# Relativistic effects in lanthanides and actinides

**Brian G Wybourne‡% and Lidia Smentek†§**

‡ Instytut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziądzka 5/7, 87-100 Toruń, Poland

† Instytut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziądzka 5/7, 87-100 Toruń, Poland and Chemistry Department, Vanderbilt University, Nashville, Tennessee, USA

5 June 2001

**Abstract.** The Judd-Ofelt theory of $f \longleftrightarrow f$ transitions was originally developed as a non-relativistic theory nearly 40years ago. Modifications to include the effects of spin-orbit effects have been developed by various researchers. The inclusion of relativistic effects both for the Judd-Ofelt theory of intensities and for crystal field effects has been hindered, until recent times, by the lack of adequate relativistic radial integrals. It is now possible to obtain reliable relativistic integrals and we show how both the Judd-Ofelt theory and crystal field theory may be modified to accommodate relativistic effects. These extensions involve new effective operators. We include some historical remarks on the development of the Judd-Ofelt theory.

% E-mail: bgw@phys.uni.torun.pl

§ E-mail: smentek@phys.uni.torun.pl

## 1. Introduction

The first successful theoretical treatment of the transition probabilities of the $f \longleftrightarrow f$ transitions so characteristic of the lanthanides and actinides in solid and liquid environments was developed, independently, almost forty years ago by Judd[1] and Ofelt[2] forming what has been commonly known as the Judd-Ofelt theory of intensities. For a general reference see[3] and references contained therein. In this account, one of us (BGW) gives a brief personal account of the origins of the Judd-Ofelt theory and then we outline the implications for crystal field theory and the Judd-Ofelt theory of relativistic effects.

## 2. A Historical Note (BGW)

The possibility of calculating the spectroscopic properties lanthanides and actinides owes much to Giulio Racah's paper[4] *The Theory of Complex Spectra IV* (Unna[5] gives a fascinating account of Racah's appointment to the Hebrew University of Jerusalem). That paper, together with his three earlier papers on complex spectra[6–8] created the machinery for calculating properties of $f^n$ configurations. Nuclear physicists such as Jahn[9], Flowers[10] and others were quick to exploit Racah's methods. Atomic spectroscopists were slow to abandon the tried and trusted methods ensconced in the book of Condon and Shortley[11]. In 1953 Edith Reilly[12] used Racah's methods to calculate the electrostatic interaction matrices for the $f^4$ configuration. The mid-1950's saw Judd[13–15] in England and Jørgensen[16,17] in Denmark starting to make specific applications to rare earths. The publication, in 1958, by Elliott, Judd and Runciman[18] showed to a much wider audience how Racah's methods could be applied to the making of practical calculations. In 1957 Alan Runciman came as a senior lecturer to the University of Canterbury and I commenced my PhD thesis under his supervision. The objective was to calculate as much as possible of the properties of rare earths using Racah's methods and a Monroe calculator and eventually the Sydney SILLIAC computer. Runciman and I reported our first results at a conference in Melbourne. W M Lomer reported[18] in *Nature*

*A CONFERENCE was held at Melbourne on "Solid State Physics" during August 17-21 under the auspices of the Australian Branch of the Institute of Physics. Grants ... enabled several Americans, a Canadian and three Englishmen to attend. Other States of the Commonwealth of Australia and New Zealand were well represented..... On the third day attention was swung to optical properties of solids... The analysis of rare-earth spectra in crystals is getting steadily more detailed and very large-scale calculations are rapidly elucidating the details of interactions within the f electron shell. ...*

Attending the conference was fortunate because in a Sydney bookshop I came across a book[20] that I bought, at what seemed to a poor student an exorbinant price. I returned to New Zealand, wrote up my thesis and completed my PhD with B R

Judd being my "Overseas Examiner". The following year, with family, I went by boat through the Panama Canal and train to Baltimore to become a very young Assistant Professor at Johns Hopkins University in the group of G H Dieke. I had read the book bought in Sydney while on the boat. By then I knew how to calculate matrix elements, energy levels etc but what about Van Vleck's rare earth puzzle[21] - the intensities of transitions in rare earths in crystals and in solutions? The time was ripe to tackle the problem. Fano and Racah's book[20] supplied some of the tools and the masterly book of Griffith[22] a number of ideas. It was clear how to proceed - use the odd terms in the crystal field to couple configurations of opposite parity and make use of perturbation theory - an ideal PhD student project - which I assigned to my very first PhD student - George Ofelt. George completed the problem at speed and I told him to write it up for the Journal of Chemical Physics. Little did we know that on the opposite side of the continent at Berkeley B R Judd was, completely independently, writing a paper on the same subject for the Physical Review and thus was the celebrated Judd-Ofelt theory of intensities of rare earth ions born.

## 3. Relativistic crystal field theory

Relativistic crystal field theory[23] started with attempts to calculate the electric quadrupole moment of the ground state $4f^76s^2[^8S_{\frac{7}{2}}]$ of neutral europium in an atomic beam[24,25], a problem very analogous to the crystal field splitting of the ground state $4f^7[^8S_{\frac{7}{2}}]$ of trivalent gadolinium. If we solve Dirac's equation for an electron $n\ell j$ in a central field we obtain two radial functions, $F$ and $G$, that are associated with the small and large components of the Dirac wavefunction, respectively, and which depend on the total angular momentum $j$ of the electron. To give a specific example, assume a crystal field potential

$$V = A_2^0 r^2 C_0^{(2)} + A_4^0 r^4 C_0^{(4)} + A_6^0 r^6 C_0^{(6)} + A_6^6 r^6 (C_6^{(6)} + C_{-6}^{(6)}) \tag{1}$$

For a single $f-$electron we have the fourteen states

$$|\tfrac{7}{2} \pm \tfrac{1}{2}\rangle,\ |\tfrac{7}{2} \pm \tfrac{3}{2}\rangle,\ |\tfrac{7}{2} \pm \tfrac{5}{2}\rangle,\ |\tfrac{7}{2} \pm \tfrac{7}{2}\rangle,\ |\tfrac{5}{2} \pm \tfrac{1}{2}\rangle,\ |\tfrac{5}{2} \pm \tfrac{3}{2}\rangle,\ |\tfrac{5}{2} \pm \tfrac{5}{2}\rangle \tag{2}$$

Noting that[26]

$$\langle s\ell j||C^{(k)}||s\ell j'\rangle = \langle \ell||C^{(k)}||\ell\rangle(-1)^{s+\ell+j+k}\sqrt{(2j+1)(2j'+1)}\begin{Bmatrix} j & k & j' \\ \ell & s & \ell \end{Bmatrix} \tag{3}$$

leading to

$$\begin{aligned}
&\langle s\ell jm|r^k C_q^{(k)}|s\ell j'm'\rangle \\
&= \langle \ell||C^{(k)}||\ell\rangle R_{jj'}(-1)^{j-m}\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \\
&\times (-1)^{s+\ell+j+k}\sqrt{(2j+1)(2j'+1)}\begin{Bmatrix} j & k & j' \\ \ell & s & \ell \end{Bmatrix}
\end{aligned} \tag{4}$$

where each non-relativistic radial integral

$$R^k_{\ell\ell} = \int_0^\infty R_{n\ell}(r) r^k R_{n\ell} dr, \tag{5}$$

is now replaced three relativistic radial integrals $R^k_{jj'}$ such that

$$\begin{aligned} R^k_{++} &= \int_0^\infty r^k (F_+^2 + G_+^2) dr, \\ R^k_{+-} &= \int_0^\infty r^k (F_+F_- + G_+G_-) dr, \\ R^k_{--} &= \int_0^\infty r^k (F_-^2 + G_-^2) dr, \end{aligned} \tag{6}$$

with the $+$ referring to $j = \ell + \frac{1}{2}$ and the $-$ to $j = \ell - \frac{1}{2}$.

For fourteen states of a single $f-$electron we obtain the crystal field matrices

$$\begin{array}{lll} \mu = \pm\frac{1}{2} & |\frac{7}{2} \pm \frac{1}{2}\rangle & |\frac{5}{2} \pm \frac{1}{2}\rangle \\ \langle\frac{7}{2} \pm \frac{1}{2}| & \frac{5}{21}A_2^0R^2_{++} + \frac{9}{77}A_4^0R^4_{++} + \frac{25}{429}A_6^0R^6_{++} & \begin{array}{l} \sqrt{3}(\pm\frac{2}{105}A_2^0R^2_{+-} \pm \frac{10}{231}A_4^0R^4_{+-} \\ \pm\frac{50}{429}A_6^0R^6_{+-}) \end{array} \\ \langle\frac{5}{2} \pm \frac{1}{2}| & \begin{array}{l} \sqrt{3}(\pm\frac{2}{105}A_2^0R^2_{+-} \pm \frac{10}{231}A_4^0R^4_{+-} \\ \pm\frac{50}{429}A_6^0R^6_{+-}) \end{array} & \frac{8}{35}A_2^0R^2_{--} + \frac{2}{21}A_4^0R^4_{--} \end{array} \tag{7a}$$

$$\begin{array}{lll} \mu = \pm\frac{3}{2} & |\frac{7}{2} \pm \frac{3}{2}\rangle & |\frac{5}{2} \pm \frac{3}{2}\rangle \\ \langle\frac{7}{2} \pm \frac{3}{2}| & \frac{1}{7}A_2^0R^2_{++} - \frac{3}{77}A_4^07R^4_{++} - \frac{15}{143}A_6^0R^6_{++} & \begin{array}{l} \sqrt{10}(\pm\frac{1}{35}A_2^0R^2_{+-} \pm \frac{8}{231}A_4^0R^4_{+-} \\ \mp\frac{5}{143}A_6^0R^6_{+-}) \end{array} \\ \langle\frac{5}{2} \pm \frac{3}{2}| & \sqrt{10}(\pm\frac{1}{35}A_2^0R^2_{+-} \pm \frac{8}{231}A_4^0R^4_{+-} \mp \frac{5}{143}A_6^0R^6_{+-}) & \frac{2}{35}A_2^0R^2_{--} - \frac{1}{7}A_4^0R^4_{--} \end{array} \tag{7b}$$

$$\begin{array}{llll} \mu = \pm\frac{5}{2} & |\frac{7}{2} \pm \frac{7}{2}\rangle & |\frac{7}{2} \mp \frac{5}{2}\rangle & |\frac{5}{2} \mp \frac{5}{2}\rangle \\ \langle\frac{7}{2} \pm \frac{7}{2}| & \begin{array}{l} -\frac{1}{3}A_2^0R^2_{++} + \frac{1}{11}A_4^0R^4_{++} \\ -\frac{5}{429}A_6^0R^6_{++} \end{array} & -\frac{10\sqrt{33}}{429}A_6^6R^6_{++} & \mp\frac{10\sqrt{22}}{143}A_6^6R^6_{+-} \\ \langle\frac{7}{2} \mp \frac{5}{2}| & -\frac{10\sqrt{33}}{429}A_6^6R^6_{++} & \begin{array}{l} -\frac{1}{21}A_2^0R^2_{++} - \frac{13}{77}A_4^0R^4_{++} \\ +\frac{25}{429}A_6^0R^6_{++} \end{array} & \begin{array}{l} \sqrt{6}(\mp\frac{1}{21}A_2^0R^2_{+-} \pm \frac{10}{231}A_4^0R^4_{+-} \\ \mp\frac{5}{429}A_6^0R^6_{+-}) \end{array} \\ \langle\frac{5}{2} \mp \frac{5}{2}| & \mp\frac{10\sqrt{22}}{143}A_6^6R^6_{+-} & \begin{array}{l} \sqrt{6}(\mp\frac{1}{21}A_2^0R^2_{+-} \pm \frac{10}{231}A_4^0R^4_{+-} \\ \mp\frac{5}{429}A_6^0R^6_{+-}) \end{array} & -\frac{2}{7}A_2^0R^2_{--} + \frac{1}{21}A_4^0R^4_{--} \end{array} \tag{7c}$$

If in the above matrices we were to make all the radial integrals $R^k_{jj'}$ of the same rank $k$ equal we would obtain the standard non-relativistic crystal field matrices. The next problem is to extend the formulation to many-electron configurations. Two ways are open (1). Do the entire calculation in a $jj-$coupling basis; or (2). Follow Sandars and Beck[24] and continue to use the traditional $LS-$coupling basis by making the operator replacements

$$r^k \mathbf{C}^{(k)} \to \sum_{\kappa,\kappa'} b_k(\kappa\kappa')\mathbf{w}^{(\kappa\kappa')k}, \tag{8}$$

where the $\mathbf{w}^{(\kappa\kappa')k}$ are single-particle tensor operators[26] and the $b_k(\kappa\kappa')$ involve the relativistic radial integrals. One finds that

$$r^2\mathbf{C}^{(2)} \to b_2(11)\mathbf{w}^{(11)2} + b_2(13)\mathbf{w}^{(13)2} + b_2(02)\mathbf{w}^{(02)2}, \tag{9a}$$
$$r^4\mathbf{C}^{(4)} \to b_4(13)\mathbf{w}^{(13)4} + b_4(15)\mathbf{w}^{(15)4} + b_4(04)\mathbf{w}^{(04)4}, \tag{9b}$$
$$r^6\mathbf{C}^{(6)} \to b_6(15)\mathbf{w}^{(15)6} + b_6(06)\mathbf{w}^{(06)6}, \tag{9c}$$

where

$$\begin{aligned} b_2(11) &= 4\sqrt{21}\left[-5R^2_{++} + 3R^2_{+-} + 2R^2_{--}\right]/245 \\ b_2(13) &= 4\sqrt{7}\left[5R^2_{++} + 4R^2_{+-} - 9R^2_{--}\right]/245 \\ b_2(02) &= -2\sqrt{42}\left[25R^2_{++} + 6R^2_{+-} + 18R^2_{--}\right]/735 \end{aligned} \tag{10a}$$

$$\begin{aligned} b_4(13) &= 4\sqrt{21}\left[6R^4_{++} - 5R^4_{+-} - R^4_{--}\right]/441 \\ b_4(15) &= 2\sqrt{2310}\left[-3R^4_{++} - 8R^4_{+-} + 11R^4_{--}\right]/4851 \\ b_4(04) &= 2\sqrt{77}\left[18R^4_{++} + 20R^4_{+-} + 11R^4_{--}\right]/1617 \end{aligned} \tag{10b}$$

$$\begin{aligned} b_6(15) &= 20\sqrt{77}\left[-R^6_{++} + R^6_{+-}\right]/1001 \\ b_6(06) &= -10\sqrt{462}\left[R^6_{++} + 6R^6_{+-}\right]/3003 \end{aligned} \tag{10c}$$

Not surprisingly, calculation with the replacement operators yields exactly the same results, for a single electron, as found in Eq.(7a-c). For states involving $n$ equivalent electrons the $\mathbf{w}^{(\kappa\kappa')}$ are simply replaced by

$$\mathbf{W}^{(\kappa\kappa')} \to \sum_{i=1}^{n} \mathbf{w}^{(\kappa\kappa')} \tag{11}$$

and the matrix elements may be evaluated in the usual non-relativistic $LS-$coupling basis but with the associated radial integrals being taken from appropriate relativistic Dirac-Hartree-Fock wavefunctions. The important point to notice is that the replacement operators are *double tensor operators* that act in *both* the spin and orbital spaces whereas the non-relativistic crystal field operators act only in the orbital space.

It is this property that leads to a second-order contribution to the ground state splitting for rare earth and actinide ions having a half-filled $f-$shell[23,27,28]. We have recently given detailed calculations of a relativistic crystal field for $S-$state $f$ electron ions[28]. Free ion non-relativistic calculations were performed using Froese-Fischer's MCHF programme while the relativistic radial integrals were evaluated using the GRASP[2] package. The inner $s$ and $p$ orbitals are contracted and hence the effective nuclear charge seen by the $f-$orbitals is *decreased* and the orbitals *expand.* It is planned to present further numerical calculations in the near future.

## 4. Relativistic $f \longleftrightarrow f$ transitions in crystal fields

Here we have products of the electric dipole and crystal field matrix elements coupling the $f^N$ configuration to those of opposite parity. Again, whereas in the non-relativistic Judd-Ofelt theory transitions depend on the tensor operators $\mathbf{U}^{(k)}$ the relativistic treatment leads to double-tensor operators $\mathbf{W}^{(\kappa\kappa')k}$. In the Judd-Ofelt theory the single particle unit tensor operators $\mathbf{u}(n\ell, n'\ell')^{(k_{odd})}$ link a ground configuration orbital $n\ell$ to an orbital $n'\ell'$ in an excited configuration and closure results in single particle tensor operators $\mathbf{u}(n\ell, n\ell)^{(k_{even})}$. In the relativistic extension the double tensor operators $\mathbf{w}(n\ell, n'\ell')^{(\kappa\kappa')k}$ couple the orbitals and closure results in single particle double tensor operators $\mathbf{w}(n\ell, n\ell)^{(\kappa\kappa')k}$ where again $k$ is *even* but $\kappa'$ is *even* or *odd* as $\kappa$ is 0 or 1 respectively. The effective operators obtained in the detailed analysis[29−32] generalize the standard Judd-Ofelt effective operators, the latter becoming a limiting case of the former. Whereas in our discussion of relativistic crystal field theory we limited ourselves to action within the $f-$shell here the action takes place between configurations and the radial functions are more complex, involving $f-$orbitals and orbitals of opposite parity.

## 5. Concluding Remarks

In terms of the *angular* parts which reflect the symmetry properties of $f-$orbitals there is a remarkable, and understandable, similarity between crystal field theory and the theory of $f \longleftrightarrow f$ transitions. In the non-relativistic theory both involve, to second-order, the matrix elements of the unit tensor operators $\mathbf{U}^{(k)}$ with $k = 0, 2, 4, 6$ while in the extension to the relativistic theory both involve the replacement of the $\mathbf{U}^{(k)}$ operators by the double tensor operators $\mathbf{W}^{(\kappa\kappa')k}$. The fundamental difference comes in the radial integrals involved. It is only in relatively recent times that it has become possible to give serious consideration to detailed calculation of such integrals. Future work will undoubtedly be more directed to such calculations and to estimates of the significance of relativistic effects both for crystal field interactions and transition intensities. One expects these effects to become increasingly important as the calculations, and hopefully experiments, are made on the heavy actinides. It may well be that in the future studies will be directed towards calculations in the

$jj-$coupling basis which is the natural basis to use when relativistice effects become significant.

## Acknowledgments

This research has been performed under grants from the National Science Foundation of Poland (KBN) (Contracts No. 2 P03B 064 16 and 2 P03B 076 13). BGW acknowledges, with pleasure, the inspiration to reconsider relativistic effects coming from a lecture given in Toruń by Roberto Acevedo.

## References

[1] Judd B R 1962 *Phys. Rev.* **127** 750
[2] Ofelt G S 1962 *J. Chem. Phys.* **37** 511
[3] Smentek L 1998 Phys Rept **297** 155
[4] Racah G 1949 *Phys. Rev.* **76** 1352
[5] Unna I 2000 Phys. perspect **2** 336
[6] Racah G 1941 *Phys. Rev.* **61** 186
[7] Racah G 1942 *Phys. Rev.* **62** 438
[8] Racah G 1943 *Phys. Rev.* **63** 367
[9] Jahn H A 1950 *Proc. R. Soc.* **A201** 516
[10] Flowers B H 1952 *Proc. R. Soc.* **A212** 248
[11] Condon E U and Shortley G H 1935 *The theory of atomic spectra*, (Cambridge: Cambridge University Press)
[12] Reilly E F 1953 *Phys. Rev.* **91** 876
[13] Judd B R 1955 *Proc. R. Soc.* **A227** 552
[14] Judd B R 1955 *Proc. R. Soc.* **228** 120
[15] Judd B R 1955 *Proc. R. Soc.* **232** 458
[16] Jørgensen C K 1955 *K. danske vidensk. Selsk. Mat. Fys. Medd.* **29** no. 11
[17] Jørgensen C K 1955 *Acta chem. scand.* **9** 540
[18] Elliott J P, Judd B R and Runciman W A, 1957 *Proc. R. Soc.* **A240** 509
[19] Lomer W M 1959 *Nature* **184** 1117
[20] Fano U and Racah G 1959 *Irreducible Tensorial Sets*(New York: Academic Press Inc.)
[21] Van Vleck J H 1937 *J. Phys. Chem.* **41** 67
[22] Griffith J S 1961 *The Theory of Transition-Metal Ions* (Cambridge: Cambridge University Press)
[23] Wybourne B G 1965 *J. Chem. Phys.* **43** 4506
[24] Sandars P G H and Beck J 1965 *Proc. R. Soc.* **A289** 97
[25] Bordarier Y, Judd B R and Klapisch M 1965 *Proc. R. Soc.* **A289** 81
[26] Judd B R 1998 *Operator Techniques in Atomic Spectroscopy* (Princeton, NJ: Princeton University Press)
[27] Wybourne B G 1966 *Phys. Rev.* **148** 317
[28] Smentek L, Wybourne B G and Kobus J 2001 *J. Phys. B: At. Mol. Phys.* **34** 1513
[29] Smentek L and Wybourne B G 2000 *J. Phys. B: At. Mol. Phys.* **33** 3647
[30] Smentek L and Wybourne B G 2001 *J. Phys. B: At. Mol. Phys.* **34** 625
[31] Smentek L, Wybourne B G and Hess Jr. B A 2001 J All. Comp. **XX**XX
[32] Smentek L, Wybourne B G and Hess Jr. B A (In these proceedings)