

Basics of Lanthanide Photophysics

Jean-Claude G. Bünzli and Svetlana V. Eliseeva

Abstract The fascination for lanthanide optical spectroscopy dates back to the 1880s when renowned scientists such as Sir William Crookes, LeCoq de Boisbaudran, Eugène Demarçay or, later, Georges Urbain were using luminescence as an analytical tool to test the purity of their crystallizations and to identify potential new elements. The richness and complexity of lanthanide optical spectra are reflected in an article published in 1937 by J.H. van Vleck: *The Puzzle of Rare Earth Spectra in Solids*. After this analytical and exploratory period, lanthanide unique optical properties were taken advantage of in optical glasses, filters, and lasers. In the mid-1970s, E. Soini and I. Hemmilä proposed lanthanide luminescent probes for time-resolved immunoassays (Soini and Hemmilä in Clin Chem 25:353–361, 1979) and this has been the starting point of the present numerous bio-applications based on optical properties of lanthanides. In this chapter, we first briefly outline the principles underlying the simplest models used for describing the electronic structure and spectroscopic properties of trivalent lanthanide ions Ln^{III} ($4f^n$) with special emphasis on luminescence. Since the book is intended for a broad readership within the sciences, we start from scratch defining all quantities used, but we stay at a descriptive level, leaving out detailed mathematical developments. For the latter, the reader is referred to references Liu and Jacquier, Spectroscopic properties of rare earths in optical materials. Tsinghua University Press & Springer, Beijing & Heidelberg, 2005 and Görrler-Walrand and Binnemans, Rationalization of crystal field parameters. In: Gschneidner, Eyring (eds) Handbook on the physics and chemistry of rare earths, vol 23. Elsevier BV, Amsterdam, Ch 155, 1996. The second part of the chapter is devoted to practical aspects of lanthanide luminescent probes, both from the point of view of their design and of their potential utility.

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Keywords Crystal-field analysis · Energy transfer · f–f Transition · Intrinsic quantum yield · Lanthanide bioprobe · Lanthanide luminescence · Lanthanide spectroscopy · Lifetime · Luminescence sensitization · Population analysis · Quantum yield · Radiative lifetime · Selection rule · Site symmetry · Stern–Volmer quenching

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Abbreviations

AO	Acridine orange
CF	Crystal field
CT	Charge transfer
DMF	Dimethylformamide
DNA	Deoxyribonucleic acid
dpa	Dipicolinate (2,6-pyridine dicarboxylate)
dtpa	Diethylenetrinitrilopentaacetate
EB	Ethidium bromide
ED	Electric dipole

EQ	Electric quadrupole
FRET	Förster resonant energy transfer
hfa	Hexafluoroacetylacetonate
ILCT	Intraligand charge transfer
ISC	Intersystem crossing
JO	Judd–Ofelt
LLB	Lanthanide luminescent bioprobe
LMCT	Ligand-to-metal charge transfer
MD	Magnetic dipole
MLCT	Metal-to-ligand charge transfer
NIR	Near-infrared
PCR	Polymerase chain reaction
SO	Spin–orbit
tta	Thenoyltrifluoroacetylacetonate
YAG	Yttrium aluminum garnet

1 Electronic Structure of Trivalent Lanthanide Ions

1.1 Atomic Orbitals

In quantum mechanics, three variables depict the movement of the electrons around the positively-charged nucleus, these electrons being considered as waves with wavelength $\lambda = h/mv$ where h is Planck's constant ($6.626 \times 10^{-34} \text{ J s}^{-1}$), m and v the mass ($9.109 \times 10^{-31} \text{ kg}$) and velocity of the electron, respectively:

- The time-dependent Hamiltonian operator \mathcal{H} describing the sum of kinetic and potential energies in the system; it is a function of the coordinates of the electrons and nucleus.
- The wavefunction, Ψ_n , also depending on the coordinates and time, related to the movement of the particles, and not directly observable; its square $(\Psi_n)^2$ though gives the probability that the particle it describes will be found at the position given by the coordinates; the set of all probabilities for a given electronic Ψ_n , is called an *orbital*.
- The quantified energy E_n associated with a specific wavefunction, and independent of the coordinates.

These quantities are related by the dramatically simple Schrödinger equation, which replaces the fundamental equations of classical mechanics for atomic systems:

$$\mathcal{H}\Psi_n = E_n\Psi_n. \quad (1)$$

Energies E_n are eigenvalues of Ψ_n , themselves called eigenfunctions. In view of the complexity brought by the multidimensional aspect of this equation

(3 coordinates for each electron and nucleus, in addition to time) several simplifications are made. Firstly, the energy is assumed to be constant with time, which removes one coordinate. Secondly, nuclei being much heavier than electrons, they are considered as being fixed (Born–Oppenheimer approximation). Thirdly, since the equation can only be solved precisely for the hydrogen atom, the resulting hydrogenoid or one-electron wavefunction is used for the other elements, with a scaling taking into account the apparent nucleus charge, i.e., including screening effects from the other electrons. Finally, to ease solving the equation for non-H atoms, the various interactions occurring in the electron-nucleus system are treated separately, in order of decreasing importance (*perturbation method*).

For hydrogen, the Hamiltonian simply reflects Coulomb’s attraction between the nucleus and the electron, separated by a distance r_i , and the kinetic energy of the latter:¹

$$\mathcal{H}_0 = -\frac{1}{r_i} - \frac{1}{2}\Delta_i \quad \left(\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right). \quad (2)$$

Each wavefunction (or orbital: the two terms are very often, but wrongly, taken as synonyms) resulting from solving (1) is defined by four quantum numbers reflecting the quantified energy of the two motions of the electrons: the orbital motion, defined by the angular momentum $\vec{\ell}$, and the spin, characterized by the angular momentum \vec{s} . If polar coordinates (r, ϑ, φ) are used, wavefunctions are expressed as the product of a normalizing factor N , of a radial function $\mathcal{R}_{n,\ell}$, of an angular function Φ_{ℓ,m_ℓ} , and of a spin function S_{m_s} :

$$\Psi_{n,\ell,m_\ell,m_s} = N \cdot \mathcal{R}_{n,\ell}(r) \cdot \Phi_{\ell,m_\ell}(\vartheta, \varphi) \cdot S_{m_s}. \quad (3)$$

The principal quantum number n is an integer (1, 2, 3, ...) and represents the radial expansion of the orbital. The angular quantum number ℓ varies from 0 to $(n - 1)$ and characterizes the shape of the orbital (designed by letters: s, p, d, f, g, \dots for $\ell = 0, 1, 2, 3, 4, \dots$). The magnetic quantum number m_ℓ is the projection of the vector $\vec{\ell}$ onto the z axis and is linked to the orientation of the orbital in space; it varies between $-\ell$ and $+\ell$. Finally, m_s is the projection of the vector \vec{s} and takes values of $\pm \frac{1}{2}$. Pauli’s principle requires that two electrons of the same atom must at least differ by the value of one quantum number; this implies that only two electrons of opposite spin can be associated with a given orbital. An electronic shell consists in all electrons having the same quantum number n . A sub-shell regroups electrons with same n and ℓ numbers, has therefore $(2\ell + 1)$ orbitals, and may contain a maximum of $(4\ell + 2)$ electrons. The shapes of the seven 4f orbitals ($n = 4, \ell = 3$) are represented on top of Fig. 1.

¹We use the atomic system units (a.u.) in order to simplify the equations as much as possible.

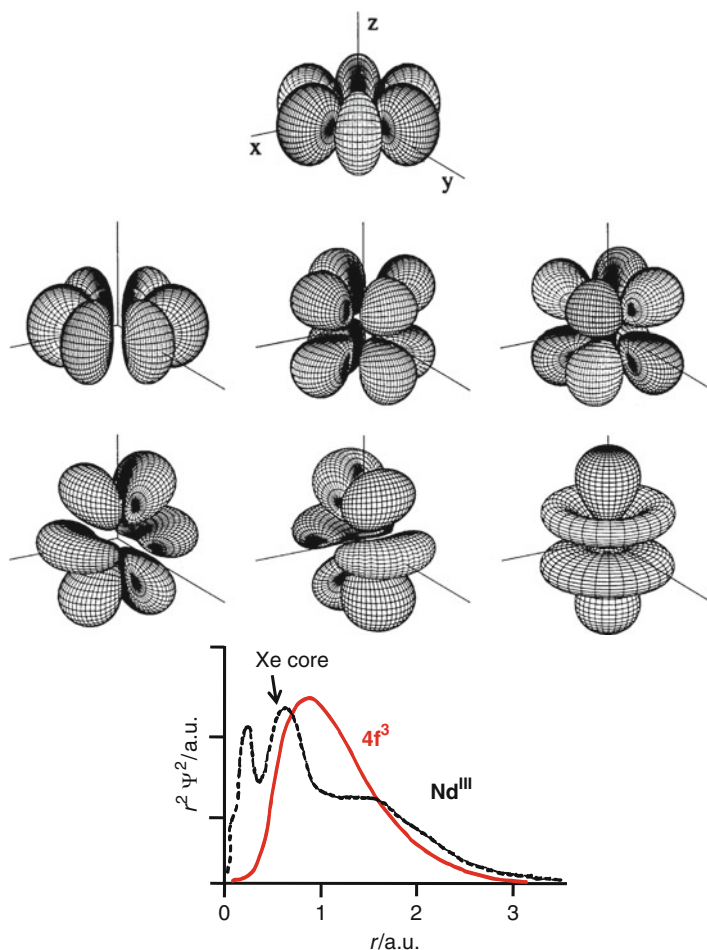


Fig. 1 *Top:* Shape of the one-electron (hydrogenoid) 4f orbitals in a Cartesian space. From *top* to *bottom* and *left to right*: $4f_{x(x^2 - 3y^2)}$, $4f_{y(3y^2 - x^2)}$, $4f_{xyz}$, $4f_{z(x^2 - y^2)}$, $4f_{xz^2}$, $4f_{yz^2}$, and $4f_{z^2}$ (combinations of Cartesian coordinates represent the angular functions). *Bottom:* Radial wavefunction of the three 4f electrons of Nd^{III} compared with the radial wavefunction of the xenon core (a.u. = atomic units); redrawn after [1]

1.2 Electronic Configuration

The ground state electronic configuration of Ln^{III} ions is $[\text{Xe}]4f^n$ ($n = 0-14$). It is energetically well separated from the $[\text{Xe}]4f^{n-1}5d^1$ configuration ($\Delta E > 32,000 \text{ cm}^{-1}$). A far reaching fact is the shielding of the 4f orbitals by the xenon core (54 electrons), particularly the larger radial expansion of the $5s^2 5p^6$ subshells, making the valence 4f orbitals “inner orbitals” (bottom of Fig. 1). This is the key to the chemical and spectroscopic properties of these metal ions.

Lanthanide Luminescence

Photophysical, Analytical and Biological Aspects

Hänninen, P.; Härmä, H. (Eds.)

2011, XII, 388 p., Hardcover

ISBN: 978-3-642-21022-8