

Intensity Relations in Chromium Spectra

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The relative intensities of lines in four multiplets in the spectrum of Cr I, and eight multiplets in the spectrum of Cr II, have been measured with a concave-grating spectrograph and photographic photometry. The intensities in many cases deviate from those calculated for Russell-Saunders coupling, the deviations being in accord with observations of others on intensities in the spectra of

elements of the iron group. Perturbing energy levels offer a possible explanation of many of the deviations. Two multiplets in the septet system of Cr II have been corrected for excitation. The temperature of the chromium arc source consistent with this correction was found to be 4060°K.

I. INTRODUCTION

INTENSITY measurements in the complex spectra of the elements composing the iron group are particularly interesting because of the increasing divergence from intensity rules for Russell-Saunders coupling as the atomic number increases. The elements at the beginning of the group show fairly good agreement with these intensity rules, but there is an increase in the proportion of anomalous line intensities as one passes through this group to nickel. This is shown by the intensity studies of titanium (22),¹ vanadium (23),² chromium (24),³ manganese (25),⁴ iron (26),⁵ cobalt (27)⁶ and nickel (28).⁷ This investigation was undertaken to determine some of the intensity relations in chromium.

II. EXPERIMENTAL

The method of photographic photometry as described by G. R. Harrison was used for the determination of relative intensities of spectral lines.

Excitation of spectrum

Two pieces of purified chromium metal were clamped in water-cooled holders in a glass bulb, 19 cm in diameter, where the pressure was maintained at 7 to 15 cm of mercury. The arc

was excited by approximately 2.4 amperes, furnished by a 110-volt storage battery with a large reactance in series. The glass bulb was provided with a quartz window which transmitted the desired wavelengths.

Spectrograph

A concave grating with a radius of curvature of 6.4 meters, having 6000 lines per cm for a length of 11.6 cm, was used in the second order with a dispersion of 1.25Å/mm, on a Paschen-type mounting. The intensity of the light was varied by absorbing screens made of screen wire of different mesh placed between the lens and the slit. The intensity could be varied from 100 to 3 percent. The plateholders were held in position and manipulated by means of cassettes, making it possible to expose any portion of the plate. The cassettes, taking 4×10-inch plates, were placed on two concentric rails on a rigid circular table. The plate was raised 4 mm between each exposure, making it possible to take 22 exposures on one plate. These exposures were accurately timed by an automatic timing device consisting of a pendulum, vacuum-tube relay, and magnetic shutter. The two central exposures were of the chromium arc. Above and below these were three exposures of the mercury arc for calibration purposes. Exposures were made simultaneously on both sides of the normal in such a way that there was a 40-Å overlap, thus giving a continuous exposure to the chromium or other sources. Eastman 36 plates were used.

Determination of intensities of spectral lines

The photographic plates were calibrated, as described by Harrison, with a series of exposures

¹ G. R. Harrison, *J. O. S. A.* **17**, 389 (1928).

² G. R. Harrison, unpublished material.

³ C. E. Hesthal, unpublished material.

⁴ R. S. Seward, *Phys. Rev.* **37**, 344 (1931).

⁵ J. B. van Milaan, *Zeits. f. Physik* **34**, 921 (1925); R. Frerichs, *Ann. d. Physik* **81**, 807 (1926).

⁶ L. S. Ornstein and T. Bouma, *Phys. Rev.* **36**, 679 (1930).

⁷ H. N. Russell, *Astrophys. J.* **66**, 335 (1927); but modified later, see *J. O. S. A.* **18**, 296 (1929).

to a mercury arc operated on a 110-volt storage battery. To get the intensity of a given chromium line the percentage transmissions were measured by means of a densitometer employing a photoelectric cell and a Wynn-Williams⁸ Wheatstone-bridge amplifier as described by C. E. Hesthal and G. R. Harrison.⁹ The transmissions as given by the densitometer were then converted to the corresponding intensities by means of a calibration curve. To correct for variations in the arc, 48 exposures were made of each chromium line.

Corrections and errors

1. The intensity of the background upon which the spectrum was superimposed was determined separately and subtracted from the intensity of the line.

2. A correction for self-reversal was made by adding to the intensity that fraction of the light which was absorbed as the radiation passed through the cooler layers of chromium vapor surrounding the arc, in the manner described by Harrison.

3. The transmissions of the most intense lines could not be read accurately in the stronger exposures, and very weak lines could be measured only in the more intense exposures, while other lines could be obtained in all exposures. To correct for this experimental limitation, weighted averages were used, the proper weight for each exposure (or group of exposures) being determined from the intensity readings of four lines that appeared in all exposures on all photographic plates. In this way all exposures were converted to the same arbitrary scale.

4. Since the rate of radiation of an oscillator is proportional to the fourth power of the frequency, it is necessary to divide each intensity by the fourth power of its frequency in order to compare theoretically intensities of different frequencies.

5. The variation in sensitivity of the spectrograph with wavelength was determined in a separate experiment, and the results were used to correct all intensities for this variation.

6. All measured intensities have been checked for superimposed lines of aluminum and iron,

the two most abundant impurities in the chromium arc.

7. In a few cases the superposition of ghosts upon spectral lines has augmented the measured intensities. These cases have been indicated in the results.

8. In varying the intensity of the calibrating source of light, it was necessary to move the screens with an irregular motion to average out the effect of moire patterns. This gives rise to three kinds of errors. (a) Intermittency effect of the photographic plate introduces an error because of the small variations in the intensity due to the motion of the absorbing screens. This variation is under 10 percent and results in an intermittency error of less than 1 percent.¹⁰ (b) The error due to the diffraction of light in passing through the screens was reduced to a minimum by removing the slit, flooding the grating with light. (c) The error due to lack of achromatism is negligible. Landsberg¹¹ has found wire screens to be neutral in their absorption to within 1 or 2 percent over the wavelength region from 2000A to 5000A.

III. RESULTS

In Table I and Table II observed intensities of the lines of each multiplet have been compared with the theoretical relative intensities¹² calculated for Russell-Saunders coupling. The notation here used is that given by Bacher and Goudsmit.¹³

Chromium I

Multiplet $a^5D - y^5D^0$ ($3d^4 4s^2 - 3d^4 4s(4D) 4p$). Some of the abnormally high intensities may be attributed to overlapping ghosts. Other anomalies may arise from perturbations between the terms of y^5D^0 and y^5F^0 which overlap.

Multiplet $a^5D - x^5D^0$ ($3d^4 4s^2 - ?$). Line 2889.3A of this multiplet is coincident with 2889.2A of $a^4D - z^4D^0$ of Cr II. The observed intensity was arbitrarily divided so that the latter line would be approximately normal. The results show both lines to be normal. The self-reversal curves of $a^5D - w^5P^0$, $a^5D - x^5D^0$, and $a^5D - y^5D^0$ are similar

¹⁰ G. R. Harrison, J. O. S. A. **18**, 492 (1929).

¹¹ Landsberg, Zeits. f. Physik **46**, 106 (1927).

¹² H. E. White, *Introduction to Atomic Spectra*, p. 205 *et seq.*

¹³ R. F. Bacher and S. Goudsmit, *Atomic Energy States*, McGraw-Hill, 1932.

⁸ C. E. Wynn-Williams, Phil. Mag. **6**, 324 (1928).

⁹ C. E. Hesthal and G. R. Harrison, Phys. Rev. **34**, 543 (1929).

TABLE I. *Chromium I*. $I_{\text{obs.}}$, observed intensities after applying corrections for background, self-reversal, ν^4 , and variation in sensitivity. I^* , intensity measurements by C. E. Hesthal.

Wavelength	Transition	$I_{\text{theor.}}$	$I_{\text{obs.}}$	I^*	Wavelength	Transition	$I_{\text{theor.}}$	$I_{\text{obs.}}$	I^*
<i>Multiplet</i>	$a^5D - y^5D^0$				2893.2	3-3	269	269	
3005.1	4-3	359	522	490	2889.3	4-4	577	581 ²	
3000.9	3-2	478	593	578	2887.0	1-2	134	99.3	
2996.6	2-1	419	502 ¹	480	2879.3	2-3	154	91.5	
2992.0	1-0	240	274 ¹	269	2871.6	3-4	115	55.8	
2986.5	4-4	1790	821	1600					
2986.1	1-1	900	803	1060	<i>Multiplet</i>	$a^5D - w^5P^0$			
2986.0	3-3				2780.7	4-3	237	237	
2985.9	2-2				2769.9	3-2	123	125	
2980.8	0-1				2764.3	3-3	61.4	71.0 ¹	
2975.5	1-2	419	362	337	2761.7	2-1	46.0	48.2	
2971.1	2-3	478	409	423	2757.1	2-2	76.8	81.5	
2967.6	3-4	359	359	365	2752.9	1-1	59.2	57.7	
					2751.6	2-3	8.76	9.24	
					2748.3	0-1	46.0	43.9	
					2748.2	1-2			
<i>Multiplet</i>	$a^5D - x^5D^0$				<i>Multiplet</i>	$a^5S - w^5P^0$			
2911.1	4-3	115	118		2736.5	2-1	45.2	45.0	
2910.9	3-2	154	175		2731.9	2-2	75.3	74.5	
2909.1	2-1	134	160		2726.5	2-3	105	105	
2905.5	1-0	77.0	87.6						
2899.2	1-1	19.2	29.9						
2896.8	2-2	96.2	130						
2894.2	0-1	77.0	74.1						

¹ Superimposed ghost.² Two coincident lines—intensity arbitrarily divided.

because all three multiplets have the same lower term, a^5D . The terms a^7D , x^7P^0 , and z^5G^0 overlap x^5D^0 ; and there are other terms lying close enough to x^5D^0 to cause anomalous intensities.

Multiplet $a^5D - w^5P^0$ ($3d^4 4s^2 - ?$). The agreement between the observed and calculated intensities is good throughout the entire range of intensities from 10 to 250, with one exception which is explained by a superimposed ghost. The self-reversal curve of this multiplet resembles that of $a^5D - x^5D^0$ and $a^5D - y^5D^0$ because the three multiplets have the same lower term.

Multiplet $a^5S - w^5P^0$ ($3d^5(^6S)4s - ?$). The observed intensities agree very well with the theoretical intensities in this multiplet, which would indicate that the type of coupling is Russell-Saunders, and that the energy levels involved are quite free from perturbations although w^5P^0 is only 40 cm^{-1} from y^5G^0 and 407 cm^{-1} from v^5P^0 . Russell-Saunders coupling seems to hold completely although the separations in the levels of w^5P^0 are in the ratio of 3 : 2.5 instead of 3 : 2 as predicted by the Landé interval rule for Russell-Saunders coupling. Both Frerichs and Harrison have failed to find a correlation between deviations from the intensity rules and deviations from Landé's rule in the iron group.

Chromium II

Multiplet $a^4D - z^4F^0$ ($3d^4(^5D)4s - 3d^4(^5D)4p$). The first-order ghost of the comparatively strong line 3147.2A falls upon 3145.1A causing an abnormally high reading for the latter line intensity. The nearest energy level to z^4F^0 is $y^4P^0_{5/2}$ (separation, 1878 cm^{-1}). Appreciable perturbations may exist between the energy levels of these two terms. However, the observed intensities of this multiplet agree with the theoretical values much better than in the case of the multiplet $a^4F - z^4G^0$, in which a perturbing term y^4D^0 is only 231.8 cm^{-1} removed from z^4G^0 . The self-reversal curve of the above multiplet is quite similar to the curve for $a^4D - z^4D^0$, since both have the same lower term.

Multiplet $a^4P - y^4D^0$. Intensities of two lines are missing from this multiplet because they were too weak to measure accurately. The observed intensities in this multiplet show good agreement with the calculated values.

Multiplet $a^4F - z^4G^0$ ($3d^4(^3F)4s - 3d^44p?$). The transition $a^4F_{9/2} - z^4G^0_{11/2}$ is not listed because the level $z^4G^0_{11/2}$ has not been identified. The energy levels $z^4G^0_{7/2}$ and $y^4D^0_{7/2}$ are only 332 cm^{-1} apart. According to Harrison and Johnson,¹⁴

¹⁴ G. R. Harrison and M. H. Johnson, Jr., Phys. Rev. **38**, 757 (1931).

TABLE II. *Chromium II*. $I_{\text{obs.}}$, observed intensities after applying corrections for background, self-reversal, ν^4 , and variation in sensitivity. I^* , intensity measurements by C. E. Hesthal.

Wavelength	Transition	$I_{\text{theor.}}$	$I_{\text{obs.}}$	I^*	Wavelength	Transition	$I_{\text{theor.}}$	$I_{\text{obs.}}$	I^*
<i>Multiplet</i> $a^4D - z^4F^0$					<i>Multiplet</i> $a^6D - z^6F^0$				
3159.1	7/2-5/2	4.83	3.6		2878.5	9/2-7/2	14.4	32.1	<89.6
3147.2	7/2-7/2	100	102		2878.0	7/2-5/2	33.2	82.9	<89.6
3145.1	5/2-3/2	6.89	10.8 ¹		2876.3	5/2-3/2	47.1	136	<89.6
3136.7	5/2-5/2	128	123		2873.5	3/2-1/2	43.8	95.5	<89.6
3132.0	7/2-9/2	861	855		2867.6	1/2-1/2	347	328	347
3128.7	3/2-3/2	96.5	108		2866.8	3/2-3/2	536	471	496
3125.0	5/2-7/2	589	589		2865.1	5/2-5/2	621	610	568
3120.4	3/2-5/2	386	404		2862.6	7/2-7/2	582	582	533
3118.7	1/2-3/2	241	264		2860.9	1/2-3/2	203	269	275
<i>Multiplet</i> $a^4P - y^4D^0$					<i>Multiplet</i> $b^6G - y^6H^0$				
3011.4	5/2-3/2	1.37	— ⁴		2858.9	9/2-9/2	379	417	424
2984.7	3/2-1/2	2.28	— ⁴		2855.7	3/2-5/2	517	555	525
2976.7	5/2-5/2	12.4	8.95		2849.8	5/2-7/2	967	924	741
2961.7	3/2-3/2	14.6	15.4		2843.2	7/2-9/2	1580	1240	930
2953.4	1/2-1/2	11.4	11.5		2835.6	9/2-11/2	2350	2050	1100
2935.1	5/2-7/2	54.7	54.7		<i>Multiplet</i> $a^6D - z^6P^0$				
2930.9	1/2-3/2	11.4	11.7		2766.5	9/2-7/2	703	694	523
2928.2	3/2-5/2	28.7	27.4 ⁵		2762.6	7/2-5/2	361	402 ¹	353
<i>Multiplet</i> $a^4F - z^4G^0$					<i>Multiplet</i> $a^6D - z^6D^0$				
2941.4	7/2-5/2	2.41	9.99		2757.7	5/2-3/2	131	164	171
2937.1	9/2-7/2	72.1	107		2751.9	7/2-7/2	201	208	209
2937.0	5/2-5/2				2750.7	5/2-5/2	256	256	236
2934.0	3/2-5/2	436	318		2749.0	3/2-3/2	199	199	199
2932.7	7/2-7/2	92.0	83.0		2743.6	1/2-3/2	140	122 ¹	133
2928.3	5/2-7/2	583	693 ⁶		2742.0	3/2-5/2	83.8	100 ^{1, 6}	133
2926.2	9/2-9/2	70.2	72.4		2740.1	5/2-7/2	33.4	33.0	36.6
2921.8	7/2-9/2	777	311		<i>Multiplet</i> $a^6D - z^6D^0$				
<i>Multiplet</i> $a^4D - z^4D^0$					2691.1	9/2-7/2	119	108	
2889.2	7/2-5/2	36.9	38.8 ²		2677.2	9/2-9/2	827	687	
2880.9	5/2-3/2	46.5	49.7		2677.2	7/2-7/2			
2876.0	7/2-7/2	225	227		2677.2	5/2-5/2			
2873.8	3/2-1/2	32.8	32.0		2666.0	5/2-7/2	167	167	
2870.4	5/2-5/2	113	114		2663.4	7/2-9/2	119	128 ⁴	
2867.1	3/2-3/2	52.0	68.9 ¹						
2865.3	1/2-1/2	32.8	35.6						
2858.7	1/2-3/2	32.8	31.0						
2857.4	5/2-7/2	36.9	14.3 ³						
2856.8	3/2-5/2	46.5	10.4 ³						

¹ Superimposed ghost.
² Two coincident lines—intensity arbitrarily divided.
³ Uncertain because of strong neighboring line.

⁴ Very weak line.
⁵ Incomplete multiplet because of unknown term values.
⁶ Overlapping line.

appreciable perturbations may exist between levels in Ti I that are separated by as much as 2000 cm⁻¹, and weaker lines will show a greater percentage deviation from their normal intensities, when there is a weak spin-orbit interaction such as exists in the chromium atom. The first line in the above multiplet illustrates this case.

Multiplet $a^4D - z^4D^0$ ($3d^4(^5D)4s - 3d^4(^3D)4p$). Line 2889.2A of this multiplet is coincident with 2889.3A of $a^5D - x^5D^0$. The intensity reading was arbitrarily divided so as to make the former line approximately normal. The observed intensities

of the lines 2857.4A and 2856.8A in this multiplet are not dependable because strong adjacent lines interfered with the densitometer readings. The remaining line intensities are in fair agreement with the theoretical values. This indicates a lack of perturbations which is to be expected since the nearest known energy level to z^4D^0 is z^4F^0 ; and the separation is 2475 cm⁻¹. The self-reversal curves of $a^4D - z^4D^0$ and $a^4D - z^4F^0$ are quite similar. This is to be expected, since both multiplets have the same lower term.

Multiplet $a^6D - z^6F^0$ ($3d^4(^5D)4s - 3d^4(^5D)4p$).

As in multiplet $a^4F-z^4G^0$ the observed intensities of the weak lines differ greatly from the calculated values. The correlation between Hesthal's observed intensities and those of the present observers is especially poor for both the weaker and stronger lines. No explanation of this discrepancy was found.

Multiplet $b^4G-y^4H^0$ ($3d^4(^3G)4s-3d^4(^3G)4p$). Two indicated lines of this multiplet are too weak to be measured on the densitometer. There is practically no self-reversal in this multiplet because b^4G is the highest term value of all known even terms; and, hence, it should be poorly populated with electrons. Consequently, there are fewer absorption transitions upward from b^4G to y^4H^0 . As in the multiplets $a^4F-z^4G^0$ and $a^6D-z^6F^0$, we find an anomalous intensity for the weak line.

Multiplet $a^6D-z^6P^0$ ($3d^4(^5D)4s-3d^4(^5D)4p$). There are three cases of superimposed ghosts and one case of an overlapping line which help to explain some of the anomalous intensities in this multiplet.

Multiplet $a^6D-z^6D^0$ ($3d^4(^5D)4s-3d^4(^5D)4p$). Five of the seven lines missing from this multiplet involve the levels of z^6D^0 for which J equals $1/2$ and $3/2$. The term values of these two levels were not known, and so the wavelengths could not be calculated. The observed intensity of the three superimposed lines is much less than the sum of the three corresponding theoretical intensities. The explanation of this may be that the three lines are not exactly superimposed.

Sextet supermultiplet $a^6D-z^6F^0$, $a^6D-z^6D^0$, $a^6D-z^6P^0$. The multiplets forming this sextet supermultiplet have already been considered but the intensity data of such a supermultiplet may be used to compute the theoretical temperature T of the arc by means of the formula,¹⁵ $T = 0.625\Delta\sigma/\log_{10} R$, where T is the absolute temperature of the arc, $\Delta\sigma$ is the wave-number separation of the levels of the upper term, and R is the excitation factor. R is the factor by which the sum of the observed intensities of all lines originating in the same upper level is multiplied to make it equal to the sum of the corresponding theoretical intensities. The higher the level, the greater will be the value of R , because of the

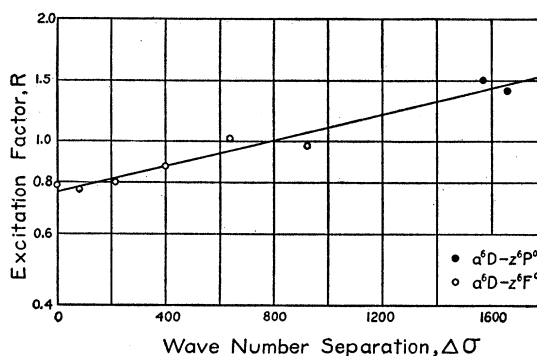


FIG. 1. Excitation curve for the sextet supermultiplet.

decreasing electronic population of the higher levels. When the values of $\log_{10} R$ are plotted against the corresponding wave-number separations $\Delta\sigma$ of the upper levels, the points¹⁶ fall along a straight line (Fig. 1) which demonstrates

TABLE III. Excitation corrections in the sextet supermultiplet. $I_{\text{obs.}}$, observed intensities after applying corrections for background, self-reversal, ν^4 , and variation in sensitivity. R , excitation factor. I_c , observed intensities corrected for excitation.

Wavelength	Transition	$I_{\text{obs.}}$	R	I_c	$I_{\text{theor.}}$
<i>Multiplet $a^6D-z^6F^0$</i>					
2878.5	9/2-7/2	32.1	0.872	28.0	12.5
2878.0	7/2-5/2	82.9	.816	67.6	29.2
2876.3	5/2-3/2	136	.778	106	41.1
2873.5	3/2-1/2	95.5	.757	72.3	38.2
2867.6	1/2-1/2	382	.757	248	303
2866.8	3/2-3/2	471	.778	366	367
2865.1	5/2-5/2	610	.816	498	542
2862.6	7/2-7/2	582	.872	507	507
2860.9	1/2-3/2	269	.778	209	177
2858.9	9/2-9/2	417	.947	395	331
2855.7	3/2-5/2	555	.816	453	450
2849.8	5/2-7/2	924	.872	805	850
2843.2	7/2-9/2	1240	.947	1170	1380
2835.6	9/2-11/2	2050	1.05	2150	2050
Sum 7075					
<i>Multiplet $a^6D-z^6P^0$</i>					
2766.5	9/2-7/2	694	1.43	993	1040
2762.6	7/2-5/2	402	1.37	551	536
2757.7	5/2-3/2	164	1.32	217	194
2751.9	7/2-7/2	208	1.43	298	298
2750.7	5/2-5/2	256	1.37	351	379
2749.0	3/2-3/2	199	1.32	263	295
2743.6	1/2-3/2	122	1.32	161	208
2742.0	3/2-5/2	100	1.37	137	124
2740.1	5/2-7/2	33.0	1.43	47.2	49.6
Sum 3018					

¹⁶ Seven of the thirteen lines of multiplet $a^6D-z^6D^0$ are missing, and the remaining meager data are not used in the calculation of the arc temperature.

¹⁵ G. R. Harrison, J. O. S. A. 19, 109 (1929).

the existence of an excitation function. The slope of this line determines the calculated temperature of the chromium arc, which was 4060°K, with a current of 2.4 amperes and a pressure of 7 to 15 cm of mercury.

By multiplying the intensities by the proper values of the excitation factor R , as determined from the excitation curve, we obtain the intensities that would have been observed if the temperature of the arc had been infinite. This

excitation correction is applied only to this supermultiplet; and the results are reported in Table III. Since this correction applies only to multiplets having the lowest term a^6D , it cannot be applied to the data on other multiplets here reported.

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Note on the Relative Transition Probabilities for Almost Closed Shells

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Three simplifications are given for calculating the relative transition probabilities of different multiplets from spectroscopic stability. They apply to configurations involving almost closed shells in Russell-Saunders coupling.

THE calculation of the relative transition probabilities of different multiplets in Russell-Saunders coupling from spectroscopic stability¹ can be simplified for electron configurations involving almost closed shells, so that transition probabilities for these configurations may be calculated as easily as those for the configurations containing the electrons missing from the almost closed shells. This simplification for transition probabilities is of the same type as that given by Shortley² for the energies. The simplifications apply to calculating the matrix elements of the electric moment in the zero order scheme. The first simplification is to represent the almost closed shells present in the zero order state by the quantum numbers of the electrons missing from these shells. This means that the representations for the states containing almost closed shells are obtained simply by changing the signs of m_l and m_s in the states of the electrons required to complete the shells.

In the second place, it is necessary to write the zero order states of but one of the two electron configurations³ between which a single electron jumps. For simplicity, one chooses from the LSM_LM_S scheme the configuration with the fewer terms. It is possible to simplify the calculation further by writing only one zero order state for each set of values of m_l . The group of states with this set of values of m_l , obtained for different sets of values of m_s , will give multiples, constant throughout the matrix, of the matrix elements of a single state of the group. Once these numbers are found by inspection of a single group of states with a given set of values of m_l , they may be used as factors for each subsequent set of m_l values, having the same number of sets of m_s values associated with it. These simplifications enable one to alter the states already used previously for partially filled shells, so that the relative transition probabilities for the multiplets of the corresponding almost closed shells may be calculated from them.

¹ E. U. Condon and C. W. Ufford, *Phys. Rev.* **44**, 740 (1933); C. W. Ufford and F. M. Miller, *Phys. Rev.* **46**, 283 (1934).

² G. H. Shortley, *Phys. Rev.* **40**, 185 (1932).

³ L. Goldberg found that this was sufficient for the case where a closed shell was represented by all its electrons. It is also sufficient for the representation considered here.