LIGAND POLARIZATIONS AND LANTHANIDE ION SPECTRA*

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In 1949, Racah introduced the non-invariance groups $O(7)$ and G_2 to aid in the classification of the states of the atomic f shell.[1] By similarly classifying all physical operators in terms of these groups, full use can be made of the Wigner-Eckart theorem to extract the dependence of the matrix elements of the operators on the various quantum numbers appearing in the bras and the kets. In this brief paper, we report some work on the effect of polarizable neighbors on the energy spectrum of triply-ionized lanthanide (i.e., rare-earth) ions in crystals. Such ions possess $4f^N$ as the ground electronic configuration. As Newman has emphasized,[2] a 4f electron (distinguished by the label i) induces various electric multipole moments in the neighbors (the so-called ligands). These moments then interact with a second 4f electron (labelled j) with the result that the ordinary direct Coulomb interaction e^2/r_{ij} requires modification. When $1/r_{ij}$ is expanded by means of the addition theorem, terms involving the tensorial scalar products $C_i^{(k)} \cdot C_j^{(k)}$ (where $C_i^{(k)}$ is a tensor whose components are proportional to the spherical harmonics $Y_{km}(\theta_i, \phi_i)$) are augmented by terms in which the non-scalar products of the type $(C_i^{(k)} C_j^{(p)})_q^{(t)}$ appear. Unlike the scalar operators, the latter can contribute to splittings of the LSJ levels.[3] Since the standard crystal-field analysis[4] involves a Hamiltonian that is a sum of single-electron operators $(C_q^{(t)})_i$ prefaced by the coefficients B_q^t, consideration of the polarizable neighbors offers the possibility of accounting for some of the discrepancies that have arisen over the years when the standard theory has been applied to such levels as $^1D_2$ of Pr^{3+} $4f^2$, ^6I_J and ^6P_J of Gd^{3+} $4f^7$, and ^3K_J of Ho^{3+} $4f^{10}$.

Uncertainties over the multipole polarizabilities of such ions as Cl^- and O^{2-} in crystals (as well as the screening effects of the outer shells of the lanthanide ions) make it difficult to estimate a priori the strengths of the two-electron operators $(C_i^{(k)} C_j^{(p)})_q^{(t)}$. From a formal standpoint, their coefficients involve (among other factors) such products as

$$\alpha_n \, r_i^k \, r_j^p \, R^{-k-p-2n-2} \, (C_{-q}^{(t)})_L,$$

where α_n is the n-pole polarizability of the ligand L whose polar coordinates (R, θ_L, ϕ_L) (with respect to the nucleus of the lanthanide ion) appear in $C_L^{(t)}$.

For f electrons, we need consider k, p = 2, 4, and 6 only. The screening by the outer shells of the lanthanide ion of the low-rank tensors (k = 2 or p = 2), coupled with the enhancement of $\langle r_i^6 \rangle$ and $\langle r_j^6 \rangle$ due to the extension of the tail of the 4f wavefunction when a lanthanide ion is situated in a crystal, has the effect of increasing the relative importance of the high-rank tensors. It is well-known[5] that the two-particle delta-function interaction $\delta(r_i - r_j)$ weights the tensor products $C_i^{(k)} \cdot C_j^{(k)}$ by the factor $2k + 1$, thereby enhancing the operators with large k. The analog for an intervening ligand is

$$I = - A\delta(r_i - R)\delta(r_j - R)$$

where A is necessarily a positive constant. Although the model interaction I may not produce, when expanded, terms $(C_i^{(k)} C_j^{(p)})_q^{(t)}$ whose coefficients are accurately proportional to those required in a detailed calculation, at least the signs will be correct as well as the general trends of their magnitudes.

More significantly, I possesses several interesting group-theoretical properties. It can be expressed as a sum of operators $g_s^{(t)}$ (with even t), each one of which is labelled by a set of irreducible representations $\langle \sigma \rangle (w_1 w_2 w_3)(u_1 u_2)t$ of the respective groups Sp(14), O(7), G_2, and O(3).[6] The only sequences to occur are $\langle 11 \rangle (200)(20)t$ (for s = 1, 2), $\langle 22 \rangle (200)(20)t$ for s = 3), and $\langle 22 \rangle (400)(40)\tau t$ (for s = 10). The symbol τ separates duplicated terms when t = 4, 6, or 8. Unlike the general two-electron operator, no O(7) representations of the type (220) arise. Their absence corresponds to the vanishing of all matrix elements of I for the triplets of f^2, since from the Pauli Exclusion Principle, no two electrons with similarly aligned spins can be located simultaneously at R. Thus the inclusion of I in the Hamiltonian would not disturb the generally good agreement found between experiment and theory for the terms of f^N of maximum multiplicity.

A detailed decomposition of I into the tensors $g_s^{(t)}$ has been performed for t = 2 and t = 4. The ratio of the relative strengths $G_{10,A}^4$ and $G_{10,B}^4$, corresponding to $\tau = A$ and $\tau = B$ (in Nielson and Koster's notation[7]) is given by

$$G_{10,A}^4/G_{10,B}^4 = (187/686)^{1/2},$$

which is pleasantly free from unusual prime numbers, the common bugbear of multiplicity separations.

When the matrix elements for I are calculated for the states ^{2S+1}L of f^2 in the presence of a single ligand lying on the z axis, it is found that all the sums over products of 3-j and 6-j symbols can be performed. The result can be expressed very simply in terms of Slater determinants: all matrix elements of I between determinantal product states of the type $\{m_1^\pm \, m_2^\pm\}$ vanish except for the one that is diagonal with respect to $\{0^+ \, 0^-\}$. Its value is necessarily negative. This result enables one to calculate the sign of the effect very quickly if expansions in determinantal product states are available. In fact, it may be quicker to actually work out the determinantal expansions. For example, there are

at most seven determinants in the expansions of $|f^7 {}^6I, M_S=5/2, M_L\rangle$ for $-6 \leq M_L \leq 6$. The pair $0^+ 0^-$ appears only for $M_L = \pm 3, \pm 2, \pm 1$. From their coefficients we can rapidly verify that I is diagonal with respect to M_L (for a ligand on the z axis) and that the energy shifts are proportional to $0, 0, 0, -6, -16, -25, 0$ for $M_L = \pm 6, \pm 5, \ldots, \pm 1, 0$. It is straightforward to project out particular components of rank t from this sequence: and it soon becomes clear that ranks t as large as 12 play an important role.

For Pr^{3+} $4f^2$ ^1D, we find that the effect reduces the intrinsic (i.e., single-ligand) parameter $\bar{B}_0^4$ and increases $\bar{B}_0^2$. The changes in B_0^4 and B_0^2 can be inferred from the superposition model.[8] If the nearest chlorine ions are assumed to be equidistant from the praseodymium nucleus, we can conclude that $|B_q^4|$ is decreased and $|B_q^2|$ increased. Preliminary calculations showed that this reduced the discrepancies between experiment and theory for $Pr_2Mg_3(NO_3)_{12} \cdot 24H_2O$. However, this seems to be an atypical case, as the ^1D state is rendered rather impure by the substantial icosahedral field produced by the twelve neighboring oxygen ions. For both $PrCl_3$ and $Pr(C_2H_5SO_4)_3 \cdot 9H_2O$, the corrections are in the opposite sense. Further calculations, which, it is hoped, will be reported in detail at a later date, also suggest that the presence of polarizable neighbors is not the principal mechanism for introducing two-electron crystal-field terms in the Hamiltonian. Recent studies[9] have, in fact, provided evidence that spinpolarized 4f wavefunctions lead to a consistent interpretation of the general trends of the discrepancies in the standard crystal-field model.

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