5Este, Lądek Zdrój, POLSKA 6 - 11 June 2001

Relativistic effects in lanthanides and actinides

Brian G Wybourne and Lidia Smentek

Instytut Fizyki,

Uniwersytet Mikołaja Kopernika, Toruń - Polska

6 - 11 June 2001

Introduction

- The Origins of the Judd-Ofelt Theory of Intensities
- The Basics of the Judd-Ofelt Theory
- Relativistic Crystal Field Theory
- Relativistic Extensions of the Judd-Ofelt Theory
- Back to the Future
- Acknowledgements

The Origins of the Judd-Ofelt Theory of Intensities

- Van Vleck's Rare Earth Puzzle 1937
- Johns Hopkins 1960
- George S Ofelt 1962
- Brian R Judd 1962
- *"One can measure the importance of a scientific work by the number of earlier publications rendered superfluous by it"* David Hilbert

Nature October 10, 1959 p1117

SOLID STATE PHYSICS

- 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. ... W. M. LOMER

J.CHEM.PHYS. V37 AUGUST 1, 1962

Intensities of Crystal Spectra of Rare-Earth Ions*

G. S. OFELT

The Johns Hopkins University, Baltimore, Maryland

(Received February 26, 1962)

Magnetic and electric dipole transitions between levels of the $4f^x$ configuration perturbed by a static crystalline field are treated. The expression obtained for the pure-electronic electric-dipole transition probability involves matrix elements of an even-order unit tensor between the two $4f^x$ states involved in the transition. The contributions to the transition probability from interactions, via the crystalline field, with the $nd^9 4f^{x-1}, 4f^{x-1}nd, 4f^{x-1}ng$ configurations are shown to add linearly, in such a manner as to multiply each odd k crystal-field parameter A_k^q by a constant. If "J mixing" ...

ACKNOWLEDGMENTS

I would like to express my sincere thanks to Professor Brian G. Wybourne for suggesting this problem. I would also like to thank both Professor Wybourne and Dr. John D. Axe for many helpful discussions and suggestions.

PHYS.REV. V127 AUGUST 1, 1962

Optical Absorption Intensities of Rare-Earth Ions

B. R. JUDD

Lawrence Radiation Laboratory, University of California, Berkeley, Ca.

(Received March 12, 1962)

Electric dipole transitions within the $4f$ shell of a rare-earth ion are permitted if the surroundings of the ion are such that its nucleus is not situated at a center of inversion. An expression is found for the oscillator strength of a transition between two states of the ground configuration $4f^N$, on the assumption that the levels of each excited configuration of the type $4f^N n'd$ or $4f^N n'g$ extended over an energy range small as compared to the energy of the configuration above the ground configuration. On summing over all transitions between the components of the ground level Ψ_J and those of an excited ....

The Basics of the Judd-Ofelt Theory of Intensities

- The transitions between states of a f^n are electric dipole forbidden
- Electric dipole transitions become possible through the odd parity part of the crystal field coupling the states of electron configurations of opposite parity
- Second-order perturbation theory, with closure, is used to produce a description of transition probablities in terms of effective operators
- The matrix elements of the effective operators are evaluated within the f^n configuration

The Basics of the Judd-Ofelt Theory of Intensities

- The effective operators are what one would expect from simple symmetry considerations. They involve angular parts and radial parts. In most applications the angular part is evaluated exactly with the radial parts being treated as empirical parameters
- The angular parts simply reflect the symmetry of the problem while the parameters largely bury the physics of the problem
- The parameters accommodate many contributions that are not explicitly contained in the Judd-Ofelt formulation

The Basics of the Judd-Ofelt Theory of Intensities

- At the time of the Judd-Ofelt theory (1962) reliable atomic wavefunctions were unavailable for heavy elements such as the lanthanides, and more so for the heavier actinides
- This is no longer the situation and it is time for the Judd-Ofelt theory to move from a convenient data summarising formulation to a more quantitative theory that reflects the detailed physics of the transitions
- Relativistic wavefunctions are now possible and their use in crystal field theory and in the extension of the Judd-Ofelt formulation can be seriously explored

J.CHEM.PHYS. V43 15 DECEMBER , 1965

Use of Relativistic Wavefunctions in Crystal Field Theory

B. G. WYBOURNE

(Received 18 August 1965)

The purpose of this paper is to indicate some of the consequences of using relativistic wavefunctions in crystal-field calculations. Substitutional expressions are developed which permit the calculation of relativistic crystal-field matrix elements using LS basis states following the method of Sandars. In these expressions the *angular* parts of the matrix elements are evaluated using LS basis states while the radial part uses the radial integrals computed from relativistic Hartree-Fock-type wavefunctions....

Use of Relativistic Wavefunctions in Crystal Field Theory

- Non-relativistic Hartree-Fock wavefunctions produce radial integrals for the expectation value of r^k for an electron for an orbital $n\ell$ of the form

$$\int_0^\infty R_{n\ell}(r) r^k R_{n\ell} dr \tag{1}$$

- Dirac's equation for an electron $n\ell j$ in a central field leads to *two* radial functions, F and G, associated with the small and large components of the Dirac wavefunction and which depend on j.

Use of Relativistic Wavefunctions in Crystal Field Theory

- The reduced matrix element for a single relativistic electron in a crystal field becomes

$$\begin{aligned}\langle n\ell j' \| r^k C^{(k)} \| n\ell j\rangle =& (-1)^{j'+\frac{1}{2}} \int_0^\infty r^k (FF' + GG')dr \\ & \times \left[(2j'+1)(2j+1)\right]^{\frac{1}{2}} \begin{pmatrix} j' & k & j \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}\end{aligned}$$

Use of Relativistic Wavefunctions in Crystal Field Theory

- In the relativistic treatment the crystal field parameters are no longer independent of j. We have three radial integrals to consider

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

$\pm \rightarrow j = \ell \pm \frac{1}{2}$

In relativistic crystal field theory we write the crystal field operator as essentially

$$V_{CF}^{R} = \sum_{k,q} A_q^k \sum_{\kappa,t} b_k(\kappa t) W_q^{(\kappa t)k}$$

where

$$W_q^{(\kappa t)k} = \sum_i w_{i,q}^{(\kappa t)k}(\ell\ell)$$

and

$$b_k(\kappa t) = (-1)^{\kappa+k+\ell} \sum_{j_\pm, j'_\pm} (-1)^{j'_\pm + \frac{1}{2}} [k]^{-\frac{1}{2}} [\kappa, t]^{\frac{1}{2}} [j_\pm, j'_\pm]$$

$$\times \begin{pmatrix} j'_\pm & k & j_\pm \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{Bmatrix} \ell & \ell & t \\ \frac{1}{2} & \frac{1}{2} & \kappa \\ j'_\pm & j_\pm & k \end{Bmatrix} R_{j_\pm, j'_\pm}.$$

$$
\begin{aligned}
b_2(11) &= 4(21)^{\frac{1}{2}}\left[-5R^2_{++} + 3R^2_{+-} + 2R^2_{--}\right]/245 \\
b_2(13) &= 4(7)^{\frac{1}{2}}\left[5R^2_{++} + 4R^2_{+-} - 9R^2_{--}\right]/245 \\
b_2(02) &= -2(42)^{\frac{1}{2}}\left[25R^2_{++} + 6R^2_{+-} + 18R^2_{--}\right]/735 \\
b_4(13) &= 4(21)^{\frac{1}{2}}\left[6R^4_{++} - 5R^4_{+-} - R^4_{--}\right]/231 \\
b_4(15) &= 2(2310)^{\frac{1}{2}}\left[-3R^4_{++} - 8R^4_{+-} + 11R^4_{--}\right]/4851 \\
b_4(04) &= 2(77)^{\frac{1}{2}}\left[18R^4_{++} + 20R^4_{+-} + 11R^4_{--}\right]/1617 \\
b_6(15) &= 20(77)^{\frac{1}{2}}\left[-R^6_{++} + R^6_{+-}\right]/1001 \\
b_6(06) &= -10(462)^{\frac{1}{2}}\left[R^6_{++} + R^6_{+-}\right]/3003
\end{aligned}
$$

Calculation of Radial Integrals

- 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*.
- Whereas in non-relativistic crystal field theory the operators act only in the orbital space in relativistic crystal field theory they act in the spin-orbital space. i.e. The tensor operators $\mathbf{U}^{(K)}$ become replaced by double-tensor operators $\mathbf{W}^{(\kappa k)K}$.

An example

- Let us assume a crystal field potential

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

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

$$|\tfrac{7}{2} \pm \tfrac{1}{2}\rangle,\ |\tfrac{7}{2} \pm \tfrac{3}{2}\rangle,\ |\tfrac{7}{2} \pm \tfrac{5}{2}\rangle,\ |\tfrac{7}{2} \pm \tfrac{7}{2}\rangle,\ |\tfrac{5}{2} \pm \tfrac{1}{2}\rangle,\ |\tfrac{5}{2} \pm \tfrac{3}{2}\rangle,\ |\tfrac{5}{2} \pm \tfrac{5}{2}\rangle \quad (2)$$

- and

$$\langle s\ell j || C^{(k)} || s\ell j' \rangle = \quad (3)$$

$$\langle \ell || C^{(k)} || \ell \rangle (-1)^{s+\ell+j+k} \sqrt{(2j+1)(2j'+1)} \left\{ \begin{array}{ccc} j & k & j' \\ \ell & s & \ell \end{array} \right\} \quad (4)$$

The example continued

- leading to

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

Example of a crystal field matrix for f^1

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

Relativistic $f \leftrightarrow f$ 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 $\mathbf{W}^{(\kappa k)K}$.
- 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 $\mathbf{u}(n\ell, n\ell)^{(k_{even})}$.

Relativistic $f \leftrightarrow f$ transitions in crystal fields

- 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 κ' is *even* or *odd* as κ is 0 or 1 respectively.

- Note the similarities between the formalism for crystal field theory and the theory of transitions. Both involve similar effective operators acting within the $f-$shell though their origins are quite different. The fundamental difference comes in the radial functions which are very different.

Relativistic $f \leftrightarrow f$ transitions in crystal fields

- In terms of the *angular* parts which reflect the symmetry properties of $f-$orbitals the similarity is understandable
- 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 κ' is *even* or *odd* as κ is 0 or 1 respectively.

Back to the Future

- 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.

References

- 1. L Smentek and B G Wybourne, *Relativistic $f \leftrightarrow f$ transitions in crystal fields*, J.Phys.B: At.Mol.Opt.Phys.**33**, 3647 (2000).
- 2. L Smentek and B G Wybourne, *Relativistic $f \leftrightarrow f$ transitions in crystal fields: II. Beyond the single-configuration approximation*, J.Phys.B: At.Mol.Opt.Phys.**34**, 625 (2001).
- 3. L Smentek, B G Wybourne and J Kobus, *A relativistic crystal field for $S-$state f electron ions*, J.Phys.B: At.Mol.Opt.Phys.**34**, 1513 (2001).

I don't know

- "Had my compatriot Marie Sklodowska-Curie never said to herself "I don't know", she probably would have wound up teaching chemistry at some private high school for young ladies from good families, and ended her days performing this otherwise perfectly respectable job. But she kept on saying "I don't know", and these words led her, not just once but twice, to Stockholm, where restless, questing spirits are occasionally rewarded with the Nobel Prize."

- *Wisława Szymborska* (Nobel Lecture 1996)