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LETTER TO THE EDITOR

Three-electron matrix elements near the middle of the atomic f shell

B R Judd and Edwin Lo

Henry A Rowland Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, MD 21218, USA

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Abstract. A number of minor errors have been detected in the computer output frequently used to fit the strengths of the three-electron operators t_i to the experimental spectroscopic data for lanthanide and actinide ions in crystals. A table of corrections is given. The five new zeros appearing in this table can be accounted for on the basis of the quark model for the atomic f shell.

The spectroscopic properties of lanthanide and actinide ions situated in crystal lattices are significantly affected by perturbations on the ground configurations f^N coming from excited configurations. The leading terms in a treatment by perturbation theory involve the Coulomb interaction taken between a particular f^N and configurations that differ from f^N with respect to a single electron. It has become commonplace to allow for such perturbations by including six three-electron operators t_i in the Hamiltonian, where $i = 2, 3, 4, 6, 7$, and 8 (Judd 1966). Among the many examples in the literature, we cite the work reported during the present year by Beaury *et al* (1994) and Rukmini *et al* (1994) for Nd^{3+}, Renuka Devi *et al* (1994) for Er^{3+}, Qian *et al* (1994) for Sm^{3+}, Görller-Walrand *et al* (1994) for Eu^{3+}, and Thouvenot *et al* (1994) for Cm^{3+}. The empirical strengths T^i of the operators t_i are usually found by fitting procedures in which the matrix elements of the t_i are taken from a computer program written by Hannah Crosswhite and based on an iterative procedure similar to what Racah (1949, equation (1)) envisaged for the Coulomb interactions between the f electrons themselves. This requires a knowledge of the coefficients of fractional parentage (CFP), which Crosswhite took from the tabulation by Nielson and Koster (1963). Her results have been made available to the scientific community by Dr W T Carnall and, more recently, by Dr G K Liu of the Chemistry Division of the Argonne National Laboratory.

We have recently taken advantage of this computer output to factorize the matrix elements of the t_i by applying the Wigner–Eckart theorem to the Lie group G_2. This has enabled us to represent the numerical results in a compact form, similar to what Racah (1949) achieved for the parts e_2 and e_3 of the Coulomb interaction in his tables VI–XI and XIV–XXIV. It is planned to report this work elsewhere. However, in the course of our analysis we discovered that the CFP $(f^6\ 1S3\{|f^5\ 2F3)$, which we write in the notation of Nielson and Koster (1963), had been entered into the computer program with the wrong sign (+1 instead of −1). This error escaped orthonormality checks because 2F3 is the sole parent of 1S3. Fortunately, the affected spectroscopic terms, namely those of the type ^1S of f^6 and ^2F of f^7, are too high to be directly observed, and their admixtures into lower terms are expected to be quite small. Although we do not anticipate any revisions of work that has

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Table 1. Matrix elements of the t_i (i = 2, 3, 4, 6, 7) subject to correction. No changes are needed for t_8. The notation of Nielson and Koster (1963) is used to define the states.

Configuration	Matrix element	Corrected value
f^6	$\langle 1S2\|t_2\|1S3\rangle$	$-(1083/5390)^{1/2} = -0.448\,250$
	$\langle 1S3\|t_4\|1S4\rangle$	$(3/35)^{1/2} = 0.292\,770$
	$\langle 1S2\|t_6\|1S3\rangle$	$(975/77)^{1/2} = 3.558\,418$
	$\langle 1S3\|t_7\|1S4\rangle$	$-(45/7)^{1/2} = -2.535\,463$
f^7	$\langle 2F2\|t_2\|2F3\rangle$	$(49/880)^{1/2} = 0.234\,970$
	$\langle 2F2\|t_2\|2F8\rangle$	$-(33/196)^{1/2} = -0.410\,326$
	$\langle 2F3\|t_2\|2F4\rangle$	$-(1849/2940)^{1/2} = -0.793\,039$
	$\langle 2F3\|t_2\|2F6\rangle$	$-(24/49)^{1/2} = -0.699\,854$
	$\langle 2F4\|t_2\|2F8\rangle$	$1/4 = 0.25$
	$\langle 2F6\|t_2\|2F8\rangle$	0
	$\langle 2F3\|t_3\|2F8\rangle$	$-(144/7)^{1/2} = -4.535\,574$
	$\langle 2F3\|t_4\|2F9\rangle$	$(8/35)^{1/2} = 0.478\,091$
	$\langle 2F3\|t_4\|2F10\rangle$	$-(9/70)^{1/2} = -0.358\,569$
	$\langle 2F5\|t_4\|2F8\rangle$	$-(1/7)^{1/2} = -0.377\,964$
	$\langle 2F7\|t_4\|2F8\rangle$	0
	$\langle 2F2\|t_6\|2F3\rangle$	$-(325/154)^{1/2} = -1.452\,718$
	$\langle 2F4\|t_6\|2F8\rangle$	0
	$\langle 2F6\|t_6\|2F8\rangle$	$-(52/7)^{1/2} = -2.725\,541$
	$\langle 2F3\|t_7\|2F9\rangle$	0
	$\langle 2F3\|t_7\|2F10\rangle$	$(125/42)^{1/2} = 1.725\,164$
	$\langle 2F5\|t_7\|2F8\rangle$	0
	$\langle 2F7\|t_7\|2F8\rangle$	$(25/7)^{1/2} = 1.889\,822$

already been published, it nevertheless seems appropriate to list the corrections that should be made. This is done in table 1. An independent iterative calculation by Dr J E Hansen of the Van der Waals–Zeeman Laboratory in Amsterdam has confirmed these corrections.

It is interesting to note from table 1 that five matrix elements of the t_i for the ^{2}F terms of f^7 turn out to be zero. None of them can be accounted for on the basis of the classic group labels provided by Racah (1949). However, the are all explicable in terms of the recently developed quark model of the atomic f shell (Judd and Lister 1991, 1993a, Judd 1994). In this scheme, an alternative basis for the 16 384 states of the entire f shell is provided by the quark configuration $(s + f)^4$, augmented with two parity labels. The null matrix elements of t_2 and t_4 in table 1 are zero because in these cases both t_2 and t_4 are effectively f-quark-conserving operators set between states that, in the quark picture, belong to the quark configurations f^4 and f^3s. The detailed arguments leading to this result are similar to those already described for t_2 and t_4 in other situations (Judd and Lister 1991, 1993b). The remaining three zeros in table 1 can be accounted for by embedding G_2 in an $SO(7)$ group different from the one used by Racah, and called SO(7)′. The method depends on applying the Wigner–Eckart theorem to the irreducible representations of SO(7)′. It has been described for other doublet states belonging to f^7 (Judd and Lister (1993a), section 5), and the analysis for the present case proceeds as before, with minor modifications.

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References

Beaury L, Derouet J, Escorne M and Porcher P 1994 *J. Phys.: Condens. Matter* **6** 5169–80

Görller-Walrand C, Huygens E, Binnemans K and Fluyt L 1994 *J. Phys.: Condens. Matter* **6** 7797–812
Judd B R 1966 *Phys. Rev.* **141** 4–14
—— 1994 *Comment. At. Mol. Phys.* **30** 27–35
Judd B R and Lister G M S 1991 *Phys. Rev. Lett.* **67** 1720–2
—— 1993a *J. Phys. B: At. Mol. Opt. Phys.* **26** 3177–88
—— 1993b *J. Alloys Compounds* **193** 155–9
Nielson C W and Koster G F 1963 *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (Cambridge, MA: MIT Press)
Qian C, Wang B, Edelstein N, Reddmann H, Hagen C and Amberger H-D 1994 *J. Alloys Compounds* **207/208** 87–9
Racah G 1949 *Phys. Rev.* **76** 1352–65
Renuka Devi A, Jayasankar C K and Reid M F 1994 *J. Alloys Compounds* **207/208** 74–7
Rukmini E, Jayasankar C K and Reid M F 1994 *J. Phys.: Condens. Matter* **6** 5919–36
Thouvenot P, Hubert S and Edelstein N 1994 *Phys. Rev.* B **50** 9715–20