LXXXI. On the principal series in the spectra of the alkali metals

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inversely as the fourth power of the distance, seems to show that the atom of iron must come under one of the special cases above mentioned, having a centre ring with only one or two electrons. The force in this case may be inversely as the square of the distance. This is shown by the equations for the hydrogen atom, (48) and (49) above, where the first term due to the magnetic force contains the inverse second power of the distance, showing that for hydrogen atoms at a great distance, having parallel axes, the attraction is inversely as the square of the distance. This suggests that possibly the rings of electrons in fig. 3* of the former paper are correct, for there iron and cobalt have a single central electron, and nickel two central electrons, which will give rise to the same law of variation of the force with the distance as that in hydrogen.

In this paper the positive charge in each atom is supposed to be at rest free from vibration of its whole mass, and long waves of radiant heat are attributed to the vibration of this mass. The period of this vibration in the hydrogen molecule was given in the former paper. It should be considered, therefore, that the work in this paper applies to the state of matter at the absolute zero of temperature.

LXXXI. *On the Principal Series in the Spectra of the Alkali Metals.* By W. MARSHALL WATTS, D.Sc.†

IN the Philosophical Magazine for 1908 (xvi. p. 945) Wood describes the absorption spectrum of sodium vapour in which he measured 48 lines of the principal series forming the most extended "Balmer series" hitherto observed.

Bevan‡ applied Wood's method to the other alkali metals, and observed extended series in lithium, potassium, rubidium, and caesium. He also discusses the representation of these long series by formulæ, obtaining very close results by the use of the formula employed by Mogendorff in 1906 and by Hicks in 1910, viz.,

$$\text{O.F.} = \text{C.F.} - \frac{109675}{\left(m + \mu + \frac{c}{m}\right)^2}.$$

* *Loc. cit.*

† Communicated by the Author.

‡ Proc. Roy. Soc. lxxxiii. p. 423 (1910), lxxxiv. p. 209, lxxxv. pp. 54, 55, lxxxvi. p. 300 (1911).

The Principal Series in Sodium.

OBSERVED.					m.	OBSERVED—CALCULATED.			
Arc.		Spark.		Absorption.		CALCULATED.			
Kayser & Runge.	Eder & Valenta.	Exner & Haschek.	Exner & Haschek.	Schillinger.	Wood.		Birge.	Hicks.	Lohuizen.
{ 5896.16 5890.19 3303.07 3302.47	{ 5896.15 5890.18 3303.12 3302.50	{ 5896.17 5890.20 3303.11 3302.56	{ 5896.18 5890.21 3303.17 3302.52	{ 5896.16 5890.19 3303.16 3302.49		{ 5896.16 5890.19 3303.07 3302.47	-01 0 +06 +04	0 0 0	0 -01 -01
2852.91	2852.91	2853.00	2852.9	2853.00	2852.91	{ 2853.04 2852.84	0 -04	0	0
2680.46	2680.46	2680.50			2680.46	2680.39	+09	+03	+11
2593.98	2593.98				2594.05	2593.89	+09	+02	+11
2543.85					2543.82	2543.86	-05	-09	0
2512.23					2512.15	2512.16	+03	-01	0
					2490.70	2490.74	-04	-13	-04
					2475.60	2475.56	+04	-07	-03
					2464.53	2464.42	+11	+01	+11
					2456.02	2455.97	+05	+05	+04
					2449.46	2449.42	+04	+04	+03
					2444.24	2444.23	+01	-03	0
					2440.06	2440.06	0	+01	0
					2436.70	2436.64	+06	-05	+05
					2433.85	2433.82	+03	+04	+03
					2431.43	2431.45	-02	-01	-02
					2429.42	2429.44	-02	-02	-03

2427.72	20	2427.73	-01	-01	-01	-02
2426.28	21	2426.26	+02	+02	+01	+01
2425.00	22	2424.99	+01	+03	0	0
2423.88	23	2423.88	0	+01	-01	-01
2422.90	24	2422.90	0	0	-01	-01
2422.04	25	2422.04	0	0	-01	-01
2421.29	26	2421.29	0	+02	0	0
2420.60	27	2420.59	+01	+01	-01	-01
2420.02	28	2420.00	+02	+04	+02	+02
2419.50	29	2419.45	+05	+07	+05	+05
2419.00	30	2418.96	+04	+06	+04	+04
2418.44	31	2418.51	-07	-05	-07	-07
2418.09	32	2418.11	-02	0	-02	-02
2417.71	33	2417.74	-03	-01	-01	-01
2417.38	34	2417.40	-02	+01	-02	-02
2417.10	35	2417.09	+01	+02	+01	+01
2416.80	36	2416.81	-01	0	-01	-01
2416.56	37	2416.55	+01	+03	+01	+01
2416.33	38	2416.31	+02	+04	+02	+02
2416.11	39	2416.09	+02	+03	+02	+02
2415.89	40	2415.88	+01	+02	+02	+02
2415.70	41	2415.69	+01	+03	+01	+01
2415.52	42	2415.50	+02	+02	+02	+02
2415.37	43	2415.35	+02	+03	+02	+02
2415.21	44	2415.19	+02	+04	+02	+02
2415.06	45	2415.05	+01	+03	+02	+02
2414.94	46	2414.91	+03	+05	+03	+03
2414.78	47	2414.79	-01	+01	+01	+01
2414.64	48	2414.67	-03	-03	-01	-01
2414.50	49	2414.56	-06	-04	-04	-06

Birge has the convergence-frequency 41448.71, Hicks 41446.76, and von Lohuizen 41448.5.

Other formulæ which have been employed (besides that of Kayser and Runge, which is not sufficient) are the Ritz form

$$\text{O.F.} = \text{C.F.} - \frac{109675}{\left(m + \mu + \frac{c}{m^2}\right)^2},$$

and that of Lohuizen

$$\text{O.F.} = \text{C.F.} - \frac{109675}{\left(m + \mu + \frac{c}{\text{O.F.}}\right)^2}.$$

A comparison of the results given by these different formulæ is calculated to afford useful guidance in the examination of less extended series.

The case of Sodium has been examined at length by Birge*, who gives wave-lengths on the Fabry and Perot scale reduced to vacuum, and employs the Ritz formula with 109678·6 as the value of N instead of 109675.

In the table on pp. 776-7 I give the wave-lengths calculated from the formula

$$\text{O.F.} = 41448\cdot67 - \frac{109675}{\left(m + \cdot147408 - \frac{\cdot031328}{m-1}\right)^2}$$

for the less refrangible component, and

$$\text{O.F.} = 41448\cdot67 - \frac{109675}{\left(m + \cdot148204 - \frac{\cdot031380}{m-1}\right)^2}$$

for the more refrangible component of the pairs of lines.

In Potassium the formulæ

$$\text{O.F.} = 35005\cdot56 - \frac{109675}{\left(m + \cdot293076 - \frac{\cdot061356}{m-1}\right)^2},$$

$$\text{O.F.} = 35005\cdot56 - \frac{109675}{\left(m + \cdot296228 - \frac{\cdot061628}{m-1}\right)^2}$$

give the following values :—

* Astrophys. Journ. xxxii. p. 112 (1910).

give the following results :—

The Principal Series in Rubidium.

Flame.	Arc.		Spark.	Kayser & Runge. (Arc.)	m.	Calculated		Observed—Calculated.		
	Lehmann.	Saunders.	Exner & Haschek.					Birge.	Hicks.	Bevan.
Eder & Valenta.										
{ 7950·4	{ 7950·46	{ 7947·6		{ 7950	2	{ 7949·03	+·01	0	0	
{ 7806·2	{ 7805·98	{ 7800·2		{ 7811*		{ 7803·13	+·04	-2·5		
Ramage.		Exner & Haschek.								
4215·63		{ 4215·75	{ 4215·73	{ 4215·72	3	{ 4215·72	-·01	0	0	
4202·04		{ 4202·06	{ 4201·97	{ 4201·98		{ 4201·99	+·01		0	
3591·86		{ 3591·74		{ 3591·74	4	{ 3591·74	+·04	+20	0	
3587·27		{ 3587·21		{ 3587·23		{ 3587·22	+·02		0	
3350·98		{ 3351·00		{ 3351·03	5	{ 3350·94	+·06	+16	0	
3348·84		{ 3348·89		{ 3348·86		{ 3348·93	-·07		+·06	
3229·26					6	{ 3229·27	-·01	-·01	+·02	
3228·18				Bevan. (Absorption.)		{ 3228·10	+·08	-	·04	
				{ 3158·25†	7	{ 3158·39	+·08	-22	+1·00	-19
				{ 3157·69		{ 3157·67	+·02		+·27	-03
				3112·95	8	3112·95	0	-23		-11
				3082·39	9	3082·34	+·05	-65		+·01
				3060·62	10	3060·56	+·06	-41		-·01
				3044·33	11	3044·47	-14	-40		-20
				3032·20	12	3032·25	-·05	-26		-11
				3022·70	13	3022·74	-·04	-23		-09
				3015·16	14	3015·20	-·04	-18		-11
				3009·03	15	3009·11	-·08	-08		-15
				3004·11	16	3004·12	-·01	-27		-08
				2999·96	17	2999·98	-·02	-03		-08
				2996·51	18	2996·51	0	-26		-06
				2993·52	19	2993·57	-·05	-21		-12
				2991·12	20	2991·06	+·06	-09		+·01
				2988·94	21	2988·89	+·05	-13		-01
				2987·01	22	2987·02	-·01	-14		-06
				2985·45	23	2985·38	+·07	0		+·02
				2984·05	24	2983·94	+·11	+14		+·06
				2982·68	25	2982·67	+·01	+41		-05
				2981·51	26	2981·53	-·02	+53		-08
				2980·52	27	2980·53	-·01			-07
				2979·62	28	2979·62	0			-07
				2978·81	29	2978·81	0			-07
				2978·10	30	2978·08	+·02			-05
				2977·39	31	2977·42	-·03			-09

* { 7947·7 Eder & Valenta (Arc.)

† 3158·7 Saunders.

Birge has the convergence-frequency 33687·82, Hicks 33687·50, and Bevan 33687·5.

For Cæsium the formulæ

$$\text{O.F.} = 31404 \cdot 31 - \frac{109675}{\left(m + 418202 - \frac{090052}{m-1}\right)^2},$$

$$\text{O.F.} = 31404 \cdot 31 - \frac{109675}{\left(m + \cdot 449969 - \frac{\cdot 089326}{m-1}\right)^2}$$

give the following results :

The Principal Series in Cæsium.

Observed.						m.	Calculated	Observed-Calculated	
Randall. (Arc.)	Lehmann. (Arc.)	Kayser & Runge. (Arc.)	Exner & Haschek. (Arc.)	Runge. (Flame.)	Bevan. (Absorp- tion.)			Bevan.	Hicks.
{ 8945·0 8522·4	{ 8949·92 8527·72					2	{ 8949·92 8527·72		0
		{ 4593·34 4555·44 3888·83 3876·7 3617·08 3611·84	{ 4593·29 4555·34 3889·1 3876·7	{ 4593·30 4555·46 3888·75 3876·31 3617·49 3611·70	{ 3888·80 3876·53 3617·56 3611·54	3	{ 4593·19 4555·29 3888·66 3876·34		−·02 +·04 +·42
						4	{ 3888·66 3876·34 3617·31 3611·54	+·04 +·17 +·13 +·05	+·42 −·09 −·22
						5	{ 3617·31 3611·54 3480·09 3476·88	+·05 +·09 +·19 +·15	−·05 −·05 −·10 −·10
				3477·25	3477·03	6	{ 3476·88 3400·05 3398·06 3348·93	−·10 0 +·21 −·09	−·14 +·13 −·09 −·12
				3398·40	3398·27	7	{ 3348·93 3347·63 3314·18 3313·26	+·13 −·09 −·02 +·02	+·67 −·09 −·09 −·05
				3348·72	3347·56	8	{ 3314·18 3313·26 3289·25 3288·68	−·12 −·02 −·18 −·08	+·30 −·21 −·25 −·16
				3314	3313·28	9	{ 3289·25 3288·68 3270·66 3256·77	−·08 −·16 +·02 −·09	−·16 −·15 −·16 −·07
				3287	3288·68	10	{ 3270·66 3256·77 3246·02 3237·58	−·02 −·09 −·10 0	−·16 −·15 −·16 −·07
						11	{ 3237·58 3230·88 3225·11 3220·34	0 −·07 +·01 −·06	−·07 −·09 0 −·09
						12	{ 3230·88 3225·03 3225·03 3220·40	−·07 −·02 0 −·01	−·08 −·08 −·02 −·03
						13	{ 3220·40 3216·45 3213·02 3210·18	−·01 −·01 −·09 −·07	−·03 −·03 −·09 −·08
						14	{ 3210·18 3207·78 3205·64 3203·80	−·07 0 +·01 +·04	−·08 −·02 −·02 +·01
						15	{ 3203·80 3202·13 3200·71 3199·45	+·04 +·01 +·05 +·08	+·01 −·02 +·01 +·03
						16	{ 3200·71 3199·45 3198·25 3197·28	+·08 +·03 +·03 +·09	+·03 −·01 −·01 +·05
						17	{ 3197·28 3196·20 3195·42 3194·59	+·09 −·07 −·01 −·08	+·05 −·11 −·05 −·13
						18	{ 3196·20 3195·42 3194·59 3193·24	−·07 −·01 −·08 −·04	−·11 −·05 −·13 −·10

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In the case of Lithium the results are not quite so satisfactory. Hicks finds the convergence-frequency to be $43482\cdot20 \pm 1\cdot18$. Bevan uses $43482\cdot98$, but points out that his latest measurements indicate a higher convergence-frequency.

In the following table I give the results calculated from

$$\text{O.F.} = 43485\cdot18 - \frac{109675}{\left(m - 0\cdot4929 + \frac{0\cdot008185}{m-1}\right)^2}$$

The Principal Series in Lithium.

Flame.	Arc.		Spark.		Absorption.	Calculated.	Observed--Calculated.		
	Kayser & Runge.	Exner & Haschek.	Eder & Valenta.	Exner & Haschek.			Bevan.	Hicks.	Birge.
Ramage.					Bevan.	m.			
6708·0	6708·2	6708·10	6708·07	6708·09		2	6707·94 +·06	0	0
3232·82	3232·77	3232·8	3232·98	3232·80		3	3232·89 -·09	0	0
2741·43	2741·39	2741·37	2741·57	2741·32		4	2741·34 +·08	0	+·07
	2562·60					5	2562·44 +·16	+·07	0
	2475·13					6	2475·15 -·02	-·11	+·20
	2425·55					7	2425·52 +·03	-·08	+·01
	2394·54					8	2394·46 +·08	-·02	+·03
					2373·9	9	2373·65 +·25	+·09	+·10
					2359·4	10	2359·03 +·37	+·22	+·22
					2348·5	11	2348·33 +·17	+·03	
					2340·5	12	2340·27 +·23	+·08	
					2334·3	13	2334·04 +·26	+·12	
					2329·0	14	2329·12 -·12	-·28	
					2325·2	15	2325·17 +·03	-·13	
					2321·9	16	2321·97 -·07	-·20	
					2319·3	17	2319·31 -·01	-·15	
					2317·1	18	2317·08 +·02	-·12	
					2315·2	19	2315·21 -·01	-·15	
					2313·6	20	2313·61 -·01	-·15	
					2312·2	21	2312·23 -·03	-·17	
					2311·1	22	2311·04 +·06	-·08	
					2310·0	23	2310·01 -·01	-·15	
					2309·0	24	2309·10 -·10	-·24	
					2308·3	25	2308·30 0	-·14	
					2307·5	26	2307·59 -·09	-·23	
					2306·90	27	2306·96 -·06	-·18	
					2306·48	28	2306·39 +·09	-·03	
					2305·87	29	2305·88 -·01	-·11	
					2305·41	30	2305·42 -·01	-·11	
					2304·99	31	2305·01 -·02	-·11	
					2304·63	32	2304·63 0	-·15	
					2304·29	33	2304·30 -·01	-·10	
					2304·00	34	2303·99 +·01	-·07	
					2303·73	35	2303·70 +·03	-·06	
					2303·46	36	2303·44 +·02	-·12	
					2303·24	37	2303·20 +·04	-·05	
					2303·03	38	2302·98 +·05	-·03	
					2302·83	39	2302·77 +·06	-·03	
					2302·59	40	2302·58 +·01	-·08	
					2302·38	41	2302·41 -·03	-·12	
					2302·20	42	2302·24 -·04	-·13	

If we take the mean observed value of the first line 6708.12, which corresponds to the oscillation-frequency 14903.26 *in vacuo*, and, applying the Rydberg-Schuster rule, add 28579.71, Hicks's mean value for the convergence-frequency of the subordinate series, we obtain 43482.97 for the convergence-frequency of the principal series.

LXXXII. *Ionization by Positive Rays.*

By NORMAN CAMPBELL*.

1. **T**HE chief facts concerning the ionization of gases by electrons seem to be now thoroughly established, but comparatively little is known concerning ionization by the impact of atoms except when the atoms are those constituting α -rays. The first direct attack on this problem is described in the recent papers of v. Bahr and Franck† and of Pawlow‡, who come to the surprising conclusion that the positively charged particles from hot platinum and hot phosphates can ionize gases when their energy is less than that required by electrons. This result is of the greatest importance for theories of the structure of the atom, for it would seem to indicate that the "ionization potential" for electrons has not the fundamental significance which has often been attributed to it; it appears that further experiments, especially on the variation of the ionizing power of positive particles with their speed, energy or charge, are desirable.

It is not easy to conduct such quantitative experiments on a gas, into which rays of such low speed as are here considered have practically no power of penetration. But recent work has tended to show § that the liberation of electrons, which takes place when ionizing rays of any kind fall on a metal surface, varies with the properties of those rays in precisely the same manner as the ionization which the rays cause in a gas. Indeed it is highly probable that, when the surface of the metal has been recently polished, the electrons are actually liberated from a layer of gas on the surface of the metal. Experiments on such metal surfaces are free from many of the difficulties which attend experiments on ionization in a gas which has any appreciable volume.

* Communicated by the Author.

† E. v. Bahr and J. Franck, *Deutsch. Phys. Gesell. Verh.* xvi. 1. p. 57 (1914).

‡ W. Pawlow, *Roy. Soc. Proc. A.* vol. xc. p. 398 (1914).

§ See, *e.g.*, N. Campbell, *Phil. Mag.* June 1913, p. 803, and March 1915, p. 369.