

17. Calculate the spin-orbit splitting pattern for the ground state of a d^3 ion and a d^7 ion.

Equate the matrix elements of $\lambda \hat{L} \cdot \hat{S}$ and

$$\sum_{nd} \sum_i \hat{l}_i \hat{s}_i$$

	d^3	d^7
Ground state	$4F$	$4F$
M_L	3	3
M_S	$3/2$	$3/2$
Determinantal wave function $\Psi = \phi_1 \phi_2 \dots $	$ \uparrow \uparrow \uparrow $	$ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow $
Diagonal element $\langle \Psi \lambda \hat{L} \cdot \hat{S} \Psi \rangle$ $= \lambda \langle \Psi \hat{L}_z \hat{S}_z \Psi \rangle$ $= \lambda M_L M_S$	$\lambda \cdot 3 \cdot \frac{3}{2}$	$\lambda \cdot 3 \cdot \frac{3}{2}$
$\sum_{nl} \langle \Psi \sum_i \hat{l}_i \hat{s}_i \Psi \rangle$ $= \sum_{nl} \sum_i \langle \phi_i \hat{l}_i \hat{s}_i \phi_i \rangle$ (Slater-Condon Rules) $= \sum_{nl} \sum_i \langle \phi_i \hat{l}_{z_i} \hat{s}_{z_i} \phi_i \rangle$	$\sum_{nd} [2 \cdot \frac{1}{2} + 1 \cdot \frac{1}{2} + 0 \cdot \frac{1}{2}]$ $= \frac{3}{2} \sum_{nd}$	$\sum_{nd} [2 \cdot \frac{1}{2} + 2 \cdot \frac{1}{2} + 1 \cdot \frac{1}{2}$ $+ 1 \cdot \frac{1}{2} + 0 \cdot \frac{1}{2} +$ $(-1 \cdot \frac{1}{2}) + (-2 \cdot \frac{1}{2})]$ $= -\frac{3}{2} \sum_{nd}$
	$\therefore \lambda = \frac{1}{3} \sum_{nd}$	$\lambda = -\frac{1}{3} \sum_{nd}$

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Verify that ^{for the ground state,} in general $\lambda = \frac{1}{2S} \sum_{nd}$ (less than half filled)
 $\lambda = -\frac{1}{2S} \sum_{nd}$ (more than " " " ")

