APPLICATION OF THE CORRESPONDENCE PRINCIPLE TO RELATIVE INTENSITIES IN SERIES SPECTRA

BY FRANK C. HOYT

ABSTRACT

A brief discussion is given of the representation of intensities in emission and absorption in terms of the probabilities of transition and of the estimation of the probability $A'_{''}$ of spontaneous transition in the usual way based on the correspondence principle. It is shown that on the basis of the Bohr theory approximate values of $A'_{''}$ may be obtained in many cases from the information as to the parameters of the stationary orbits which is given by the values of the spectral terms and their quantum numbers, together with the harmonic analysis of the penetrating orbits given in a previous paper.[1] In other cases a detailed knowledge of the intermediate orbits is shown to be necessary. Calculations are made of the ***relative probabilities of the transitions involved in the principal series of sodium.*** The values obtained by different methods of averaging are compared with the experimental results of Harrison (Phys. Rev. **25**, 768, 1925). A possible explanation is offered of the observed relative intensities in emission of certain lines with the same initial state. It is pointed out that the frequencies of the spectral lines may be approximately calculated from the orbital frequencies of the series electron when the orbits are similar as in the case of *sp* combinations.

1. INTRODUCTION

IN a previous paper[1] a method was given for obtaining an approximate harmonic representation of the so-called orbits of the second kind or penetrating orbits of the electrons in the atom, based on the atomic theory of Bohr. In the present paper a brief discussion will be given of the application of the correspondence principle to the estimation of relative intensities in emission and absorption, followed by an outline of the way in which the analysis of the previous paper may be applied to line spectra. No data at present available on emission intensities appear to be sufficiently reliable for a comparison with the theoretical predictions, but in the case of some recent measurements on intensities in absorption in the principal series of sodium a quantitative comparison will be made with the calculations.

2. THEORY OF THE ESTIMATION OF THE INTENSITIES OF SPECTRAL LINES ON THE BASIS OF THE CORRESPONDENCE PRINCIPLE

We shall assume that the intensity I in emission of a spectral line of frequency ν is given by the expression

$$I=N'A'_{''}h\nu \tag{1}$$

---

[1] F. C. Hoyt, Phys. Rev. **25**, 174 (1925). In what follows the results and notation of this previous paper will be used.

where N' is the number of atoms present in the initial state, h is Planck's constant and $A'_{\prime\prime}$ the probability as introduced by Einstein[2] that a given atom undergo in unit time a spontaneous transition from one stationary state indicated by a single prime to one of lesser energy indicated by a double prime.[3] An estimate of the probability $A'_{\prime\prime}$ may now be made on the basis of the correspondence principle in the well-known way[4] if the rate of emission of energy given by (1) is equated to that of an equivalent harmonic oscillator radiating according to the classical laws. This gives

$$A'_{\prime\prime} = \frac{1}{h\nu} \; \frac{32\pi^4 e^2}{3c^3} (Q^2\nu_0^4) \tag{2}$$

where Q is the effective amplitude and ν_0 the effective frequency of the equivalent or "virtual" oscillator. The fact that the frequency ν may be represented for multiply periodic systems as an average value of the "corresponding" harmonic $\omega_0 = \tau_1\omega_1 + \ldots\ldots + \tau_s\omega_s$ by an expression of the form

$$\nu = \int_0^1 \omega_0 d\lambda \tag{3}$$

where λ is a parameter defining a set of states intermediate between the initial and final states, suggests that $(Q^2\nu_0^4)$ may also be obtained from an average value of the same type of the quantity $C^2\omega_0^4$ or of some function of this quantity, where C is the resultant amplitude of the corresponding harmonic component of the electric moment of the atom.[5]

A great variety of possible types of average[6] have been suggested but their evaluation is possible only in the simplest cases. However, in certain instances a sufficiently accurate estimate of $A'_{\prime\prime}$ may be obtained by representing Q as a simple average of its values in the initial and final stationary states, as for example by

$$Q^2 = \tfrac{1}{2}(C'^2 + C''^2) \tag{4}$$

with

$$\nu_0 = \nu$$

in which case

$$A'_{\prime\prime} = \left(\frac{32\pi^4 e^2}{3c^3 h}\right) Q^2\nu^3$$

---

[2] A. Einstein, Phys. Zeits. **18**, 121 (1917).

[3] In what follows quantities referring to the state of greater energy will always be denoted by a prime, while those referring to the state of lesser energy will be denoted by a double prime.

[4] See, for example, Ladenburg and Reiche, Naturwissenschaften **11**, 584 (1923).

[5] N. Bohr, Zeits. f. Physik **13**, 142 (1923).

[6] For a brief discussion of the possible types of average see F. C. Hoyt, Phil. Mag. **46**, 135 (1923).

and from Eq. (1)

$$I = \text{const.} \times Q^2\nu^4. \tag{5}$$

We must remember, however, that in many cases it will be necessary to take into account the amplitudes C in the intermediate states. Such will in general be the case when these amplitudes differ greatly from those in the stationary states, and a certain criterion for the applicability of so simple an average as Eq. (4) may be found in the possibility of representing the frequency ν with sufficient accuracy by an average of the type

$$\nu = \tfrac{1}{2}(\omega_0{}' + \omega_0{}'') \tag{6}$$

involving only the orbital frequencies in the stationary states.

3. The Estimation of the Corresponding Amplitudes

In the previous paper a brief discussion was given of the character of the electron orbits involved in the emission of line spectra and the method of estimating the corresponding amplitudes was outlined. Here we shall consider in more detail the determination of these amplitudes in simple cases, using the results and notation of that paper. It is assumed that to a high degree of approximation the motion of the series electron may be regarded as a central motion, and hence the stationary states may be designated by the quantum symbol n_k, where n is the principal quantum number and k the subordinate quantum number. The value of the given spectral term is then a function of n and k and the terms may be arranged in series, each series corresponding to a certain value of k and the terms within a given series being approximately representable by a Rydberg formula with successive integral values of n. In the case of the simple systems of series occurring in a large number of elements the values of the terms are given by series expressions

$$mt = p^2R/(n - q_t)^2 \tag{7}$$

where the q's, which are ordinarily called the quantum defects, are to a first approximation independent of n. Here p is the degree of ionization of the atom (i.e. p, which is the same as the $N - N_i$ of the previous paper, is 1 for the arc spectra, 2 for first spark spectra, etc.). The integer m is merely the serial number of the term and is not to be confused with the quantum integer n, while t stands for any one of the characteristic term series $s, p, d, f, \ldots.$ for which $k = 1, 2, 3, 4, \ldots.$ respectively.

The values of the k's for the various series are readily assigned from simple considerations, but the fixation of the principal quantum numbers n is a matter of greater difficulty. Obviously the quantum defects will be dependent on the values of n, as the denominator $(n - q)^2$ only is fixed by the value of the term. Assuming any assignment of the n's, however, we have the following approximate method of finding the corresponding amplitudes.

According to the formula derived in the previous paper the amplitudes C_τ of the circular vibrations

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

into which the motion of the series electron referred to axes in the plane of the orbit may be resolved, are represented for a given value of τ as

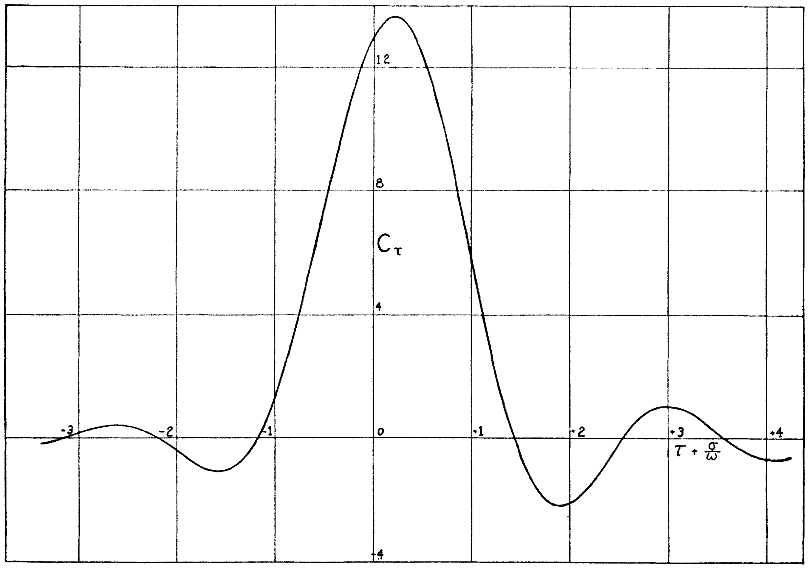

Fig. 1. Plot of C_τ/a as a function of $\rho=\tau+\sigma/\omega$ for $\epsilon=.8660$.

functions of the major axis a, the eccentricity ϵ of the outer loop, and the quantity σ/ω which for the penetrating type of orbit assumed is equal to the ratio of the frequency of precession to the radial frequency of the motion. The coefficients are of course directly proportional to the major axis. It will be seen from Eq. (22) of that paper, however, that in reality the amplitudes for given values of a and ϵ are continuous functions of the quantity $\rho=\tau+\sigma/\omega$ in the case of penetrating orbits.[7] Fig. 1 shows the computed values of C_τ/a plotted as a function of ρ for $\epsilon=.8660$, the eccentricity of a 2_1 orbit in hydrogen. This plot may then be interpreted in two ways. If we consider only values of σ/ω between 0 and 1 the portion

---

[7] For orbits of the non-penetrating type the coefficients C_τ are given to a first approximation by Eq. (22) with $\sigma/\omega=0$.

of the curve from $\rho=0$ to $\rho=1$ represents C_0 as a function of σ/ω while that from $\rho=1$ to $\rho=2$ represents C_1 as a function of σ/ω, and so on. If, however, we consider values of σ/ω greater than 1 as seems to be necessary in certain cases, we may think of the whole curve for positive ρ as representing C_0 as a function of σ/ω, or by proper shift of the origin as giving any C_τ as a function of σ/ω. For the actual estimation of the amplitudes by graphical interpolation a plot of C_τ as a function of ϵ for discrete values of σ/ω is more convenient, but the diagram given here shows more clearly the effect of increasing rotation on the coefficients. The character of the curve does not depend greatly on the value of ϵ if ϵ is near 1. For $\epsilon=1$ the curve is symmetrical with respect to the vertical axis.

From a consideration of spectral data alone it is possible to estimate the value of C_τ corresponding to an assignment of the n's and k's to the various terms, as these data give approximate values of ϵ, a, and σ/ω. As already pointed out τ is given by the changes in the quantum numbers. Thus $\tau=\pm\Delta n$, the positive sign being taken if it changes in the same sense as k and the negative sign being taken if it changes in the opposite sense.[8] The quantities a and ϵ may be found in the well-known way from the effective quantum numbers by means of Eqs. (7), (8), and (9) of the previous paper. The values of σ/ω can be estimated as follows[9]: From the general theory of multiply periodic systems the values of ω and σ satisfy the relations $\omega=\partial E/\partial J$, $\sigma=\partial E/\partial P$ where J and P are the "uniformization variables" conjugate to ω and σ respectively. Since in the stationary states $J=nh$ and $P=kh$ we have,

$$\omega=\frac{1}{h}\frac{\partial E}{\partial n}, \quad \sigma=\frac{1}{h}\frac{\partial E}{\partial k} \tag{8}$$

where E is the total energy of the motion. If we suppose this energy to be given by the formula

$$E=Rh/(n-q)^2$$

we get by carrying out the differentiation, remembering that q depends only on k,

$$\sigma/\omega=-dq/dk. \tag{9}$$

Thus σ/ω is given approximately by the negative of the slope of the curve obtained by plotting q as a function of k for a constant value of n. It must be remembered that the values of q depend on the n's, and consequently the values of the corresponding amplitudes depend on the

---

[8] See p. 184 of the previous paper.

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

assignment of the principal quantum numbers not only through the order of the harmonic but also through the values of σ/ω.

4. CALCULATION OF TRANSITION PROBABILITIES FOR THE ALKALI METALS

In this section we shall discuss the application of the general considerations outlined above to some special types of transition in the arc spectra of the alkalis and give the quantitative results for the principal series transitions of sodium.

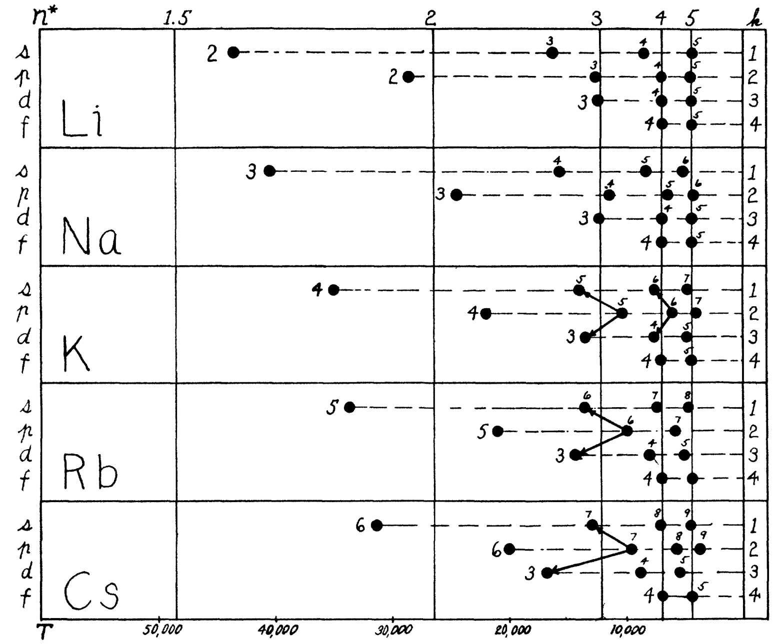

Fig. 2. Bohr diagrams for the arc spectra of the alkalies. The numbers attached to the terms are the principal quantum numbers n.

In Fig. 2 are shown Bohr diagrams for these alkali spectra. The numbers attached to the terms give the principal quantum numbers n according to the assignment of Bohr, which is based on special considerations of quantum dynamics in relation to the periodic properties of the elements. The values of n and k give at once the order of the harmonic corresponding to any given transition.

In the diagrams the fine structure of the terms has been omitted. In disregarding this fine structure in the calculations we are proceeding as though we had to do with a plane doubly-periodic motion and assuming that this gives the total transition probability for the sum of the components. Such a procedure cannot be strictly justified and in fact as pointed out by Kemble[10] and others the transition probability in such a case of degeneracy may be expected to depend in some way on the statistical weights of both initial and final states. It should be noted, however, that in comparing relative probabilities of transition of lines of the same series within which the statistical weights of initial and final states are the same, the existence of such a factor would not influence the results. In comparing lines of different series, however, it would probably have to be taken into account.

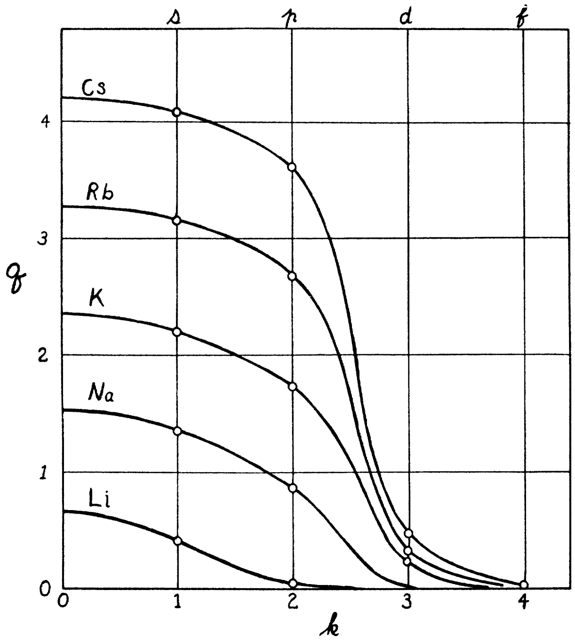

Fig. 3. Plot of the quantum defect q (cf Eq. (7)) as a function of k for the arc spectra of the alkalies.

The values of σ/ω for the s and p states necessary for the estimation of the corresponding amplitudes as determined from Eq. (9) by means of a plot of the quantum defect q against k for constant n (Fig. 3) are given in Table I. The variations of q with n have been neglected, as they are small compared to the uncertainties in drawing the curves and finding the slopes. For the $d, f, \ldots.$ terms we may suppose that the values of σ/ω are zero or at any rate very small, as according to Bohr[11] they are due to orbits of the non-penetrating type, while the s and p terms are due to orbits of the penetrating type.

---

[10] E. C. Kemble, Phys. Rev. **25**, 1 (1925).

[11] N. Bohr, Ann. der Phys. **71**, 228 (1923).

Values of the corresponding amplitudes in the stationary states may now be found for any desired transition, as described in Section 3. For this purpose plots of C_τ as a function of ϵ for different values of σ/ω were found most convenient. In estimating the transition probabilities, however, some consideration must be given to the probable values of the amplitudes in the "intermediate" states. In fact, as pointed out in Section 2, it is only in certain cases that we can hope to represent these probabilities in terms of the amplitudes in the stationary states alone, and a reasonable criterion for the possibility of representing the probabilities in this way may be found in the degree of approximation with which the frequency ν may be represented as an average of the type of Eq. (6), involving only the corresponding orbital frequencies in initial and final states.

TABLE I

Values of σ/ω in the s and p states.

Element	*s* states	*p* states
Na	.35	.70
K	.31	.67
Rb	.29	.86
Cs	.28	1.00

TABLE II

Comparison of computed and observed frequencies.

Element	Line	Calc. (1)	Calc. (2)	Obs.	$\overline{\sigma/\omega}$
Na	$2s-3p$	4590		4529	
	$3d-3p$	5330	1170	1093	.856
K	$2s-3p$	3660		3683	
	$3d-3p$	13680	3900	3179	1.51
K	$3s-4p$	1550		1550	
	$4d-4p$	4780	1730	1611	1.51
Rb	$2s-3p$	3940		3660	
	$3d-3p$	21900	5270	4437	2.35
Rb	$3s-4p$	1720		1553	
	$4d-4p$	9350	2260	2164	2.35
Cs	$2s-3p$	4050		3410	
	$3d-3p$	25000	8040	7348	3.15

Calc. (1) : Frequencies computed from the equations $\nu = \frac{1}{2}(\omega_0' + \omega_0'')$; $\omega_0 = (\tau + \sigma/\omega)(2R/n^{*3})$.

Calc. (2) : Frequencies computed from the equation $\nu = (\tau + \overline{\sigma/\omega})\bar{\omega}$ where $\overline{\sigma/\omega}$ is the slope of the straight line joining the stationary states in Fig. 3 and $\bar{\omega} = \frac{1}{2}(\omega' + \omega'')$. Values of $\overline{\sigma/\omega}$ used are given in the last column.

If we apply this criterion to the transitions involved in the alkali spectra we find that for transition between *s* and *p* terms the frequencies may be represented with a fair degree of accuracy by Eq. (6). For *pd* combinations, on the other hand, Eq. (6) does not give even a first approximation. The results of computations of the frequencies for certain *sp* and *pd* combinations are shown in the first column of Table II. The frequencies $\omega_0 = \tau\omega + \sigma = (\tau + \sigma/\omega)\omega$ of the corresponding harmonics have been found from the values of σ/ω in Table I and values of ω computed from the spectral terms by means of the relation $\omega = 2R/n^{*3}$. In the second column are given values of ν computed from the harmonic of an intermediate orbit for which σ/ω is taken as the slope of a straight line joining the stationary states in Fig. 3. In this case the agreement is better, although not quantitative.

This difference between *sp* and *pd* combinations is probably due to the fact that the former are transitions between orbits both of which are of the same type (penetrating orbits) while the latter are transitions between penetrating and non-penetrating orbits, in which case one may expect very large values of the frequency of precession when the series electron penetrates almost tangentially into the inner region.

We may then conclude that for *sp* combinations the transition probabilities may be approximately represented by an average of corresponding amplitudes in the stationary states. Computations have been made for various transitions, but it is only in the case of the principal series of sodium that a satisfactory comparison with experimental data seems possible at present, and hence only the results for these transitions are reproduced here. Table III gives the computed corresponding amplitudes necessary for a calculation of the transition probabilities for the first five lines.

TABLE III

Computed values of corresponding harmonics for the principal series of sodium.

Term	C_0	C_1	C_2	C_3	C_4
1*s*	$3.38a_0$	$.506a_0$	$.356a_0$	$.217a_0$	$.143a_0$
2*p*	4.55	....	....	....	....
3*p*	....	1.28	....	....	....
4*p*	....	....	1.14	....	....
5*p*	....	....	....	0.971	....
6*p*	....	....	....	....	0.830

The values are in terms of $a_0 = .532 \times 10^{-8}$cm as unit.

The probability of spontaneous transition $A'_{,}$, may now be found from Eq. (2), but as mentioned in Section 2 the representation of $Q^2\nu_0^4$ as an average of $C^2\omega_0^4$ may be made in several different ways. Since the results depend very considerably on the method of averaging the following six methods have been employed:

$$Q^2\nu_0^4=\tfrac{1}{2}(C'^2+C''^2)\nu^4 \qquad (A)$$

$$Q^2\nu_0^4=\tfrac{1}{4}(C'+C'')^2\nu^4 \qquad (B)$$

$$\log Q=\tfrac{1}{2}(\log C'+\log C'')\ ;\quad \nu_0=\nu \qquad (C)$$

$$Q^2\nu_0^4=\tfrac{1}{2}(C'^2\omega_0'^4+C''^2\omega_0''^4) \qquad (D)$$

$$Q^2\nu_0^4=\tfrac{1}{4}(C'\omega_0'^2+C''\omega_0''^2)^2 \qquad (E)$$

$$\log Q\nu_0^2=\tfrac{1}{2}(\log C'\omega_0'^2+\log C''\omega_0''^2) \qquad (F)$$

These averages correspond to the six methods of taking a continuous average which have been discussed previously in another connection.[6]

Table IV shows the computed values of $A'_{\prime\prime}$ as obtained by these six different methods.[12]

TABLE IV

Relative values of $A'_{\prime\prime}$ for the principal series of sodium.

Lines	A	B	C	D	E	F
$1s-2p$	1	1	1	1	1	1
$1s-3p$	.33	.29	.24	1.2	2.9	.20
$1s-4p$	.35	.29	.21	4.9	2.8	.16
$1s-5p$	.33	.24	.15	7.1	3.6	.013
$1s-6p$	.26	.18	.09	11.0	5.5	.046

TABLE V

Comparison of computed values of $A'_{\prime\prime}$ with Harrison's measurements.
Ratios of $A'_{\prime\prime}$ for successive lines

Lines	A	B	C	F	Experimental
$2p/3p$	3.0	3.4	4.2	5.0	(4−12)
$3p/4p$	.94	1.0	1.1	1.3	1.56
$4p/5p$	1.1	1.2	1.4	2.2	1.38
$5p/6p$	1.3	1.3	1.7	1.6	1.29

5. COMPARISON WITH EXPERIMENT

Relative values of the transition probabilities may be found directly from observed intensities in emission only in the case of two or more lines which have the same initial state. Such sets of lines are of rare occurrence in series spectra as ordinarily observed, and although in a few cases some estimates of intensities for such lines are available it would appear

---

[12] In a recent paper H. Bartels (Zeits. f. Phys. **32**, 415, 1925) has calculated transition probabilities for *sp* transitions in sodium, using a method of approximation for the amplitudes similar to that employed by the author. His calculations do not include the principal series transitions, but it is interesting to note that he also comes to the conclusion that averages involving only the stationary states are applicable to *sp* transitions, but not to *pd* transitions.

that they are too unreliable for a quantitative comparison where so many other uncertainties already enter in.

It may be mentioned here, however, that bolometric measurements of Paschen[13] and Randall[14] on infra-red combination lines of the alkalis give some information as to the relative intensities of certain *sp* and *pd* combinations with the same initial states. These transitions are marked with arrows in Fig, 2. Although probably not very accurate these measurements indicate that the *pd* combinations are in every case more intense than the corresponding *sp* combinations, even though the former correspond to harmonics of lower order than the later. For the reasons given in Section 4 it is not possible to make an estimate by the methods of approximation described here of the transition probabilities for *pd* combinations, but from Fig. 3 we can see that the intermediate states which will be of importance in determining the mean corresponding amplitudes will probably involve large values of the ratio σ/ω. This fact offers a possible explanation of the abnormally large intensities of the *pd* combinations, as may be seen from Fig. 1 which shows how the amplitudes change with increasing values of σ/ω. At the same time we must remember that since the statistical weights of initial and final states are not the same for these two types of transition, it may not be possible to compare directly the transition probabilities without taking into account this fact.

The most reliable estimates of transition probabilities at present available seem to be those of Harrison[15] and Slater[16] for the principal series of sodium. These are based on accurate measurements by Harrison of the relative absorption of these lines in sodium vapor, from which the probabilities were deduced by a method devised by Slater. These probabilities may be compared directly with the computed values of Table IV, and Table V shows the ratios of $A'_{,,}$ for successive lines calculated by different methods of averaging.[17] In the last column are the experimental results of Harrison. The averages D and E have been omitted from Table V as they give values widely at variance with the experimental results. Harrison's measurements give only a rough indication of the values for $1s-2p$ (the D-lines).

---

[13] F. Paschen, Ann. der Phys. **33**, 717 (1910).

[14] Randall, Ann. der Phys. **33**, 739 (1910).

[15] G. R. Harrison, Phys. Rev. **25**, 768 (1925).

[16] J. C. Slater, Phys. Rev. **25**, 783 (1925).

[17] That the agreement is not as good as indicated in Harrison's paper is due to the fact that the preliminary calculations sent to Dr. Harrison and published by him were found to be in error.

It must be admitted that the agreement by no one of the methods of averaging is very satisfactory. This may be attributed partly to the fact that the method of estimating the corresponding amplitudes is only an approximation, and partly to the fact that if any method of averaging is universally applicable it will certainly not be of a kind which involves only initial and final states.

National Research Fellowship,
The University of Chicago,
October, 1925