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INTENSITIES IN THE HYDROGEN SPECTRAL SERIES

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Abstract

The absolute intensities of the components of the most important lines of the first six series in the spectrum of the hydrogen atom as computed on the basis of the wave mechanics are tabulated. The components are summed to give the total line intensities per atom in the initial state. The probability coefficients for the components and lines are also tabulated. The results of comparison between experiment and theory are briefly discussed and an experiment for giving values more directly comparable with the calculated values is suggested.

In view of the current interest in intensity measurements it seems worth while to present the following tables of intensities computed for the components of the more important lines of the first several series in the spectrum of the hydrogen atom. Schrödinger,[1] Epstein,[2] Sommerfeld and Unsöld,[3] Eckart,[4] and others have computed the relative intensities of certain lines or components of lines and Y. Sugiura[5] has recently published a tabulation which the following tables duplicate and expand.

The absolute intensities given in this paper were computed from the expression given by Born and Jordan[6] for the energy radiated per second as the result of the change in state of an excited atom:

$$\text{Intensity} = (4e^2/3c^3)\ (2\pi)^4\ (\nu_{nn'})^4\ (q^{nn'})^2 \text{ ergs/sec.} \tag{1}$$

where e, c, and ν have their ordinary meanings and $(q^{nn'})$ is the matrix element depending on the space coordinates and characteristic quantum numbers of the atom in the states n and n' and is proportional to the energy radiated in a transfer from state n to n'. The n and n' here refer to the elementary quantum states characterized by three quantum numbers. Since the derivation of the expressions for the matrix element from the wave mechanics has been carried through by the above mentioned authors it is not repeated here. The expressions are taken directly from Sommerfeld and Unsöld[3] as developed by Wentzel[7] in polar coordinates. For the quantum change $n \rightarrow n'$; $l \rightarrow l' = l-1$ where n is the total quantum number and $(l+1)$ is the azimuthal quantum number:

$$(J^{nn',ll'}) = 2^6 l a_0{}^2 (\phi^{nn',ll'})^2 / (\psi^{n,l})(\psi^{n',l'})$$

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[1] E. Schrödinger, Ann. d. Physik, **80,** 437 (1926).

[2] P. S. Epstein, Phys. Rev., **28,** 695 (1926).

[3] A. Sommerfeld und A. Unsöld, Zeits. f. Physik, **38,** 237 (1926).

[4] Carl Eckart, Phys. Rev., **28,** 927 (1926).

[5] Y. Sugiura, Journal de Physique et le Radium, March (1927).

[6] M. Born und P. Jordan, Zeits. f. Physik, **34,** 858 (1925).

[7] G. Wentzel, Naturwiss., **14,** 621 (1926).

where:

$$(\phi^{nn',ll'}) = \left(\frac{nn'}{n+n'}\right)^4 \sum_{s=l}^{n-1} \sum_{s'=l'}^{n'-1} \left(\frac{-2n'}{n+n'}\right)^s \left(\frac{-2n}{n+n'}\right)^{s'} \binom{n+l}{n-s-1} \binom{n'+l'}{n'-s'-1} \frac{(s+s'+3)!}{(s-l)!\,(s'-l')!}\,.$$

$$(\psi^{n,l}) = n^3 \sum_{s=l}^{n-1} \sum_{s'=l}^{n-1} (-1)^{s+s'} \binom{n+l}{n-s-1} \binom{n+l}{n-s'-1} \frac{(s+s'+2)!}{(s-l)!\,(s'-l)!}$$

$a_0 = h^2/4\pi^2 me^2 =$ radius of first Bohr orbit.

The expression $(J^{nn',ll'})$ as here defined gives the sum of the intensities of the individual sub-states due to the magnetic splitting up without regard to the number of sub-states or their statistical weights. In order to obtain intensities for one electron per sub-state we must divide the above values by their statistical weights as defined by Sugiura,[4] that is $g_k = (2l+1)$. This will average over the degenerate states in our expression and we may write: $(q^{nn'})^2 = (J^{nn',ll'})/(2l+1)$ and substituting these values in Eq. (1) we obtain the intensities of the components as tabulated in column 3 of the Tables. Also in order to sum up the components to obtain the total line intensity per atom of total quantum number n we must multiply each of the component intensities by $(2l+1)/n^2$ before adding. (Since there are n^2 sub-states.) In this manner the values in column 5 were obtained. The probability values in columns 4 and 6 were obtained by dividing the energy radiated per second in the components and in the total lines respectively by $h\nu$, the energy of a single transfer, thus giving the number of transfers per second or the probability coefficient. It is also possible, as done by Sugiura, to obtain the total probability of line emission from any state by summing in a similar manner over all components beginning in this state.

The first column in the Tables gives the quantum change giving rise to the emission. $n_a = l+1$ is the azimuthal quantum number, n_r the radial quantum number, so that $n = n_a + n_r$. The second column gives the statistical weight of the component. The third and fourth columns give the intensities and probabilities of the components respectively and the fifth and sixth columns the line intensity and probability. The last column gives the value of ν for the line. The tables are arranged by series for convenience but since the intensities are absolute values comparison between tables is permissible. (See Table I)

The author has attempted to use the values in the above tables to compute the number of atoms in the various excited states as a function of the time elapsed after certain equilibrium conditions were reached. The object was to compute the constant of the well known "Abklingungs Kurven" of W. Wien[8] on the assumption that the atoms enter the observation chamber

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[8] W. Wien, Ann d. Physik, **73,** 483 (1924). Note: The futility of using the decay constants of the single lines is shown by Sugiura.

TABLE I

Theoretical intensities in the hydrogen spectrum.

Quantum change $n_a n_r$ $n_a' n_r'$	Stat. wt. $(2l+1)$	Component intensity ergs/sec.	Component probability	Line intensity ergs/sec.	Line prob.	Wave no. ν
			1st Series—Lyman			
20−10	3	10.2×10^{-3}	63.2×10^{7}	7.65×10^{-3}	47.4×10^{7}	82270
21−10	3	3.24	16.9	1.08	5.64	97630
22−10	3	1.38	6.83	.260	1.28	103120
23−10	3	.710	3.44	.085	.412	105310
24−10	3	.435	2.08	.036	.173	106410
25−10	3	.295	1.40	.018	.086	107510
26−10	3	.220	1.04	.011	.049	108050
			2nd Series—Balmer			
30−20	5	19.35×10^{-5}	6.47×10^{7}	13.23×10^{-5}	4.42×10^{7}	15240
21−11	3	6.78	2.26			
12−20	1	1.89	.632			
31−20	5	8.36	2.07	3.42	.845	20570
22−11	3	3.95	.975			
13−20	1	1.04	.258			
32−20	5	4.27	.946	1.15	.254	23040
23−11	3	2.25	.497			
14−20	1	.575	.127			
33−20	5	2.55	.543	.488	.102	24380
24−11	3	1.43	.298			
15−20	1	.357	.075			
34−20	5	1.60	.324	.226	.046	25180
25−11	3	.944	.191			
16−20	1	.228	.046			
35−20	5	1.04	.207	.115	.023	25710
26−11	3	.660	.131			
17−20	1	.157	.031			
36−20	5	.685	.134	.060	.012	26070
27−11	3	.446	.087			
18−20	1	.107	.021			
			3rd Series—Paschen			
40−30	7	1.45×10^{-5}	1.38×10^{7}	$.946\times10^{-5}$	$.904\times10^{7}$	5333
31−21	5	.753	.720			
22−12	3	.323	.309			
22−30	3	.037	.035			
13−21	1	.188	.180			
41−30	7	.697	.455	.338	.221	7800
32−21	5	.522	.341			
23−12	3	.252	.165			
23−30	3	.023	.015			
14−21	1	.139	.091			
42−30	7	.387	.216	.142	.079	9142
33−21	5	.346	.193			
24−12	3	.172	.096			
24−30	3	.014	.008			
15−21	1	.091	.051			
43−30	7	.240	.123	.066	.034	9950
34−21	5	.225	.115			
25−12	3	.118	.060			
25−30	3	.0090	.0046			
16−21	1	.061	.031			

TABLE I (*continued*)

Quantum change $n_a n_r$ $n_a' n_r'$	Stat. wt. $(2l+1)$	Component intensity ergs/sec.	Component probability	Line intensity ergs/sec.	Line prob.	Wave no. ν
44−30	7	$.157\times10^{-5}$	$.076\times10^{7}$	$.034\times10^{-5}$	$.017\times10^{7}$	10475
35−21	5	.157	.076			
26−12	3	.084	.041			
26−30	3	.0062	.0030			
17−21	1	.043	.021			
45−30	7	.116	.054	.020	.0095	10835
36−21	5	.128	.060			
27−12	3	.062	.029			
27−30	3	.0045	.0021			
18−21	1	.033	.016			
4th Series—Brackett						
50−40	9	20.8×10^{-7}	43.0×10^{5}	13.2×10^{-7}	27.3×10^{5}	**2468**
41−31	7	12.6	26.1			
32−22	5	7.26	15.0			
32−40	5	.246	.507			
23−13	3	3.60	7.43			
23−31	3	.0092	.019			
14−22	1	6.09	12.54			
51−40	9	9.94	13.3	5.75×10^{-7}	7.68×10^{5}	3807
42−31	7	9.85	13.2			
33−22	5	6.58	8.81			
33−40	5	.094	.126			
24−13	3	3.88	5.19			
24−31	3	.0075	.010			
15−22	1	3.11	4.16			
52−40	9	7.94	8.75	3.33×10^{-7}	3.67×10^{5}	4618
43−31	7	8.65	9.55			
34−22	5	4.28	4.73			
34−40	5	.057	.063			
25−13	3	2.38	2.63			
25−31	3	.0041	.0045			
16−22	1	1.98	2.19			
5th Series						
60−50	11	4.20×10^{-7}	16.0×10^{5}	2.60×10^{-7}	9.88×10^{5}	1338
51−41	9	2.63	10.0			
42−32	7	1.97	7.50			
42−50	7	.045	.17			
33−23	5	1.14	4.32			
33−41	5					
24−14	3	.617	2.35			
24−32	3					
15−23	1	1.97	7.50			
61−50	11	2.40	5.69	1.48×10^{-7}	3.52×10^{5}	2150
52−41	9	2.46	5.82			
43−32	7	1.97	4.66			
43−50	7	.0093	.022			
34−23	5	1.27	3.01			
34−41	5					
25−14	3	1.01	2.40			
25−32	3					
16−23	1	1.10	2.60			

TABLE I (*continued*)

Quantum change $n_a n_r$ $n_a' n_r'$	Stat. wt. $(2l+1)$	Component intensity ergs/sec.	Component probability	Line intensity ergs/sec.	Line prob.	Wave no. ν
6th Series						
70−60	13	1.13×10^{-7}	7.10×10^{5}	0.665×10^{-7}	4.18×10^{5}	809.6
61−51	11	.635	4.00			
52−42	9	.617	3.89			
52−60	9	.0113	.071			
43−33	7	.421	2.65			
43−51	7					
34−24	5	.235	1.48			
34−42	5					
25−15	3	.051	.32			
25−33	3					
16−24	1	1.04	6.53			

in more or less highly excited states and further excitation being impossible cascade down to the final normal states according to the probabilities given above. Thus Wien's curves would give simply the relative number of atoms in the initial states as a function of the time which as computed is a complicated expression depending on the probabilities of all transfers between still higher states and on the probability of leaving the state in question to all lower states. It was found that quantitative calculations on various assumptions of initial distribution among the states etc. did not check well. However from simple calculations it is seen that the ratio of the number of atoms entering the states $n=3$, $n=4$, $n=5$, giving rise to the first three Balmer lines, to the number of atoms leaving these states is very closely the same for the three states. Thus on the above assumption one would expect the same "decay constant" for the three lines as found by Wien and as denied by other theoretical considerations.[9] The theory that a large part of the intensity observed in the "decay curves" comes from "new excitation," that is atoms dropping into states capable of radiating the lines under observation from higher states, is substantiated by recent experiments of Hertel[10] and Rupp[11] where the intensity of the polarized light in the canal stream is shown to decay much more rapidly than the total intensity. The polarization is due to impacts within the discharge tube and canal and apparently disappears as soon as the atom has emitted a quantum of radiation though the atom need not necessarily return immediately to the ground state.

It is interesting to remark on the comparison of the computed relative intensities of the lines with experimental results. (For the relative component intensities the calculated and experimental values have been shown to agree reasonably well. For the fine structure as split up in the Stark

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[9] G. Mie, Ann. d. Physik, **66,** 237 (1921); J. Palacios, Ann. d. Physik, **79,** 55 (1926); R. d'E. Atkinson, Proc. Roy. Soc. **A116,** 81 (1927).

[10] K. L. Hertel, Phys. Rev., **29,** 848 (1927).

[11] E. Rupp, Ann. d. Physik, **84,** 94 (1927).

Effect by Schrödinger[1] and by Epstein,[12] for the normal components by Eckart[4] and by Sommerfeld and Unsöld.[3]) Ornstein[13] in a recent paper has made a comparison of the line intensities as computed by Schrödinger[1] with the experimental values obtained by Bongers.[14] The values quoted from Schrödinger however are computed on the basis that there are an equal number of atoms in the various initial states ready to emit the Balmer lines while actually only 9/16 of the atoms in the 4 quantum state and 9/25 of those in the 5 state etc. can emit the Balmer lines. Also there is no reason to believe that under the experimental conditions there were an equal number of atoms in each excited state. Thus the experimental results are really not comparable with the values calculated for one atom in each state. Results of Crew and Hulburt[15] and other observers show that the observed intensities depend on the mode of excitation and other conditions which may determine the number of atoms in each excited state. Only if this were the same for all states would the observed results be comparable with the calculated values above.

The author suggests the following method of obtaining a direct comparison between the calculations and experiment. If the relative intensities of the lines of two series, whose initial states overlap, are obtained simultaneously it would be possible by assuming the calculated intensities to hold for one series to compute the relative numbers of atoms in the various states and using these values to compute the relative intensities per atom for the second series for comparison with their calculated values.

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[12] P. S. Epstein, Phys. Rev., **28,** 695 (1926). Note: Certain of the intensities as calculated by Epstein are in error due to irregularities in integrating over the angular coordinate. (Counting twice instead of once the component $m=0$.)

[13] L. S. Ornstein, Phys. Zeits., **28,** 688 (1927).

[14] J. A. Bongers, Utrecht Dissertation (1927).

[15] W. H. Crew and E. O. Hulburt, Phys. Rev., **29,** 843 (1927).