in Figs. 3a, 3b, and 3c are shown the results of plotting C_0, C_1 and C_{-1} for $\sigma/\omega = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$, and 1. The case $\sigma/\omega = 0$ corresponds of course to a single Keplerian ellipse and for $\sigma/\omega = 1$ we have again a single Kep-

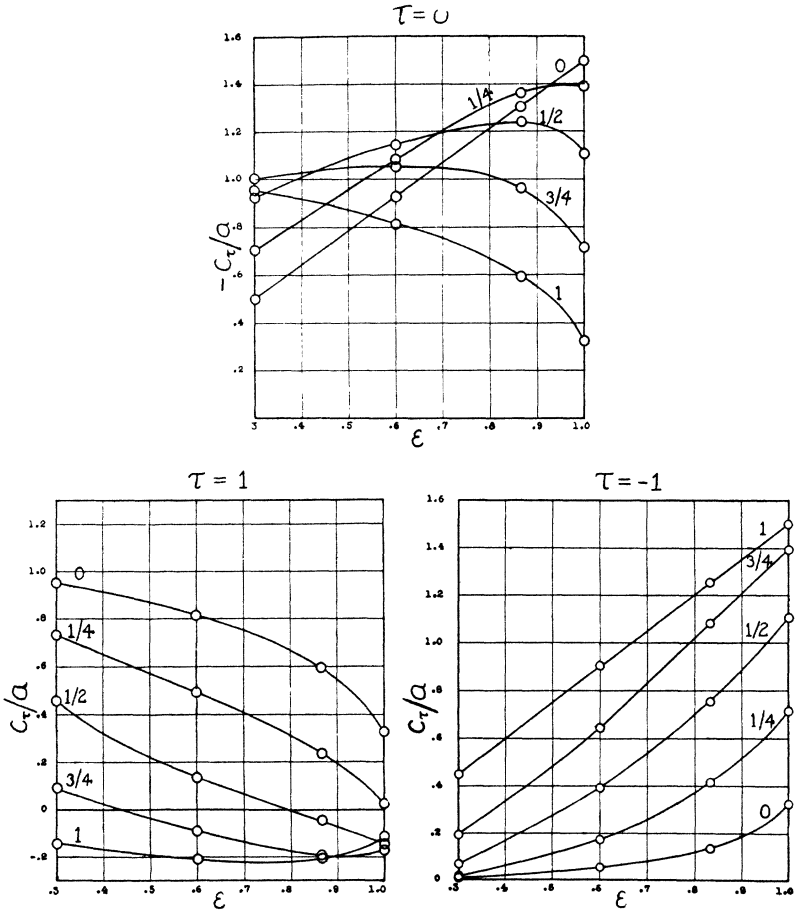

Fig. 3. Graphs of C_τ/a as a function of the eccentricity for different values of σ/ω. The numbers attached to the curves indicate the values of σ/ω.

lerian ellipse where, however, since $\tau\omega+\sigma = (\tau+1)\omega$ the amplitude of the term with frequency $\tau\omega+\sigma$ has the same value as $C_{\tau+1}$ for $\sigma/\omega = 0$, except for a change in sign. This may also be seen directly from Eq. (22) and follows from the fact that for a given value of ϵ, the amplitude is a function only of the quantity $\rho = \tau+\sigma/\omega$. The computations and plots are given only for $\epsilon > .3$ as for small values of ϵ the assumption that the

fraction of a period spent in the inner region is very small is no longer valid.

Although the applications to intensity relations are to be discussed in a later paper, it may be pointed out here that Eq. (22) may be used to compute an approximate value of the corresponding amplitude for the initial and final states of the transition involved in the emission of a spectral line in terms of the major axis and eccentricity of the outer segment, which are given directly by Eqs. (6), (7), (8), and (9) from the spectral terms, and of σ/ω which may also be roughly estimated from the spectral data. The order of the harmonic is of course given by the quantum integers. It will be seen that for a given eccentricity the effect of an increasing speed of rotation is to change continuously the value of a given amplitude from C_τ for $\sigma/\omega=0$ to $C_{\tau+1}$ for $\sigma/\omega=0$, passing in general through zero except in the case of C_0 and C_{-1}.

We must always keep in mind, however, the approximate nature of computations made in this way. The error may be very great for the higher harmonics, or even in the case of the lower harmonics when the eccentricity is small or the relative dimensions of the atomic residue and the orbit of the series electron are such that the motion in the outer segment differs greatly from a Keplerian motion. More exact calculations, however, would perhaps be of little value at present due to the uncertainties in the exact method of application of the correspondence principle.

It is of interest to compare the results obtained by the above method with the recent calculations of Thomas,[10] who has determined some Fourier coefficients for electron orbits in sodium. The work is based on a method first developed by Fues[11] for obtaining from spectroscopic data an analytic expression for the central field in which the series electron moves. In this way the kinematics of the orbits may be worked out and the Fourier coefficients evaluated numerically. In Table II are Thomas'

TABLE II

Values calculated for amplitude coefficients for sodium orbits

Orbits	Thomas' results			Values interpolated from Table I		
	C_0	C_1	C_2	C_0	C_1	C_2
3_1	3.77	.07	.03	3.2	.35	.28
3_2	4.55			4.5		
4_2		1.28			1.3	
5_2			.78			.6

[10] Thomas, Zeits. f. Phys. **24**, 169 (1924)

[11] Fues, Zeits. f. Phys. **11**, 364 (1922); **13**, 211 (1923)

results for the sodium orbits compared with the values obtained by interpolation from graphs prepared from Table I. The values of σ/ω used were taken from Thomas' paper. It will be noticed that the descrepancy is large in the case of C_1 and C_2 for the 3_1 orbit. This orbit has an eccentricity of about .35 and is probably much distorted from a Keplerian ellipse, so that a large error may be expected to occur in this case in using the method here described.

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