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# Relative Intensities of Singlet-Singlet and Singlet-Triplet Transitions

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The ratio of the intensities of singlet-triplet to singlet-singlet transitions can be calculated by means of Houston's formulae in two ways: (a) from the deviations from the interval rule, and (b) from the distance of the singlet level from the center of gravity of the triplet levels. The discrepancy of the two calculations indicates that the integral of the radial functions between the singlet and triplet differs from that for the triplet with triplet, say by a factor λ. The new parameter λ is evaluated (∼0.75) from the positions of the four levels, and gives intensity ratios in good agreement with the observed.

HOUSTON[1] showed that a forbidden transition such as $^1S_0-{}^3P_1$ is due to spin-orbit interaction,—the mixing of some of the associated singlet ($^1P_1$) with the triplet level ($^3P_1$).

Strangely enough Houston's formulae for the energy levels have never been used to calculate the relative intensity of these particular transitions. The calculations are extremely elementary, and give good agreement with the experimentally determined values.

When spin-orbit interactions are included, the energy matrix between the Russell-Saunders states

$$^3L^0{}_{l+1}\,{}^3L_l{}^0\,{}^1L_l{}^0\,{}^3L^0{}_{l-1}\quad \text{is}^2$$

$$\begin{pmatrix} F-G & & & \\ & F-G & & \\ & & F+G & \\ & & & F-G \end{pmatrix} + \tfrac{1}{2}\zeta \begin{pmatrix} l & & & \\ & -1 & (l(l+1))^{\frac{1}{2}} & \\ & (l(l+1))^{\frac{1}{2}} & 0 & \\ & & & -(l+1) \end{pmatrix}, \tag{1}$$

where $F$ and $G$ are the electrostatic energies appearing in the Russell-Saunders approximations, and $\zeta$ is the integral of the radial functions with the spin-orbit interaction operator, in a central field, *viz.*

$$\zeta = h^2Ze^2(16\pi^2m^2c^2)^{-1}\int r^{-3}R^2r^2dr, \tag{2}$$

where $R$ is the radial wave function. It is to be emphasized that Eq. (2) assumes that the radial wave function is the same for the singlet as the triplet state, an assumption not really warranted, as we shall discuss later.

The energy levels are then, for the case of $P$ states

$$^3P_2=F-G+\tfrac{1}{2}\zeta,\quad {}^3P_0=F-G-\zeta$$
$$^{1,\,3}P_1=F-\tfrac{1}{4}\zeta\pm[(G+\tfrac{1}{4}\zeta)^2+\tfrac{1}{2}\zeta^2]^2. \tag{3}$$

Equations (3) give the positions of the four levels in terms of three parameters $F$, $G$, $\zeta$. Thus the location of three of the states determine the location of the fourth.

The ratio of the $f$ values for the $^1S_0-{}^3P_1$ and $^1S_0-{}^1P_1$ transitions can be determined from the transformation matrix that diagonalizes (1), together with the fact that only $^1S_0-{}^1P_1$ is permitted in the limiting case of pure Russell-Saunders coupling (i.e., between $^1(L-1)^0{}_{l-1}$ and $^1L_l{}^0$). However, as Houston's formula does not fit exactly (does not yield the proper location for the fourth level), the results will be different according as one employs values for the param-

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[1] W. V. Houston, Phys. Rev. **33**, 297 (1929).

[2] Condon and Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 271.

eters $F$, $G$, $\zeta$ which yield the correct empirical positions either of (a), ${}^3P_1$, ${}^3P_0$, ${}^3P_2$ or (b), ${}^1P_1$, ${}^3P_0$, ${}^3P_2$ i.e., according as one adjusts the constants so as to give the proper deviations from the interval rule, or the proper singlet-triplet separation, together with, in either case, the correct over-all width for the triplet.

The corresponding formulae for the ratios of the $f$ values are:

$$\text{method (a)}: f_1/f_3 = \tfrac{2}{9}(\nu_1/\nu_3) \times ({}^3P_2 - {}^3P_0)^2/({}^3P_1 - \tfrac{2}{3}{}^3P_0 - \tfrac{1}{3}{}^3P_2)^2, \quad (4)$$

$$\text{method (b)}: f_1/f_3 = (\nu_1/\nu_3)\cot^2\{\tfrac{1}{2}\sin^{-1}[\tfrac{2}{3} \times 2^{\frac{1}{2}}({}^3P_2 - {}^3P_0)/({}^1P_1 - {}^3P_1)]\}. \quad (5)$$

It is seen from Table I that neither method (a) nor (b) gives results agreeing adequately with experiment.

The most natural explanation of the discrepancies is to blame perturbation by other levels, but none seems to be located in a suitable position to account for the anomalies. The real solution of the difficulty appears to be that the radial functions are not quite the same for singlet and triplet states, so that their Hartree, or rather Fock, self-consistent fields are slightly different. It is therefore legitimate to insert an undetermined parameter $\lambda$ in the off-diagonal matrix element of (1). Then $\zeta$ relates to (2) with $R^2 = R_3^2$, while $\lambda\zeta$ refers to (2) with $R^2$ replaced by $R_1R_3$. Here $R_1$ and $R_3$ are, of course, the singlet and triplet radial functions. (Note that the integral with $R_1^2$ does not occur due to a zero matrix element in (1).) Correspondingly, $\frac{1}{2}\zeta^2$ is replaced by $\frac{1}{2}\lambda^2\zeta^2$ in the radicand of (3). We now have four parameters $F$, $G$, $\zeta$, $\lambda$, so that (3) will now yield correctly the positions of all four energy levels. The first three can be determined from ${}^3P_2$, ${}^3P_0$ and ${}^1P_1 + {}^3P_1$ (the trace of the second order minor between ${}^3L_l{}^0$ and ${}^1L_l{}^0$ in (1)), and $\lambda$ from the determinant of this matrix ${}^1P_1 \times {}^3P_1$. Also $\lambda$ and $f_1/f_3$ can be evaluated by perturbation formulae accurately enough in the cases of Zn, Sr, Ca. With the parameters thus determined, the computed intensity ratios agree quite well with the experiment,[3] as shown in the last line of the table. Except for Hg, the calculated value is within the experimental error.

TABLE I. *Relative $f$ values of ${}^1S_0 - {}^1P_1$ and ${}^1S_0 - {}^3P_1$ transitions.*

| | Hg | Cd | Zn | Ba | Sr | Ca |
|---|---|---|---|---|---|---|
| $\lambda {}^1S_0 - {}^1P_1$ | 1,849.57 | 2,288.02 | 2,138.61 | 5,535.53 | 4,607.34 | 4,226.73 |
| $\lambda {}^1S_0 - {}^3P_1$ | 2,536.52 | 3,261.04 | 3,075.88 | 7,911.36 | 6,892.62 | 6,572.78 |
| ${}^3P_2 - {}^3P_0$ | 6,397.9 | 1,713.0 | 578.7 | 1,248.5 | 581.2 | 158.1 |
| ${}^3P_1 - {}^3P_2$ | 1,767.3 | 541.9 | 189.8 | 370.5 | 186.8 | 52.3 |
| ${}^3P_1 - \frac{2}{3}{}^3P_0 - \frac{1}{3}{}^3P_2$ | −365.4 | −29.1 | −3.1 | −45.7 | −6.8 | −1.5 |
| ${}^1P_1 - {}^3P_1$ | 14,656.1 | 13,036.0 | 14,243.5 | 5,423.6 | 7,194.1 | 8,442.2 |
| $F$ | 47,803.95 | 37,459.7 | 39,719.8 | 15,556.5 | 18,198.3 | 19,457.667 |
| $G_0$ | 5,896.4 | 6,203.4 | 7,022.2 | 2,458.1 | 3,493.35 | 4,194.3 |
| $\frac{1}{2}\zeta$ | 2,132.6 | 571.0 | 192.9 | 416.7 | 193.7 | 52.73 |
| $\lambda$ | 0.7578 | 0.7618 | 0.7702 | 0.8414 | 0.8070 | 0.8126 |
| $f_1/f_3$: | | | | | | |
| Houston (a) | 93 | 1,097 | 11,140 | 237 | 2,427 | 54,100 |
| Houston (b) | 29 | 369 | 3,995 | 127 | 1,029 | 19,500 |
| Improved method | 53.4 | 637 | 6,757 | 169 | 1,582 | 30,180 |
| Observed | 46.8±2 | 680±100 | 7,200 | 146 | 1,660 | 33,000 |

The values of $\lambda$ are of reasonable order of magnitude, as they are not far different from unity, of about the same size, ~0.75, in all cases.

Further it is probably to be expected that $\lambda$ is less than unity, since the nodes of the singlet and triplet wave functions will be at different positions. The resulting decrease in the amount of overlapping will thus make the modified integral (2) smaller with a factor $R_1R_3$ than with $R_3^2$.

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[3] Obtained from dispersion measurements by G. Wolfsohn, Zeits. f. Physik **83**, 234 (1933) (Hg, Cd, Zn) and from anomalous dispersion measurements, W. Prokofiew, Zeits. f. Physik **50**, 701 (1928) (Ba, Sr, Ca).