OVERLAPPING ATOMIC MULTIPLETS*

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ABSTRACT

It is shown that multiplets of maximum multiplicity in any atomic configuration do not interact if (a) no constituent shell $n\ell$ is more than half full; and (b) all spin-orbit coupling constants $\zeta(n\ell)$ are equal. This explains the comparatively small deviations from the Landé interval rule for many overlapping multiplets. As illustrations, we consider PrIII $4f^2\,5d$ and UI $(5f^3\,6d\,7s^2 + 5f^3\,6d^2\,7s)$.

In the Russell-Saunders limit, when the electrostatic interactions between the electrons of an atom are large compared to spin-orbit interactions, the atomic levels fall into distinct multiplets. Within each multiplet the levels are ordered with respect to J, the quantum number of the total angular momentum, and the Landé interval rule is obeyed.[1] Let us imagine a gradual increase in the strength of the spin-orbit interaction, H_{so}. At first, the multiplets expand in a way that preserves the interval rule; but as matrix elements of H_{so} between adjacent multiplets become more and more importnat, levels with similar J repel one another and distortions occur. It would be expected that multiplet structures characteristic of Russell-Saunders coupling would disappear as soon as adjacent multiplets begin to overlap. Naively, we would expect a complex scrambling of the atomic levels as the transition to jj coupling takes place. However, it has become clear over the last decade that extremely regular multiplets can be often picked out from a morass of levels. A good example is given in Figure 1, in which five low-lying multiplets of the configuration $4f^2\,5d$ of PrIII are plotted out. The data are those of Sugar.[2] Each multiplet comprises an orderly progression of levels, in spite of the fact that severe overlapping takes place. This phenomenon forms the subject of this article.

The key to the problem lies in the following theorem. For any configuration

$$(n_1 \ell_1)^a (n_2 \ell_2)^b \ldots (n_j \ell_j)^k, \tag{1}$$

in which

$$0 < a \leq 2\ell_1 + 1, \quad 0 < b \leq 2\ell_2 + 1, \ldots, \quad 0 < k \leq 2\ell_j + 1, \tag{2}$$

all matrix elements of the spin-orbit interaction, given as usual[1] by

$$H_{so} = \sum_i \xi(r_i)\, \underset{\sim}{s}_i \cdot \underset{\sim}{\ell}_i$$

vanish between states of maximum multiplicity, provided

$$\zeta(n_1 \ell_1) = \zeta(n_2 \ell_2) = \ldots = \zeta(n_j \ell_j), \tag{3}$$

where

$$\zeta(n\ell) = \langle n\ell \mid \xi(r) \mid n\ell \rangle .$$

To prove this result, we note first from (2) that no shell is more than half full. Hence, a state for which the total spin projection quantum number M_S has its maximum value corresponds to all individual spin projections m_s equal to $+\frac{1}{2}$. Such a state obviously has maximum multiplicity, $2S+1$. If we calculate the matrix element of H_{so} between two states of (1) for which $M_S = (M_S)_{max}$, we can evidently use the equivalences

$$\begin{aligned} H_{so} &\equiv \sum_i \xi(r_i)\, (s_z)_i\, (\ell_z)_i \equiv \tfrac{1}{2} \sum_i \xi(r_i)\, (\ell_z)_i \\ &\equiv \tfrac{1}{2}\, \zeta \sum_i (\ell_z)_i \equiv \tfrac{1}{2}\, \zeta L_z \\ &\equiv \tfrac{1}{2} (M_S)^{-1}_{max}\, \zeta\, S_z L_z \equiv \tfrac{1}{2} S^{-1}_{max}\, \zeta\, \underset{\sim}{S} \cdot \underset{\sim}{L} \\ &\equiv \lambda\, \underset{\sim}{S} \cdot \underset{\sim}{L}, \end{aligned}$$

where $\lambda = \frac{1}{2}\, \zeta\, (S_{max})^{-1}$. (4)

The transition to the second line above can be made if Eqs. (3) hold true. The symbol ζ stands for any one of the zetas of this equation. Now $\underset{\sim}{S} \cdot \underset{\sim}{L}$ is diagonal with respect to S, L, and any other classificatory symbol γ. Hence H_{so} cannot connect the levels of different multiplets possessing maximum multiplicity: and this proves the theorem. Its implication is self evident: multiplets with maximum multiplicity in configurations of the type (1) can overlap without interacting provided (2) and (3) are satisfied. The Landé interval rule will continue to be obeyed -- provided, of course, multiplets of next-to-maximum multiplicity are sufficiently remote. In practice, this last condition is often fulfilled.

According to the analysis of Trees,[3] $\zeta(4f) = 775\ cm^{-1}$ and $\zeta(5d) = 721\ cm^{-1}$ for PrIII $4f^2\,5d$, and the almost perfect equality of these two spin-orbit coupling constants is thus responsible for the regularities of Fig. 1. Owing to Eq. (4), the energy step from one level (J - 1) to the next (J) should be the same (and equal to $\zeta J/2S_{max}$) for every multiplet of maximum multiplicity. It is clear from the figure that this is so to a good approximation.

We conclude with another example, drawn from the actinide series. The data are those of Blaise, Diringer, Guelachvili, and Ben Osman on UI($5f^3\,6d\,7s^2 + 5f^3\,6d^2\,7s$).[4] A preliminary theoretical analysis by Bordarier[5] gives $\zeta(5f) = 1773\ cm^{-1}$ and $\zeta(6d) = 1145\ cm^{-1}$. In spite of the appreciable difference between these two numbers, many low multiplets of UI exhibit a remarkable regularity. This is shown in Fig. 2. Corresponding regularities are to be expected in other actinide and rare-earth atoms.

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REFERENCES

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2. J. Sugar, J. Opt. Soc. Am. 53, 831 (1963).

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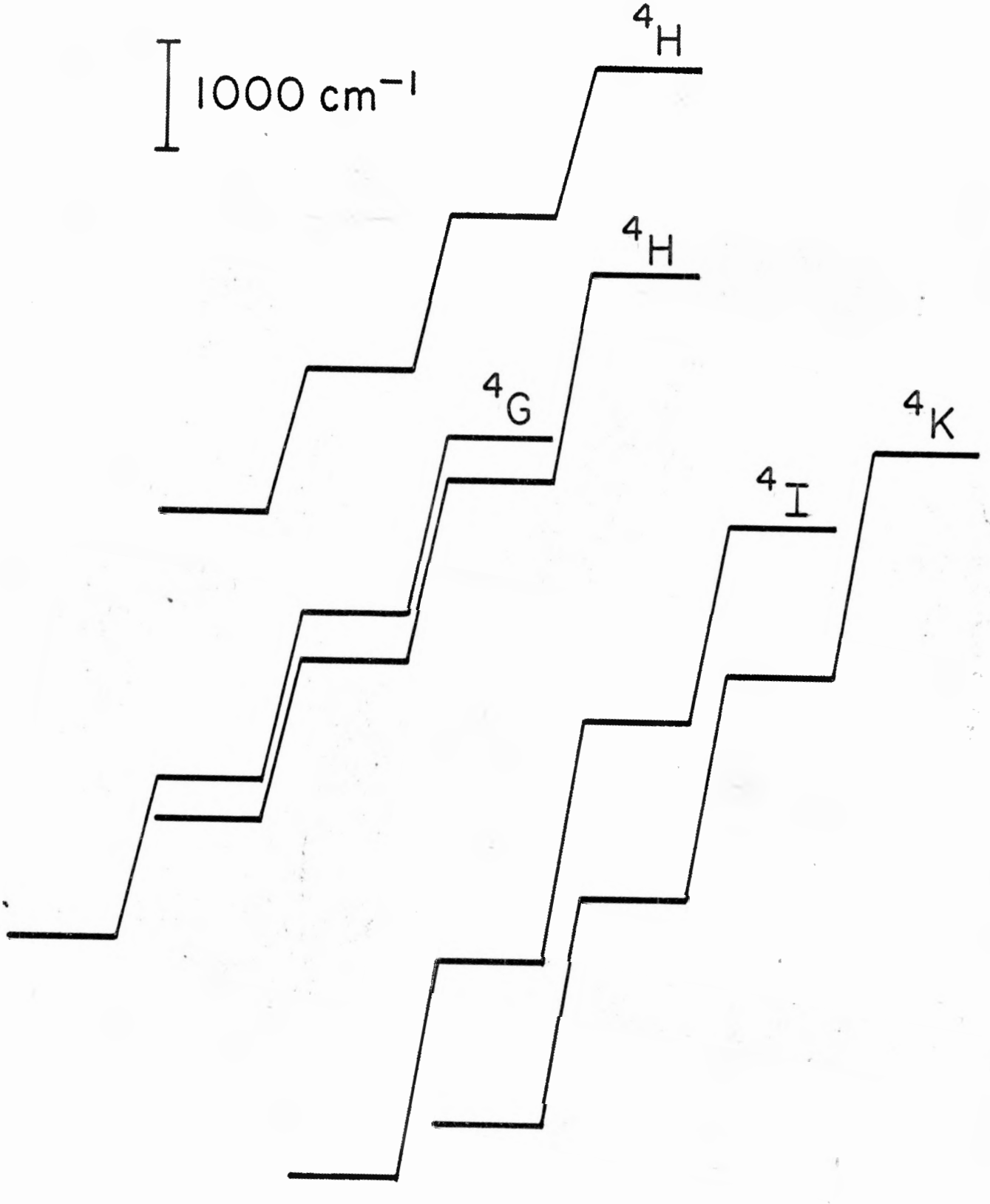
4. J. Blaise, private communication.

5. Y. Bordarier, private communication.

FIGURE CAPTIONS

Fig. 1 Five low multiplets of maximum multiplicity for PrIII $4f^2\,5d$. The numbers specify values of J. In spite of substantial overlapping, the Landé interval rule is quite well obeyed by all multiplets.

Fig. 2 Low multiplets of maximum multiplicity for UI($5f^3\,6d\,7s^2 + 5f^3\,6d^2\,7s$). Deviations from the interval rule are ascribed to the fact that the equation $\zeta(5f) = \zeta(6d)$ is only approximately true. Even so, several multiplets show regularities characteristic of Russell-Saunders coupling.


1000 cm⁻¹
⁴H
⁴H
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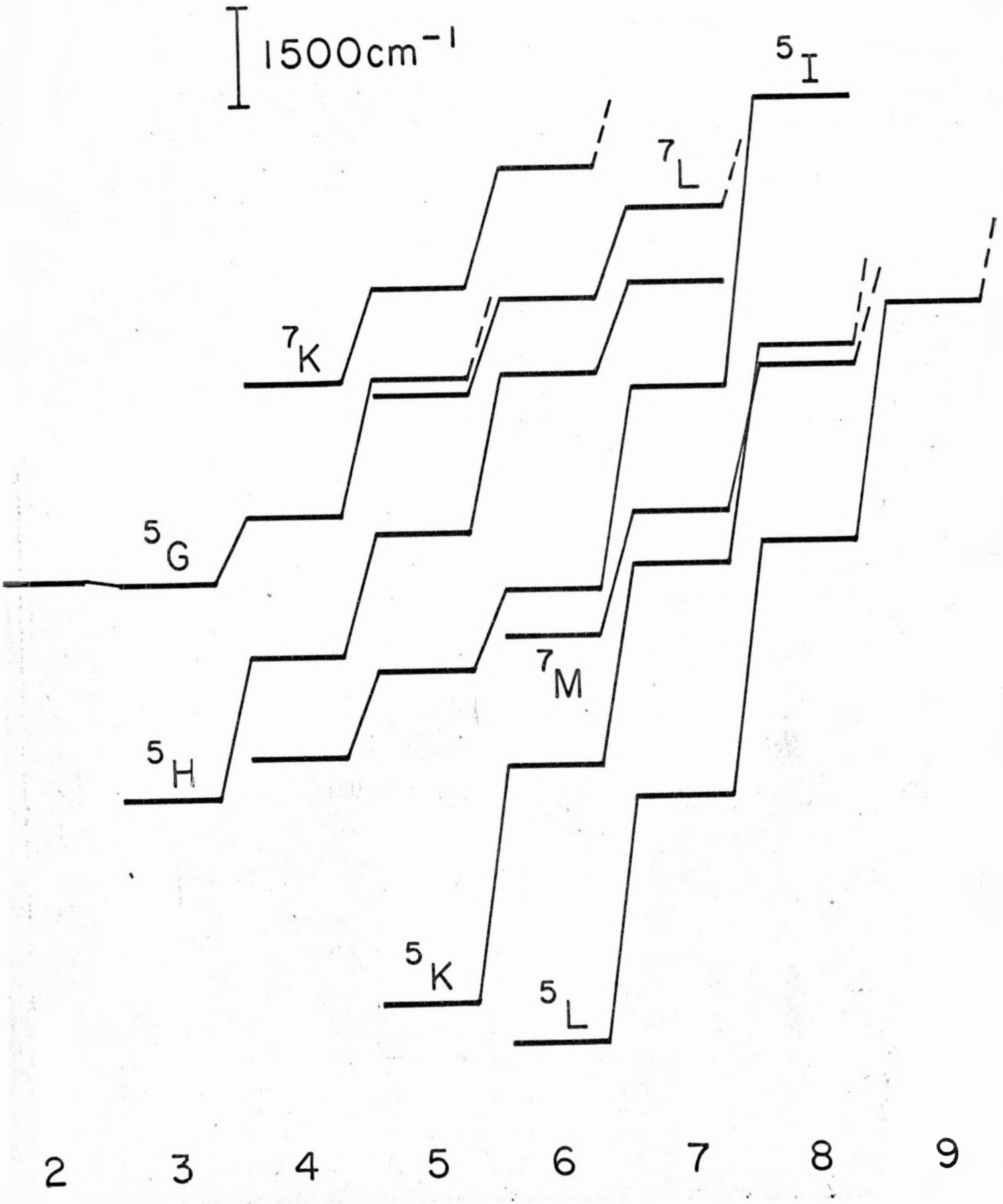
⁴K
⁴I
5/2
7/2
9/2
11/2
13/2
15/2
17/2


1500cm⁻¹
⁵I
⁷L
⁷K
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