



ELSEVIER

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Spin–orbit interactions in free lanthanide (3+) ions



Dimitar N. Petrov.*

Department of Physical Chemistry, Plovdiv University "Paisii Hilendarski", 24, Tsar Asen Str., 4000 Plovdiv, Bulgaria

ARTICLE INFO

Article history:

Received 18 March 2016

Received in revised form

18 April 2016

Accepted 20 April 2016

Available online 21 April 2016

Keywords:

Radial integrals

Spin–orbit interaction

Mean inverse-cube radii

Lanthanides

ABSTRACT

The effective nuclear charges of free Ln^{3+} ions (Ln IV in spectroscopic notation) with Ln=Pr, Nd, Er, Tm, and Yb, have been determined semiempirically from the dependence between calculated or empirical expectation values $\langle r^{-3} \rangle_{4f}$ and spin–orbit radial integrals ζ_{4f} known from experimental free-ion spectra. The variation with $\langle r^{-3} \rangle_{4f}$ of the matrix elements of spin–orbit interactions for the ground levels of the same free ions has been also discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The spin–orbit interactions (SOIs) in lanthanides lead, in the absence of external field, to coupling of L and S angular momenta into J . For most of the Ln^{3+} ions, except for Sm^{3+} and Eu^{3+} , $J=L \mp S$ is a good quantum number and designates a strong LS coupling. For the ground levels, $|L-S|$ pertains to the first half, while $L+S$ is applicable for the second half of the lanthanide series; the signs of the SOIs are positive for the former and negative for the latter [1]. This coupling removes partially the degeneracy of the terms $2S+1L$ producing multiplets of levels $2S+1LJ$. SOIs are considerable in values and dominate over the other intra-atomic magnetic interactions of the 4f electrons in Ln^{3+} ions but remain much lower than the electrostatic interactions. On the other side, the multiplet splittings arising from SOIs in lanthanides are larger than the crystal field splittings [2]. The spin–orbit radial integral ζ_{4f} is a constant for the $2S+1LJ$ levels of a $4f^N$ configuration and depends on the radial 4f wave function and the central field potential [2–7]. The simultaneous effect of Coulombic and strong SOIs results in intermediate coupling, i.e. in different admixtures of the wave functions corresponding to the levels $2S+1LJ$. Thus, the electrostatic and strong spin–orbit interactions provide an initial approximation to the experimental energy levels as well as adequate wave functions [2,3].

The spin–orbit radial integral ζ_{4f} has been often applied in conjunction with the expectation value $\langle r^{-3} \rangle_{4f}$; the calculation of the latter presents a continuous task [1] including, for example, *ab initio* model potentials for the 4f states of Ln^{3+} ions [8]. The

application of the mean inverse-cube radii for the 4f electrons has been exemplified with the combined energy matrices of Pr^{3+} [9]. The same mean values have been also related to the magnetic hyperfine structure constant a_J and used in the determination of nuclear magnetic moments either in empirical relationships [2,10] or in operator equivalent form [9]. The electrons of an open $4f^N$ configuration exert at the lanthanide nucleus hyperfine magnetic field estimated between 100 T and 800 T, higher than an external magnetic field [1]. The known values of $\langle r^{-3} \rangle_{4f}$ differ appreciably since they originate from different wave functions: relativistic [11,12], self-consistent field [13–15], and Hartree–Fock [16,17]. However, only one of these studies includes the entire lanthanide series [11].

The experimental values of ζ_{4f} have been obtained from optical spectra of Ln^{3+} ions in condensed phase. It has been generally assumed that the values of ζ_{4f} have been affected to some extent by the other ions surrounding given Ln^{3+} ion. A survey on the optical properties of lanthanides in condensed phase has included the effective nuclear charge participating in the SOIs [3].

A number of recent studies, either *ab initio* or fitting procedures, have also used the concept of SOIs for different purposes. Thus, an empirical relationship has been found relating ζ_{4f} of Ln^{3+} to the effective nuclear charge $Z^* = Z - 31.9$, where 31.9 is the 4f screening constant, in a discussion concerning crystal field parameters of Ln^{3+} in crystals of $\text{Cs}_2\text{NaLnCl}_6$ [18]. The spin–orbit coupling constant for Pr^{3+} ion has been expressed depending on ligand polarizability of various ligands in a study of the nephelauxetic effect in the electronic spectra of Pr^{3+} [19]. A semi-empirical atomic Hamiltonian with different number of varied parameters (8, 10, or 12) has been fitted for four ions with $4f^2$ electron configuration, including Pr^{3+} [20]; for ζ_{4f} of the same ion the authors have obtained values that are about 3% higher than

* Corresponding author.

E-mail address: petrov_d_n@abv.bg

that one reported by Sugar [27]. *Ab initio* determinations of atomic parameters for crystals of $\text{LaCl}_3:\text{Ln}^{3+}$ have confirmed the hypothesis for smooth trends across the Ln^{3+} series [21]; it has been also shown that the obtained values of ζ_{4f} for the free ions Pr^{3+} and Nd^{3+} depend on the number of fitted parameters. Hartree–Fock values of the spin–orbit coupling constants for Ln^{3+} ions have been obtained with small deviations in respect to the experimental ones for the free ions Ln IV, namely: Pr^{3+} (+9.0%), Nd^{3+} (+5.4%), Er^{3+} (+19.1%), Tm^{3+} (+0.1%), Yb^{3+} (–0.4%) [22]. Basic relationships in some major references have been re-examined in respect to the reduced matrix elements of the double-tensor operators z_r ($r=1, 2, 3, 4$) of rank 2 in both the orbital and spin spaces; tables have been provided for f^4 to f^7 configurations [23]. Quite recently, the role of the SOIs has been exemplified in theoretical constructions of the energy level diagrams for $(2+)$, $(3+)$, and $(4+)$ – charged lanthanides with $4f^N$ ($N=1\dots 13$) configurations [24].

The relationship between experimental radial integrals ζ_{4f} for the free ions Ln IV and the mean inverse-cube radii $\langle r^{-3} \rangle_{4f}$, however, has not been studied yet. The aim of the present work is to investigate the mentioned dependence for Ln IV ions and to exemplify certain matrix elements for $2s+1L_J$ levels occurring in the free lanthanide ions.

2. Method

The spin–orbit radial integral ζ_{4f} is defined [2–7,9] as:

$$\zeta_{4f} = \hbar^2 \int_0^\infty r^2 R_{4f}^2(r) \xi(r) dr, \quad (1)$$

where

$$\xi(r) = \frac{\hbar^2}{2m^2 c^2 r} \frac{dU(r)}{dr}, \quad U(r) = -e^2 \frac{Z^{\text{eff}}}{r}, \quad (2)$$

r is a radial coordinate of the electron, $U(r)$ is a central field potential with an effective nuclear charge Z^{eff} exerted on the 4f electrons in the SOIs, the other quantities have their usual meanings. The spin–orbit radial integral has been related to an empirical mean value $\langle r^{-3} \rangle_{4f}$ [3–7,9]:

$$\zeta_{4f} = \frac{\hbar^2 e^2}{2m^2 c^2} Z^{\text{eff}} \langle r^{-3} \rangle_{4f}. \quad (3)$$

It has been noted that the effective charges Z^{eff} relevant to the SOIs are different from those participating in the electrostatic interactions [6].

The matrix elements of the SOIs are independent of the quantum numbers M [23] and have been defined as products of 6j-symbols and doubly reduced matrix elements (DRME) $V^{(k)}$ of the $4f^N$ configuration by the expressions [2,25,26]:

$$\begin{aligned} A &= f^N \alpha L S J M | L. S | f^N \alpha' L' S' J' M' \\ &= \zeta_{4f} (-1)^{J+L+S'} [l(l+1)(2l+1)]^{1/2} \\ &\quad \times \left\{ \begin{matrix} L & L' & 1 \\ S' & S & J \end{matrix} \right\} \times \langle f^N \alpha L S || V^{11} || f^N \alpha' L' S' \rangle, \end{aligned} \quad (4)$$

$$\langle f^1 1s || V^{11} || f^1 1s \rangle = (3/2)^{1/2} \quad (5)$$

where α and α' are unspecified quantum numbers, $l=3$ for 4f electrons.

The almost closed electronic configurations $4f^{14-N}$, i.e. $4f^{11}$ (Er IV), $4f^{12}$ (Tm IV), and $4f^{13}$ (Yb IV), are complementary of the less-than-half filled open shells $4f^N$: $4f^3$ (Nd IV), $4f^2$ (Pr IV), and $4f^1$ (Ce IV), respectively. Their matrix elements are interrelated by the following expression [26]:

$$\langle f^{14-N} \nu L S || V^{11} || f^{14-N} \nu' L' S' \rangle = -(-1)^{[(\nu-\nu')/2]+2} \langle f^N \nu L S || V^{11} || f^N \nu' L' S' \rangle, \quad (6)$$

where ν and ν' designate seniority numbers. The signs of the matrix elements A depend also on those of the DRME $V^{(k)}$, i.e. for $V^{(11)}$ with $k+1=\text{even}$, as follows [26]:

$$\begin{aligned} \langle f^{14-N} \alpha L S || V^{11} || f^N \alpha' L' S' \rangle \\ = [(2l+1-N)/(2l+1-\nu)] \langle f^N \alpha L S || V^{11} || f^N \alpha' L' S' \rangle \end{aligned} \quad (7)$$

S is the total spin quantum number of the energy level $2s+1L_J$ and $\langle \psi || V^{(11)} || \psi' \rangle$ are DRME of the tensor operator $V^{(k)}$ between the wave functions ψ and ψ' . The above expressions apply only to wave functions with the same spin, $S=S'$, $\delta(S, S')=1$, so that the delta function is implicitly included in Eqs. (4), (6), (7). The DRME $V^{(11)}$ are available for all pairs of multiplets of f^2 , f^3 , and f^4 [26]. The 6j-symbols in the present study have been determined according to the procedure described by Jucys and Bandzaitis [27].

The system of atomic units has been applied in this study, namely: $m=e=\hbar=1$, $c=137.036$, $a_0=(\hbar^2/me^2)=0.52917721 \times 10^{-10}$ m, 1 a.u. of energy is equal to $2R_\infty=2 \times 109\,737.31$ cm $^{-1}$, where R_∞ is the Rydberg constant [28]. The values of the spin–orbit radial integrals ζ_{4f} used here have been experimental ones for the free ions Ln IV [29–33].

3. Results and discussion

Constants of SOIs of Ln IV and expectation values $\langle r^{-3} \rangle_{4f}$ from computations, relativistic (R) [11] and Hartree–Fock (HF) [16], or empirical (emp.) [10], are listed in Table 1. The relativistic mean values have been included in this work for two reasons: (i) they are the only set covering the entire lanthanide series as far as Pr^{3+} has not been included in [12], (ii) the spin–orbit radial integrals ζ_{4f} available in the literature from experimental free-ion spectra of Ln IV have been obtained with relativistic corrections. Obviously, the empirical values of $\langle r^{-3} \rangle_{4f}$ do not pertain to free ions Ln IV since

Table 1

Spin–orbit radial integrals ζ_{4f} , expectation values $\langle r^{-3} \rangle_{4f}$, and effective nuclear charges Z^{eff} for certain free Ln^{3+} ions with atomic number Z .

| Ln IV | Z | ζ_{4f} /cm $^{-1}$ [Ref.] | $\langle r^{-3} \rangle_{4f}$ calc.(R)/ a_0^{-3} [11] | $\langle r^{-3} \rangle_{4f}$ calc.(HF)/ a_0^{-3} [17] | $\langle r^{-3} \rangle_{4f}$ emp./ a_0^{-3} [9] | Z^{eff} calc.(R) | Z^{eff} calc.(HF) | Z^{eff} (emp.) |
|-------|----|---------------------------------|---|--|--|---------------------------|----------------------------|-------------------------|
| Pr IV | 59 | 741 [29] | 4.893 | 5.38 | 5.06 | 46 | 44 | 48 |
| Nd IV | 60 | 988 [30] | 5.479 | 6.03 | 5.64 | 51 | 48 | 53 |
| Er IV | 68 | 2012 [31] | 11.141 | 12.02 | 10.60 | 40 | 36 | 42 |
| Tm IV | 69 | 2640 [32] | 11.990 | 12.88 | 11.72 | 46 | 44 | 49 |
| Yb IV | 70 | 2918 [33] | 12.875 | 13.84 | 12.63 | 47 | 44 | 50 |

Download English Version:

<https://daneshyari.com/en/article/1808366>

Download Persian Version:

<https://daneshyari.com/article/1808366>

[Daneshyari.com](https://daneshyari.com)