

Physics 556 Spring 2007 -- HW # 4 -- Answers and discussion.

Low lying energy levels of 3-d transition metal ions. This subject is discussed in the text by Tinkham, as well as in atomic physics books, such as the classic book by Condon and Shortley. In class, we discussed the case of the Ti^{3+} ion which has a d^1 configuration, with 10 degenerate levels labeled by the quantum numbers $L=2$ and $S=1/2$. The L-S “term values” are labeled ^{2S+1}L , so this is called 2D . We also discussed the V^{3+} ion with d^2 configuration. There are 45 degenerate levels before adding the interelectronic Coulomb splitting; the corresponding L-S terms are 1G , 3F , 1D , 3P , and 1S , with 3F being the ground state according to Hund’s rules. We also discussed the more complicated case of Cr^{3+} with d^3 configuration, and 120 ways to occupy the d shell consistent with the Pauli principle. The L-S terms that appear are 2H , 2G , 4F , 2F , 2D (twice!), 4P , and 2P , with 4F being the Hund’s rule ground state. As homework, you worked out the case of Mn^{3+} with d^4 configuration. Here is the answer. The label $n \times (a,b,c,d,e)$ means that the ($m=2,1,0,-1,-2$) orbitals are occupied with a, ... e = u,d,2, or -, where u means up spin, d means down, 2 means both spin state occupied, and - means both spin states empty. The premultiplier “n x” means that there are n inequivalent allowed permutations of u and d which do not change the values of M_L or M_S or alter which m values are filled.

$Mn^{3+} (d^4)$	$M_S=2$	$M_S=1$	$M_S=0$	Rep.	Degeneracy
$M_L=6$			(2,2,-,-,-)	1I	13
$M_L=5$		(2,u,u,-,-)	2 x (2,u,d,-,-)	3H	33
$M_L=4$		(2,u,-,u,-) (u,2,u,-,-)	2 x (2,u,-,d,-) 2 x (u,2,d,-,-) (2,-,2,-,-)	3G 1G_a 1G_b	27 9 9
$M_L=3$		(2,u,-,-,u) (2,-,u,u,-) (u,2,-,u,-) (u,u,2,-,-)	2 x (2,u,-,-,d) 2 x (2,-,u,d,-) 2 x (u,2,-,d,-) 2 x (u,d,2,-,-)	3F_a 3F_b 1F	21 21 7
$M_L=2$	(u,u,u,u,-)	(2,-,u,-,u) (u,2,-,-,u) 4 x (u,u,u,d,-)	(2,-,-,2,-) (-,2,2,-,-) 2 x (2,-,u,-,d) 2 x (u,2,-,-,d) 6 x (u,u,d,d,-)	5D 3D 1D_a 1D_b	25 15 5 5
$M_L=1$	(u,u,u,-,u)	(2,-,-,u,u) (u,-,2,u,-) (-,2,u,u,-) (u,u,-,2,-) 4 x (u,u,u,-,d)	2 x (2,-,-,u,d) 2 x (-,2,u,d,-) 2 x (u,-,2,d,-) 2 x (u,d,-,d,-) 6 x (u,u,d,-,d)	3P_a 3P_b	9 9
$M_L=0$	(u,u,-,u,u)	(u,-,2,-,u) (-,u,2,u,-) (-,2,u,-,u) (u,-,u,2,-) 4 x (u,u,-,u,d)	(2,-,-,-,2) (-,2,-,2,-) 2 x (-,2,u,-,d) 2 x (u,-,2,-,d) 2 x (-,u,2,d,-) 2 x (u,-,d,2,-) 6 x (u,u,-,d,d)	1S_a 1S_b	1 1

The full table has 13 rows (M_L going from -6 to 6) and 5 columns (M_S from -2 to 2). However, the upper left part of the table is sufficient for counting states, and figuring the “L-S terms” shown in

the next to last column. In free space, if spin-orbit interactions are omitted, these are the different excitations possible for 4 electrons occupying 4 out of 10 states in the d shell. There are $10 \cdot 9 \cdot 8 \cdot 7 / 4 \cdot 3 \cdot 2 \cdot 1 = 210$ ways to construct occupancies that obey the Pauli principle. The sum of the degeneracies (rightmost column) is 210.

Within first-order degenerate perturbation theory, you would calculate the energies of these levels by constructing and diagonalizing the 210 x 210 matrix of the 2-body Coulomb part of the Hamiltonian,

$$\langle LS, M_L M_S | V | L'S', M'_L M'_S \rangle \propto \partial_{LL'} \partial_{SS'} \partial_{M'_L M_L} \partial_{M'_S M_S} .$$

The non-zero integrals are the diagonal elements, plus off-diagonal elements of some 2 x 2 submatrices that occur because some of the LS terms (irreducible representations) occur twice. For example, the ³P representation occurs twice, and results in 9 identical 2 x 2 submatrices, diagonal in M_L and M_S, coupling the two different types of ³P states. The values of the diagonal matrix elements can all be expressed as as “Slater F-functions”, which are integrals over the radial d-functions R₂(r),

$$F_k = e^2 \int_0^\infty dr_1 \int_0^\infty dr_2 \left(\frac{r_{<}^k}{r_{>}^{k+1}} \right) R_2^2(r_1) R_2^2(r_2) .$$

The Slater F₀ appears in every diagonal term and just gives an overall Coulomb shift of the d-levels; the two parameters F₂ and F₄ cause the LS term values to split. The coefficients of these energy splittings are complicated fractions arising from integrals over L=2 spherical harmonics. These splittings compare moderately well with experimental splittings, but the exact splittings are further shifted because of higher order coupling to other levels that occur when by electrons are promoted out of the d shell. The lowest energy level is the one with maximal S, and, within the possible states having this S, with maximal L (Hund’s first two rules.) The origin of Hund’s rules is in this Coulomb level splitting. Unfortunately, no corresponding rules are known which tell you how to order the higher lying LS terms.

Spin orbit splitting is contained in a smaller term in the Hamiltonian

$$H' = \sum_i \frac{\hbar^2}{2mc^2} \frac{1}{r_i} \frac{\partial U}{\partial r_i} \vec{l}_i \cdot \vec{s}_i .$$

It can be shown by symmetry arguments that within an L-S term, the matrix elements of this operator are proportional to those of $\vec{L} \cdot \vec{S}$, and that in turn, this can be simplified to

$$\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) = \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] .$$

For 3-d impurities like V, Cr, Mn, Fe, etc., these term splittings are small, of order 10² cm⁻¹. When the ions are in a crystal, the non-spherical environment of the crystal causes a larger splitting of the L-S term. The spin part S does not feel the crystal field, but the L value does, and splits into smaller dimensional irreducible representations of the point symmetry, with splittings that may be 10⁴ cm⁻¹, or 1 eV, or higher. The fact that L is no longer a good quantum number (although S still is) is called “quenching” of orbital angular momentum.