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Correlation Crystal Fields for Lanthanide Ions

B. R. Judd

Physics Department, The Johns Hopkins University, Baltimore, Maryland 21218

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To reduce the discrepancies in the crystal-field analyses of the electronic configurations $4f^N$ of lanthanide ions, it is argued that each component $(C_q^{(k)})_i$ of the single-electron tensor $C^{(k)}$ for electron i occurring in the conventional crystal-field Hamiltonian should be augmented to $c_k(\vec{s} \cdot \vec{s}_i)(C_q^{(k)})_i$. Parameters c_k of the order of -0.1 lead to significant improvements in the fit with a wide variety of experimental data.

A well-established procedure is available for calculating the energy levels deriving from the electronic configuration $4f^N$ of lanthanide ions situated in crystal lattices.[1] The crystal-field Hamiltonian H is written down as a sum of single-electron tensor operators $(C_q^{(k)})_i$ with parameters B_q^k as coefficients. Considerations of parity, of angular-momentum selection rules, and of site symmetry serve to reduce the terms in H to a manageable number. For C_{3h} symmetry, only four are required.[1] In contrast, the available data that depend on them are often very rich and varied. For example, a recent study by Crosswhite *et al.*[2] for Ho^{3+} substituted for La^{3+} in $LaCl_3$ lists 168 observed crystal-field components arising from 39 free-ion levels. Discrepancies that arise in fitting theory to experiment, although not usually pronounced, have been sufficiently unambiguous to provoke several attempts to improve matters.[3,4] The basic difficulty lies in the large number of parameters that are required to represent the various two-electron operators that can be added to H without violating any symmetry constraints. Thus, Bishton and Newman[3] report that 637 two-electron parameters can be constructed for the lowest site symmetry, while even for octahedral symmetry no fewer than 41 acceptable operators exist.[5]

Rather than attempt a complete parametrization, it seems better to examine the physical origin of the two-electron terms in the augmented Hamiltonian H'. At first sight, this seems a formidable task, particularly when it is recalled that Newman[6] distinguished as many as ten contributions to the single-electron operators in H. Even if the $4f$ electron is assumed to be localized on the lanthanide ion (and thus not subject to the renormalization effects recently considered for actinides[5]), many processes can lead to correlation effects. For example, multipole moments on the ligands induced by electron i in the $4f$ shell interact with another electron j in the $4f$ shell and produce two-electron effects. One feature of this and many other correlations is that the final rank k of such tensorial products as $(C_i^{(t)}C_j^{(p)})^{(k)}$ can run as high as 12. However, Crosswhite *et al.* find that the discrepancies in the case of Ho^{3+} $4f^{10}$ can be greatly reduced simply by making the single-electron parameters B_q^k term dependent. Evidently tensors for which $k > 6$ play a small role. This suggests that the two-electron operators should be produced by contracting products of the type $(C_i^{(t)} \cdot C_j^{(t)})(C_i^{(k)} + C_j^{(k)})$.

A general treatment of these kinds of mechanisms requires many parameters. However, there is one source of such terms that is both physically plausible and comparatively easy to treat analytically. The strong attractive exchange forces between $4f$ electrons whose spins are similarly directed leads to a less-extended radial eigenfunction and hence to smaller B_q^k. The use of variable radial functions, is, of course, a central feature of the spin-unrestricted Hartree-Fock method; to my knowledge, the only calculations for lanthanide ions appear to be made for cases where all $4f$ electrons share the same radial eigenfunction.[7] As far as the two-electron terms in H' go, the most elementary way to introduce them is to take each term $B_q^k(C_q^{(k)})_i$ in H and make the replacement

$$(C_q^{(k)})_i \rightarrow c_k(\vec{S} \cdot \vec{s}_i)(C_q^{(k)})_i. \tag{1}$$

The c_k (where $k = 2, 4, 6$) are three parameters which must necessarily be negative if the contraction of the radial function is to correspond to similarly directed spins. Since $\vec{S}$ includes $\vec{s}_j$ ($j \neq i$),

the substitution (1) introduces a true two-electron operator; but its simplicity allows us to easily construct the energy matrix of H' from that of H. In terms of the unit tensor $U^{(k)}$, the requisite substitution is then

$$(\psi \| U^{(k)} \| \psi') \to (\psi \| U^{(k)} \| \psi') + c_k [S(S+1)/(2S+1)]^{1/2}(\psi \| V^{(1k)} \| \psi'), \tag{2}$$

where $U^{(k)}$ and $V^{(1k)}$ are the respective sums of the single-electron tensors $u^{(k)}$ and $v^{(1k)}$ for which $v^{(1k)} = \vec{s}u^{(k)}$. The appearance of $V^{(1k)}$ can be most easily understood by inserting $|\psi''\rangle\langle\psi''|$ between $\vec{S}$ and $\vec{s}_i$ in (1) and summing over ψ''. The selection rules on $\vec{S}$ restrict ψ'' to the single possibility ψ, and $v^{(1k)}$ is just a renormalized form of $\vec{s}C^{(k)}$.

The operator appearing on the right-hand side in (1) has been mentioned by Newman[8] as a source of a possible contribution to the ground-state splitting of Gd^{3+} $4f^{7}$ $^8S_{7/2}$. The examples that follow indicate that its effect can be appreciable throughout the entire lanthanide series. More significantly, it acts in a direction that consistently tends to remedy the defects of the single-electron model based solely on H. Since $(\vec{S}\cdot\vec{s}_i)(C_q^{(k)})_i$ is a scalar in spin space, its inclusion does not disturb the very good agreement that H provides for the terms of maximum multiplicity. For these,

$$(\psi \| V^{(1k)} \| \psi') = \pm [(S+1)(2S+1)/4S]^{1/2}(\psi \| U^{(k)} \| \psi'), \quad k = 2, 4, 6,$$

where the plus and minus signs apply to the first and second halves of the $4f$ shell, respectively.

Unlike $U^{(k)}$ (for $k = 2, 4, 6$), the tensors $V^{(1k)}$ possess nonvanishing diagonal matrix elements for $4f^{7}$. The level $4f^{7}$ $^6I_{17/2}$ of Gd^{3+} is almost free of contributions from H, and the observed[9] splitting of 13 cm^{-1} in the anhydrous trichloride yields the approximate limits

$$|c_2| \leqslant 0.05, \quad |c_4| \leqslant 0.1, \quad |c_6| \leqslant 0.3.$$

The effect of c_2 is felt by the ^6P multiplet, for which the operator equivalent factors[10] are given by

$$\alpha(^6P_{3/2}) = -7c_2/150, \quad \alpha(^6P_{5/2}) = 2c_2/25,$$

$$\alpha(^6P_{7/2}) = -c_2/30.$$

A value of -0.03 for c_2 considerably improves the fit with experiment by expanding the crystal splitting of $^6P_{5/2}$ relative to the other two levels. The need for such a mechanism is more apparent in the hydrated chloride,[11] where we require $c_2 \sim -0.06$. From the known admixture of $^6P_{7/2}$ in $^8S_{7/2}$, I calculate that the contribution of the correlation crystal field represented by (1) to the intrinsic parameter $\bar{b}_2$ of Newman and Urban[12] is approximately $+0.05$ cm^{-1} for a single Cl$^-$ ligand. This confirms their hypothesis that the correlation-crystal-field contribution is opposite in sign to those coming from relativistic effects.

A more critical test is provided by the $^3K_8$ level of Ho^{3+} $4f^{10}$, whose operator equivalent factor γ needs to be corrected by a factor of roughly -8 according to Crosswhite et al.[2,13] Under the assumption that ^3K can be represented reasonably well by the coupling $|(IF)K\rangle$, in which four spin-up electrons provide I and six spin-down electrons F,[14] standard tensor analysis[15] yields

$$\gamma(^3K_8) = (10/429^2 \cdot 3927)(1 + 1469c_6/16).$$

The remarkably large factor associated with c_6 produces a correction factor of -9 for the quite modest value of -0.1 for c_6. The use of the correct intermediate-coupled states may modify this result somewhat, but at the very least a substantial improvement must remain.

Once the possibility of making the substitution (2) is admitted, several long-standing puzzles of crystal-field analysis in the lanthanides are resolved. For example, the splitting of $^5D_1$ of f^6 should be similar to that of $^7F_1$ but contracted by the factor $\alpha(^5D_1)/\alpha(^7F_1)$. On the assumption (an extremely good one[14]) that the lowest ^5D term of f^6 can be written, in spin-up and spin-down notation, as $|(HF)D\rangle$, the factor turns out to be $\frac{11}{45}$. The experimental results on many crystals[16,17] give a value that is consistently smaller by 20% to 50%. Using (2), I find

$$\alpha(^5D_1)/\alpha(^7F_1) = \tfrac{11}{45} + \tfrac{79}{90}c_2.$$

A value of -0.05 for c_2 thus reduces the factor by some 20%. This is of the right order of magnitude and in the right direction. It is satisfying, too, that the corresponding equation for $k = 4$, namely

$$\beta(^5D_2)/\beta(^7F_2) = -\tfrac{29}{231} + \tfrac{47}{462}c_4,$$

should predict a relative increase in the magnitude of the fourth-rank parameters for $^5D_2$, in agreement with experiment.[17]

Finally, I consider the $^1D_2$ level of Pr^{3+} $4f^2$. Its observed splittings in the trichloride[18] and the

ethylsulfate[19] appear to be too large: However, the triplet levels ^3P_J, ^3F_J, and ^3H_J, on which the parameter analysis largely depends, should be contracted by the factors $1+c_k$, and this has the effect of permitting larger parameters to be used for the singlets. The analysis of both $^1D_2$ and $^1G_4$ would yield better fits with experiment if a 5% increase in the parameters were made.

The evidence strongly suggests that it would be worthwhile to extend the standard crystal-field analysis of lanthanide ions by making the substitution (2) in the complete energy matrices. Although further refinements will undoubtedly be necessary, there is a very good chance that a large part of the correlation crystal field can be taken into account in this way.

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