Symmetry, Effective Operators and Judd-Ofelt Theory

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Abstract. Some of the developments that led up to the Judd-Ofelt theory of intensities and beyond are presented. Particular emphasis is placed upon the role of symmetry considerations and effective operators.

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1. Introduction

What an imperfect world it would be if every symmetry was perfect

Symmetry plays a key role in all physical theories none the less so than in the celebrated Judd-Ofelt theory of intensities of rare earths. Indeed symmetry considerations have been crucial in nearly all developments of our understanding of the diverse spectroscopic properties of the lanthanides and their heavier cousins, the actinides. Explicit calculation of many spectroscopic properties have centred around the construction of effective operators, limited by symmetry arguments and involving the fitting of experimental data in terms of a number of phenomenological parameters. Prior to the Judd-Ofelt theory the intensities of rare earth spectra in solutions and crystals constituted a puzzle[1]. The simultaneous and independent publication of the two papers by Judd[2] and Ofelt[3] satisfied David Hilbert's criterion for a good paper "*One can measure the importance of a scientific work by the number of earlier publications rendered superfluous*". An additional measure is the number of papers that have drawn upon the initial work of Judd-Ofelt. In this paper we trace some of the developments that led up to the Judd-Ofelt theory and beyond.

2. Symmetry and Effective Operators

The calculation of the energy levels of free atoms and ions was outlined in the classic book of Condon and Shortley[4]. With the lack of reliable Hartree-Fock wavefunctions it became a tradition to regard the radial integrals associated with the Coulomb and spin-orbit interactions as parameters to be determined by least-squares fitting to the known experimental energy levels. In the early 1950's Trees[5,6] and Racah[7] found empirically that adding a term $\alpha L(L+1)$ led to a significant reduction in the mean least-squares error for the energies of the SL terms for d^n shell ions. No explanation for the introduction of this *effective interaction* was offered. In 1959 Runciman and Wybourne[8] found that the introduction of a term $\alpha L(L+1)$ significantly improved the calculation of the terms of the $4f^2$ and $4f^{12}$ for the trivalent praseodymium and thulium ions. Initially it was thought that the $\alpha L(L+1)$ arose from the orbit-orbit interaction[9].

In 1962 Rajnak and Wybourne used second-order perturbation theory to sum over the states of generic configurations that could couple to a configuration ℓ^n of n equivalent ℓ electron orbitals[10]. They found that most of the second-order effects could be accommodated by treating the $\ell+1$ Coulomb integrals as adjustable parameters and adding ℓ additional effective two-body operators. In the case of the f^n−shell that amounts to the four Coulomb parameters and the three additional operators may be chosen as

$$\alpha L(L+1) + \beta C(G_2) + \gamma C(SO_7) \tag{1}$$

where the last two are the Casimir invariants of the groups G_2 and SO_7 that arose in Racah's classification of the states of the f^n-shell[11]. One may express the orbit-orbit interaction for the f^n-shell in precisely the same way as in Eq.(1) and obtain explicit expressions[12] for the values of α, β and γ. However, they are smaller and of the opposite sign to those found from least-squares fits. This gives a salutary warning of the dangers of parameter fitting - they may accommodate effects that are beyond those anticipated. In this case the effect of configuration interaction mimics the orbit-orbit interaction. Similar examples of different interactions mimicking one another can be found in the case of anisotropic autoionizing Rydberg systems[13]. Furthermore, at second-order, three-particle effective operators also arise[10,14].

In general, effective operators may be built up from unit tensor operators $\mathbf{u}^{(k)}$ and/or unit double tensor operators $\mathbf{w}^{(1k)}$ or equivalently in terms of coupled products of annihilation and creation operators[15-18]. In terms of energy level calculations which conserve the total angular momentum for a free atom or ion the effective operators must be scalars with respect the rotation group SO_3, or more precisely with its covering group SU_2. Technically, one is constructing an integrity basis or minimal set of invariants in terms of which other invariants are polynomials in the minimal set[19-23]. The determination of a complete list of $f-$electron scalar operators has been given by Leavitt[24].

In a crystal field the effective operators required to analyze crystal field splittings are again scalar operators but now not with respect to the groups SO_3 or SU_2 but with respect to the appropriate site symmetry point group. The explicit construction of the crystal field invariant operators is essentially the construction of the appropriate elements of an integrity basis and is largely model independent. The physics is hidden in the associated parameters. At the simplest level one-particle orbital type operators may be constructed and at a higher level effective two-particle or one-particle spin-orbital operators may be introduced with further parameters being required.

Non-scalar operators, such as the electric dipole operator

$$\mathbf{P} = -e \sum_i \mathbf{r}_i \tag{2}$$

are of particular spectroscopic interest as they induce transitions between different energy levels. The electric dipole operator is of odd parity so can only induce transitions between states of opposite parity. Unlike the energy operators which transform under the appropriate point group as the identity representation the components of the electric dipole operator span representations other than the identity representation. Selection rules follow by standard group procedures. Selection rules tell one what will not happen not what will happen. To obtain actual transitions within the $f-$shell the odd-parity electric dipole operator must be combined with other odd-parity operators to produce effective even-parity operators acting within the $f-$shell. This was the essence of the Judd-Ofelt theory in its initial formulation. The even-parity effective operators must transform with respect to the appropriate point group in the same way as the electric dipole operator and thus preserve the basic selection

rules. In terms of single particle operators one can form linear combinations of the unit tensor operators $\mathbf{u}^{(k)}$ with k even that have the appropriate point group symmetries. Essentially one is constructing terms in a generalized integrity basis. In a sense the Judd-Ofelt theory is largely model-independent. Various specific mechanisms can lead to the same parameterized effective interactions. That is one of the great achievements of the Judd-Ofelt theory - it allows the correlation of a large amount of data in terms of a small set of empirically determinable parameters.

The Judd-Ofelt theory involves the simplest possible set of one-particle spin-independent effective operators having the correct point group transformation properties that one can construct. It is not difficult to construct more complicated operators from the basic $\mathbf{u}^{(k)}$ and $\mathbf{w}^{(\kappa k)}$ operators which have the correct point group transformation properties. Many cases of explicit constructions arising from specific mechanisms have been discussed in the literature, we give but a small selection[17,18,25−35]. Higher order treatments of the Judd-Ofelt theory lead to the appearance of odd rank single particle type effective operators, two-particle effective operators and various spin-dependent effective operators. Relativistic extensions of the Judd-Ofelt theory likewise lead to additional effective operators what have been termed *doubly effective double tensor operators*. All these can be accommodated by introducing additional parameters but in the process losing the underlying simplicity of the original Judd-Ofelt formulation. A given effective operator may, unwittingly, accommodate more mechanisms than their user has anticipated. Real progress in understanding specific mechanisms requires *ab initio* calculations which are now becoming possible[36,37] and will undoubtedly mature over the next four decades but I believe that in the eight decades that will have followed the original Judd-Ofelt theory, it will still be recognized that the publication of those two papers represented a turning point in our understanding of the spectroscopic properties of the remarkable lanthanides and actinides.

Acknowledgments

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