

Article

Recovering $4f$ Electronic Shell Signatures from Collective Spectral Manifolds of Lanthanide Ions: A New Perspective for Rare-Earth Photonics

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Abstract

The electronic spectra of trivalent lanthanide ions constitute one of the most extensively characterised manifestations of partially filled $4f$ shells. Conventional rare-earth spectroscopy provides a detailed microscopic description based on assigned multiplets, angular-momentum structure, crystal-field effects and transition probabilities. Here, we examine a complementary question: whether information associated with the underlying $4f$ electronic architecture remains detectable after the spectroscopic labels normally used to identify it are deliberately removed. Using the multiplet-centre energies of Ln^{3+} ions in LaF_3 , each ion was represented as an energy-only spectral manifold, $M_n = \{E_i\}$, obtained after removing term identity, angular-momentum labels and transition assignments. The resulting manifolds were analysed through a controlled information-reduction sequence involving spectral occupancy and four complementary descriptors: spectral entropy S , compactness C , mean manifold energy μ_E and spectral dispersion σ_E . The results show that the reduced manifolds do not collapse into featureless collections of energies. Instead, they retain structured organisation across the lanthanide series, with distinctive behaviour associated with the shell-edge configurations Ce^{3+} ($4f^1$) and Yb^{3+} ($4f^{13}$), and with the half-filled-shell configuration Gd^{3+} ($4f^7$). A blind reconstruction test provides the strongest internal validation: when Gd^{3+} is excluded from the reference evolution and subsequently reintroduced, it emerges as the dominant positive deviation of the mean manifold-energy coordinate. This demonstrates that the $4f^7$ signature is not encoded only in explicit term labels or selected multiplets but leaves a measurable fingerprint in the collective energy distribution. The comparison of normalised descriptor responses further indicates that electronic shell information is distributed across state occupation, compactness, energetic displacement and spectral spreading. These results suggest that lanthanide spectra can be analysed not only as collections of assigned transitions, but also as collective spectral manifolds whose global organisation preserves physically meaningful information about shell filling. This approach does not replace conventional rare-earth spectroscopy; rather, it provides a complementary framework for testing which aspects of electronic structure remain accessible after microscopic spectroscopic identity has been removed.



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1. Introduction

Trivalent lanthanide ions represent a unique class of optical systems in which atomic-like electronic structure is preserved within condensed matter environments. The partially filled 4f shell gives rise to a rich hierarchy of electronic states whose properties are governed primarily by electron–electron interactions and spin–orbit coupling, with additional perturbations introduced by the surrounding crystal field [1–4].

Within the conventional description of rare-earth electronic structure, the energy-level hierarchy is obtained from an effective Hamiltonian containing both free-ion interactions and the perturbation introduced by the host lattice:

$$H = H_{FI} + H_{CF} \quad (1)$$

where the free-ion contribution may be written as

$$H_{FI} = H_0 + H_{ee} + H_{SO} + H_{corr} \quad (2)$$

Here, H_{ee} represents the Coulomb electron–electron interaction responsible for the formation of the Russell–Saunders terms, H_{SO} describes the spin–orbit interaction responsible for the splitting into J -resolved multiplets, and H_{corr} includes higher-order corrections required for quantitative agreement with experimental spectra. The crystal-field contribution H_{CF} further removes degeneracies according to the symmetry and strength of the local environment [1–4].

The electronic hierarchy generated by these interactions can therefore be represented as

$$4f^n \rightarrow 2S+1L \rightarrow 2S+1L_J \rightarrow \text{crystal field levels} \quad (3)$$

This hierarchy links the fundamental electronic configuration to the experimentally observed spectral structure and forms the basis of conventional lanthanide spectroscopy [1–4].

Owing to the shielding of the 4f electrons by the filled 5s and 5p orbitals, intraconfigurational 4f–4f transitions retain narrow spectral features and well-defined electronic character across a wide range of host materials [3,4].

This combination of complexity and stability has made lanthanide spectroscopy a cornerstone of optical materials research, supporting applications in upconversion and energy-transfer photonics [5–7], luminescent complexes and optical sensing [8], optical thermometry [9–11], optical-fibre and telecommunication systems [12], and photonic materials more broadly [13,14]. Decades of experimental and theoretical work have produced highly detailed descriptions of rare-earth energy-level structures, including multiplet assignments, systematic energy-level schemes, Stark splitting patterns and crystal-field parameters [1–4], radiative transition intensities and probabilities [14–17], and non-radiative relaxation and energy-transfer mechanisms [5–7,12,18]. More recently, computational approaches have been developed to standardise parameter extraction and increase the reproducibility of quantitative rare-earth spectroscopic analyses [14].

The traditional interpretation of lanthanide spectra is therefore fundamentally microscopic. Individual multiplets are assigned, their energetic positions are analysed, and

specific transitions are selected to understand optical behaviour. This approach has been extraordinarily successful and remains essential for quantitative spectroscopy.

In this conventional direction, the electronic Hamiltonian determines the sequence of states that ultimately gives rise to the observed spectra: $H \rightarrow {}^{2S+1}L_J \rightarrow E_i \rightarrow$ optical transitions.

However, the existence of such a detailed microscopic description raises a complementary inverse question:

If the spectroscopic labels generated by the electronic Hamiltonian are removed, does the remaining distribution of energy levels still retain information about the interactions and shell structure that produced it?

Although each lanthanide spectrum originates from a well-defined electronic Hamiltonian, the complete set of generated multiplet states is rarely considered as a physical object in itself. In most spectroscopic analyses, the manifold serves primarily as a repository from which selected transitions, emitting levels or energy-transfer pathways are extracted.

As a consequence, potential organisational principles existing at the scale of the complete spectral distribution remain comparatively unexplored.

This situation contrasts with many areas of physics and information theory where complex collections of microscopic states are successfully described through collective quantities. In such systems, reducing microscopic detail does not necessarily eliminate physical information. Instead, appropriate coarse-grained representations can reveal global properties associated with the organisation of the complete system [19–21]. In this sense, the relevant information may become distributed across collective descriptors rather than remain localised within individual microscopic labels.

Recent multiparametric analyses in lanthanide luminescence thermometry provide a related methodological example, showing that complementary information can be distributed across several correlated spectroscopic parameters rather than contained in a single selected quantity [22]. Although the physical problem addressed in those analyses differs from that considered here, they illustrate the broader value of collective descriptions for extracting structured information from complex lanthanide spectroscopic datasets.

The lanthanide series provides a particularly suitable platform to explore this concept. Across the sequence of $4f^n$ configurations, the occupation of the same electronic shell evolves progressively, while the same classes of free-ion and crystal-field interactions remain operative, although their relative contributions and the resulting energy-level distributions evolve across the series [1,2,13,23].

The series therefore represents a natural laboratory in which to investigate whether global spectral organisation follows the evolution of electronic shell filling.

The present work reverses the conventional direction of spectroscopic analysis. The extensive spectroscopic datasets established for Ln^{3+} ions in LaF_3 provide one of the most systematic experimentally validated descriptions of the trivalent lanthanide series [1,2]. Building upon these datasets, subsequent studies have considerably expanded the spectroscopic description of rare-earth ions through extended energy-level diagrams, analyses of alternative host lattices, and systematic investigations of high-lying $4f$ and $5d$ electronic states, thereby broadening the understanding of lanthanide spectroscopy across a wide range of photonic materials [23–27]. These studies share a common objective: extending, refining and interpreting the electronic-level scheme through increasingly complete spectroscopic assignments.

The present work addresses a complementary question. Instead of extending the energy-level diagram itself, it investigates whether the experimentally established $4f$ multiplet manifolds already retain recoverable information on electronic shell organisation after systematic removal of the spectroscopic identifiers normally used to interpret individual electronic states. In this sense, the manifold is treated not as a catalogue of assigned levels,

but as a collective physical object whose global organisation can be analysed independently of the identities of its constituent multiplets.

The present work therefore reverses the conventional direction of spectroscopic analysis. Rather than using electronic structure to explain the spectral manifold, it examines whether the manifold itself preserves recoverable signatures of the underlying electronic structure after systematic information reduction.

Operationally, we start from the experimentally established multiplet-energy structure and progressively remove spectroscopic information:

$$\{E_i, |^{2S+1}L_J, |J\rangle\} \rightarrow \{E_i\} \rightarrow \text{collective descriptors} \quad (4)$$

This transformation intentionally eliminates the quantum identifiers normally used to recognise electronic structure. The objective is therefore not to rediscover known properties such as Hund's rules or the stability of the half-filled $4f^7$ configuration, but to determine whether their consequences remain encoded in the global organisation of the energy manifold.

In this work, each lanthanide ion is represented as a spectral manifold:

$$M_n = \{E_1, E_2, \dots, E_N\} \quad (5)$$

where E_i represents the energy of an identified multiplet state associated with a given $4f^n$ configuration.

Importantly, only the energetic coordinates of the manifold are retained during the analysis. Term symbols, angular-momentum quantum numbers, degeneracies, transition probabilities and selection rules are deliberately removed.

The resulting energy-only manifold is then analysed using a hierarchy of global descriptors. First, occupancy functions describe how the spectral-energy space is populated. The manifold is subsequently compressed into four complementary quantities: spectral entropy S , compactness C , mean manifold energy μ_E , and spectral dispersion σ_E [19–21].

These descriptors provide different levels of information compression. The number of states and spectral width quantify the size of the accessible manifold, entropy and compactness describe how states occupy the available energy space, whereas the mean spectral energy represents the collective energetic displacement of the entire distribution. Spectral dispersion provides the complementary measure of the energetic spreading of the manifold around its mean position.

The central question is therefore whether any signature of the original $4f$ electronic architecture survives after this controlled reduction in information. Particular emphasis is placed on the half-filled-shell configuration Gd^{3+} ($4f^7$), since its recovery after removal of all explicit quantum labels provides a stringent internal test of information preservation.

The results show that the lanthanide spectral manifold is not reduced to a featureless collection of energies after coarse-graining. Instead, different collective descriptors preserve complementary aspects of the original electronic structure.

The present work therefore develops a complementary perspective on lanthanide spectroscopy: the spectrum is analysed not only as a set of individual transitions, but also as a collective energy landscape in which selected signatures of the underlying $4f$ shell architecture remain distributed across the complete energy-level manifold, even after the spectroscopic labels traditionally used to identify them have been removed.

2. Methodological Framework

The analysis uses only experimentally established multiplet-centre manifolds as numerical input. No synthetic spectra, theoretical reconstruction of missing levels or

machine-learning prediction is introduced. This choice allows the descriptors to be interpreted as direct properties of the retained energy distribution rather than as outputs of an additional model.

2.1. Spectroscopic Dataset and Manifold Construction

The analysis was performed using the energy-level scheme of trivalent lanthanide ions in LaF_3 reported by Carnall and co-workers [1,2]. For each Ln^{3+} ion, the reported multiplet energy centres were extracted and treated as a complete spectral manifold according to Equation (5), rather than as a collection of independently assigned electronic states. This whole-manifold representation is consistent with the systematic organisation of $4f^n$ energy-level diagrams across the trivalent lanthanide series [23].

The analysed dataset included Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} and Yb^{3+} , spanning the $4f^1$ – $4f^{13}$ filling sequence. Only ions for which complete and consistently assigned multiplet-centre manifolds were available within the adopted reference dataset were included, ensuring that all the descriptors were calculated from comparable spectroscopic information. No interpolation or reconstruction of missing $4f^n$ configurations was introduced. The absence of Eu^{3+} and Pm^{3+} therefore reflects the availability and consistency criteria of the adopted reference dataset and was not introduced as a selection criterion based on electronic configuration.

The framework is best regarded as a diagnostic manifold-level methodology. It identifies collective deviations and shell-filling signatures from complete and internally consistent multiplet-centre manifolds, as demonstrated by the blind recovery of the Gd^{3+} half-filled-shell configuration. Its present objective is therefore the interpretation of experimentally established manifolds rather than the prediction of unknown individual energy levels. For this reason, Eu^{3+} and Pm^{3+} were not reconstructed in the present analysis, since their inclusion would require either equally complete experimental manifolds or an additional model-based reconstruction step that would modify the label-free character of the comparison.

In Equation (5), E_i represents the energy of the i -th experimentally identified multiplet centre associated with a given $4f^n$ configuration, and N is the total number of multiplet centres included for that ion.

The original spectroscopic description contains information about electronic terms, angular-momentum coupling and state assignments generated by the effective Hamiltonian. In the present approach, this information is deliberately removed:

$$\left\{ E_i, {}^{2S+1}L_J, J \right\} \rightarrow M_n = \{E_i\} \quad (6)$$

The resulting object is therefore an energy-only representation of the lanthanide manifold. The objective is not to reproduce the microscopic electronic structure, but to determine which consequences of this structure remain detectable after the loss of explicit quantum labels.

The same dataset was examined at successive levels of compression: first as an unlabelled energy-level landscape, then through energy-occupancy distributions, and finally through scalar descriptors of the complete manifold.

This information-reduction sequence can be summarised as

$$M_n = \{E_i\} \rightarrow O(E, n) \rightarrow (S, C, \mu_E, \sigma_E) \quad (7)$$

where the energy-only manifold is progressively transformed into an occupancy representation and subsequently into complementary descriptors describing state distribution, compactness, energetic displacement and spectral spreading.

This sequence provides a direct test of whether information generated by the original $4f$ electronic interactions remains encoded in the collective spectral-energy distribution after removal of explicit spectroscopic labels.

2.2. Spectral Occupancy Analysis

As a first description of the global manifold organisation, the spectral occupancy function was calculated. This step represents the first reduction in the energy-only manifold, converting the discrete set of multiplet energies into a coarse-grained representation of how the spectral-energy space is populated.

The energy axis was divided into intervals of fixed width ΔE , and the number of multiplet states occupying each interval was determined. A bin width of $\Delta E = 1000 \text{ cm}^{-1}$ was used throughout the analysis as a controlled coarse-graining scale. The selected bin width reduces sensitivity to the local Stark substructure of individual multiplets, while remaining much smaller than the total spectral extension of the lanthanide manifolds [1–4,23]. The same binning parameter was maintained for all the ions to avoid introducing configuration-dependent weighting. The occupancy representation therefore probes collective energy-space organisation rather than individual level separations.

The descriptor analysis was restricted to the consistently assigned $4f^n$ multiplet-centre manifolds available across the investigated series. Extended Dieke-type compilations include additional high-energy levels for the selected ions, providing valuable information for spectroscopic assignment and high-lying electronic configurations. However, these levels are not available with the same completeness and assignment consistency for all the ions considered here. Restricting the analysis to a common $4f^n$ manifold therefore preserves descriptor comparability across the lanthanide series while maintaining a uniform physical definition of the analysed object.

For an energy interval centred at E_k , the occupancy was defined as

$$(E_k) = \sum_i I(E_i \in \Delta E_k) \quad (8)$$

where I is an indicator function equal to unity when a multiplet energy lies within the selected interval and zero otherwise.

In addition to the global occupancy function $O(E)$, a shell-resolved occupancy matrix was constructed using the same energy coarse-graining scale:

$$O(E_k, n) = \sum_i I(E_i(n) \in \Delta E_k) \quad (9)$$

where n represents the $4f$ occupation number.

This representation retains the shell-filling coordinate while eliminating the identity of individual electronic states. It therefore provides an intermediate level between the complete spectroscopic description and the fully compressed scalar descriptors.

Unlike conventional optical spectra, where intensities depend on transition probabilities and selection rules [15,16], as well as on excitation, population, non-radiative relaxation and energy-transfer mechanisms [5–7,18], the occupancy representation considers only the distribution of accessible electronic states in energy space.

2.3. Global Spectral-Manifold Descriptors

Following the occupancy analysis, the energy-only manifolds were further compressed into scalar descriptors according to the final step of the information-reduction sequence defined in Equation (7).

To quantify the collective properties of each lanthanide manifold, four complementary descriptors were considered: mean manifold energy μ_E , spectral dispersion σ_E , compactness C , and spectral entropy S .

The mean manifold energy was defined as

$$\mu_E = \frac{1}{N} \sum_{i=1}^N E_i \quad (10)$$

and represents the collective energetic position of the complete manifold.

The spectral dispersion was calculated as

$$\sigma_E = \sqrt{\frac{1}{N} \sum_{i=1}^N (E_i - \mu_E)^2} \quad (11)$$

providing a measure of the energetic spreading of the multiplet distribution around the mean manifold energy.

The spectral extension of each manifold was defined as

$$W = E_{\max} - E_{\min} \quad (12)$$

where $E_{\max}$ and $E_{\min}$ are respectively the highest and lowest multiplet energies considered.

This quantity was used to define the manifold compactness parameter introduced in the present analysis:

$$C = \frac{N}{W} \quad (13)$$

which describes the density of multiplet centres within the accessible spectral-energy window. This operational descriptor expresses the number of retained multiplet centres per unit spectral extension.

The descriptors were selected to probe complementary projections of the spectral manifold rather than to provide equivalent measures of the same property. The mean manifold energy μ_E represents the collective energetic displacement of the complete distribution, whereas σ_E quantifies the dispersion of the energy levels around this average position. The compactness parameter C , calculated from the number of multiplet centres N and the spectral extension W , describes how densely the available energy window is populated. The entropy descriptor defined below provides a complementary information-based measure of how the multiplet states are distributed across the spectral-energy space.

2.4. Spectral Entropy

The degree of energetic delocalisation of each manifold was quantified through a spectral entropy descriptor based on the Shannon information formalism [19,20]. The energy range was divided into discrete intervals using the same coarse-graining scale adopted in the occupancy analysis, and the probability of finding a multiplet within each interval was calculated as

$$p_k = \frac{N_k}{N} \quad (14)$$

where N_k is the number of multiplet centres in the k -th energy interval and N is the total number of multiplet centres in the corresponding manifold.

The spectral entropy was then obtained using

$$S = -\sum_k p_k \ln(p_k) \quad (15)$$

Higher entropy values correspond to manifolds whose multiplet states are distributed over a larger number of energetic regions, whereas lower values indicate stronger concentration of states within restricted spectral domains.

The entropy is not interpreted as a thermodynamic quantity, but as an information descriptor measuring how the multiplet manifold occupies the accessible energy landscape after removal of quantum labels.

2.5. Identification of Collective Electronic Singularities

To determine whether the global descriptors retained information about electronic shell structure, their evolution was analysed as a function of the $4f^n$ occupation number across the investigated lanthanide series.

The descriptor calculations did not include prior information about Hund's rules, term multiplicities, angular-momentum coupling or shell symmetry. Configurations known from atomic and rare-earth spectroscopy to have particular significance within the $4f^n$ filling sequence [3,4,13,23] were considered only after the descriptor values had been obtained.

The configurations $4f^1$, $4f^7$, $4f^{13}$ were therefore analysed as reference cases corresponding respectively to the beginning of shell filling, the half-filled shell and the nearly closed shell [3,4,13,23].

Special emphasis was placed on Gd^{3+} ($4f^7$), because it represents an internal electronic constraint rather than a boundary of the lanthanide series. Its recovery after removal of explicit spectroscopic labels therefore provides a stricter test of whether shell-dependent information remains encoded in the collective manifold organisation.

2.6. Validation and Descriptor Normalisation

To evaluate whether the observed signatures were intrinsic to the collective manifold organisation rather than imposed by prior knowledge of electronic structure, several validation procedures were performed.

First, a blind reconstruction test was performed for the half-filled-shell configuration. Gd^{3+} ($4f^7$) was removed from the dataset before constructing the reference behaviour of the lanthanide series. The remaining ions were used to reconstruct the expected evolution of the mean manifold energy μ_E .

After reconstruction, the Gd^{3+} manifold was reintroduced and its deviation from the reference behaviour was quantified using

$$R_n = \mu_E(n) - \mu_E^{ref}(n) \quad (16)$$

where $\mu_E^{ref}(n)$ represents the reference trend obtained without including the tested configuration.

This procedure ensures that the position of the half-filled-shell configuration is not used during construction of the reference evolution, allowing the persistence of the $4f^7$ signature to be evaluated independently.

To avoid possible boundary effects associated with the first and last members of the series, an additional internal leave-one-out analysis was performed considering only the internal configurations ($4f^2$ – $4f^{12}$). This test evaluates whether the half-filled shell represents a genuine internal deviation of the manifold evolution rather than a consequence of the shell-edge configurations.

Randomised shell-order tests were also performed by disrupting the correspondence between $4f^n$ occupation and the calculated descriptors. These tests evaluate whether the observed trends depend on the physical ordering of shell filling rather than only on the numerical distribution of descriptor values.

Finally, the response of different descriptors was compared to determine whether electronic information was concentrated in a single quantity or distributed across different projections of the spectral manifold.

For comparison of descriptors with different units and numerical ranges, each descriptor X was converted into a normalised response:

$$Z_X(n) = \frac{X(n) - \langle X \rangle}{\sigma_X} \quad (17)$$

where $\langle X \rangle$ and σ_X represent the mean value and standard deviation of descriptor X across the analysed lanthanide series respectively.

This normalisation was used only for comparative visualisation of descriptor responses and does not modify the descriptor values used in the individual analyses.

These validation steps were designed to distinguish physically meaningful information retention from trends arising solely from descriptor definition or shell ordering.

2.7. Computational Implementation

All the calculations were performed using custom scripts developed in Python 3.11. Data handling and numerical operations were carried out using pandas 2.2, NumPy 1.26 and SciPy 1.11 libraries. Graphical representations were generated using Matplotlib 3.8.

The extracted multiplet-centre energies were stored in tabulated form and used as the only numerical input for the analysis. All the descriptors, occupancy matrices, normalisation procedures and validation tests were calculated directly from these energy values without introducing spectroscopic labels, transition probabilities or additional electronic-structure parameters.

The polynomial fitting used in the blind reconstruction analysis was performed using the NumPy polynomial fitting routines. The tested configuration was removed before construction of the reference trend and reintroduced only after the fitting procedure, ensuring that the validation remained independent of the known electronic identity of the tested ion.

3. Results and Discussion

3.1. From Microscopic Energy Levels to Collective Spectral Manifolds

The electronic structure of Ln^{3+} ions is conventionally described through a hierarchy of multiplet states arising from electron–electron interactions, spin–orbit coupling and crystal-field perturbations [1–4]. This microscopic description provides detailed information on the origin and identity of individual electronic states, including their term assignments and angular-momentum character. However, it does not directly address whether the complete set of generated states possesses a collective organisation across the lanthanide series.

As a first step, the experimentally established multiplet-centre energies of Ln^{3+} ions in LaF_3 [1,2] were reorganised from an assigned spectroscopic representation into the energy-only spectral manifolds defined in Equation (5).

In the conventional description, each electronic state is associated with both its energetic position and its spectroscopic identity. Following the information-reduction procedure introduced in Equation (6), term symbols, angular-momentum labels and state assignments are deliberately removed, while only the energy coordinates are retained.

This transformation constitutes a controlled reduction in spectroscopic information. The energetic organisation generated by the underlying electronic Hamiltonian is preserved, but the microscopic labels normally used to interpret individual states are no longer available. The objective is therefore not to reconstruct the conventional electronic structure, but to determine whether information associated with $4f$ shell filling remains encoded within the collective arrangement of energy levels.

Figure 1 illustrates the application of this transformation to the Carnall multiplet-centre dataset [1,2]. The original energy-level landscape contains a large number of discrete electronic states distributed across the lanthanide series. After removal of spectroscopic identifiers, the same dataset is converted into a label-free representation where the retained energy coordinates define the collective spectral manifold.

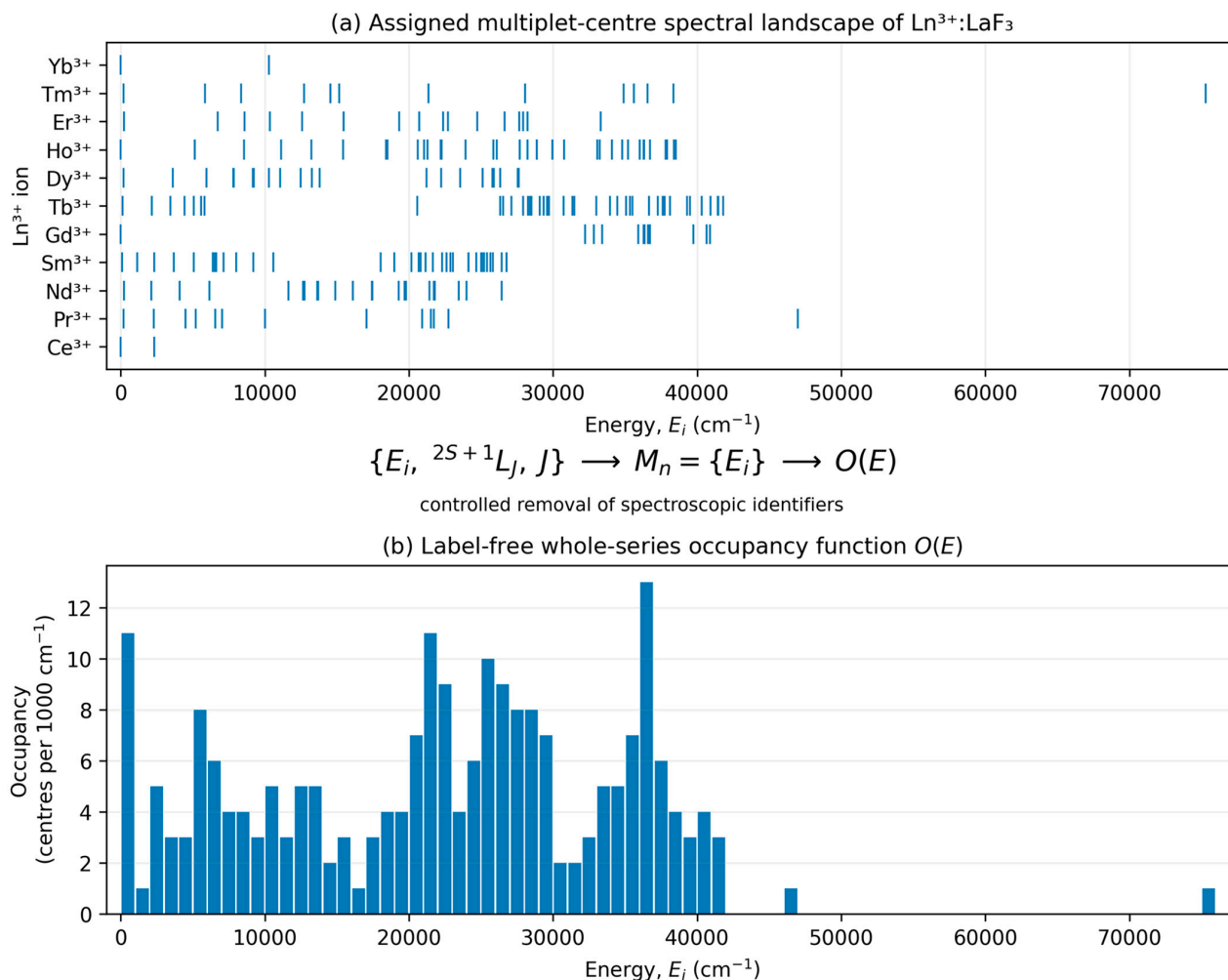


Figure 1. Transformation from assigned multiplet-centre energies to label-free collective spectral manifolds: (a) Experimentally reported multiplet-centre energies of Ln^{3+} ions in LaF_3 across the investigated lanthanide series. Each vertical mark corresponds to an identified electronic multiplet centre in the conventional spectroscopic representation, where energies are associated with term assignments and angular-momentum labels. (b) Whole-series occupancy function $O(E)$ obtained after removal of spectroscopic identifiers and retention of only the energy coordinates. The transformation $\{E_i, {}^{2S+1}L_J, J\} \rightarrow M_n = \{E_i\} \rightarrow O(E)$ represents the first stage of information reduction, converting labelled electronic states into a collective energy-space description while preserving the global organisation of the spectral manifold.

The resulting whole-series occupancy function $O(E)$ provides the first coarse-grained view of this reduced representation. It describes how the available spectral-energy space is populated after removal of state identities, without introducing information about transition probabilities, selection rules or electronic assignments.

Importantly, no information related to term identity, angular-momentum coupling, Hund-rule classification or specific electronic transitions is used in the subsequent analysis. Any systematic behaviour recovered from the manifold descriptors must therefore originate from the organisation of the energy distribution itself.

At this stage, no assumption is introduced regarding which electronic configurations should display distinctive behaviour. The purpose of the initial manifold construction is only to establish whether a collective energetic organisation remains after information reduction.

The following sections examine this question by progressively analysing the retained energy-only information, first through shell-resolved occupancy functions and subsequently through scalar descriptors of the complete manifold, following the sequence introduced in Equation (7).

This approach allows the central question of the present work to be addressed: whether the collective organisation of the lanthanide spectral manifold retains signatures of the underlying $4f$ electronic structure after removal of the microscopic labels traditionally used to interpret rare-earth spectra.

3.2. Spectral Occupancy: Evidence of Non-Uniform Energy-Space Organisation

After removing the identity of individual multiplets, the first question is whether the remaining spectral distribution contains any recognisable organisation or whether it behaves as an approximately random collection of energy states.

To address this point, the spectral occupancy analysis was extended from the global occupancy function $O(E)$, introduced in Figure 1, to the shell-resolved occupancy function $O(E, n)$, defined in Equation (9), where the population of energy intervals is followed as a function of the $4f^n$ occupation number. The same $\Delta E = 1000 \text{ cm}^{-1}$ coarse-graining scale defined in the methodology was applied, ensuring that the comparison across the lanthanide series is performed at the manifold level rather than at the individual-level scale. This representation retains the lanthanide-series coordinate while preserving the energy-only nature of the manifold.

The occupancy analysis represents the first shell-resolved level of information reduction: all the spectroscopic labels are discarded, but the distribution of energy states is preserved as a function of both energy and $4f^n$ occupation. Therefore, any remaining structure must originate from the organisation of the manifold itself rather than from predefined electronic classifications.

The resulting occupancy map, shown in Figure 2, reveals a strongly non-uniform distribution of electronic states across both energy and $4f$ occupation. Rather than filling the accessible energy range homogeneously, the lanthanide manifolds exhibit preferentially populated spectral regions separated by lower-density intervals.

In particular, the occupancy representation shows that the spectral landscape is concentrated within specific energy domains, while other regions remain weakly populated. The persistence of these occupancy features across the lanthanide series is consistent with the known constraints imposed by electron–electron interactions, spin–orbit coupling and crystal-field perturbations on Ln^{3+} multiplet structures [1–4], rather than with a random distribution of states in energy space.

This behaviour indicates that the collective manifold retains information about the constraints imposed by the underlying $4f$ electronic structure. Even after removing term labels and transition assignments, the distribution of states remains structured.

However, the occupancy representation also reveals the limitation of this first shell-resolved description. Although it preserves the global architecture of the energy landscape, it does not reduce each ion to a directly comparable quantitative fingerprint.

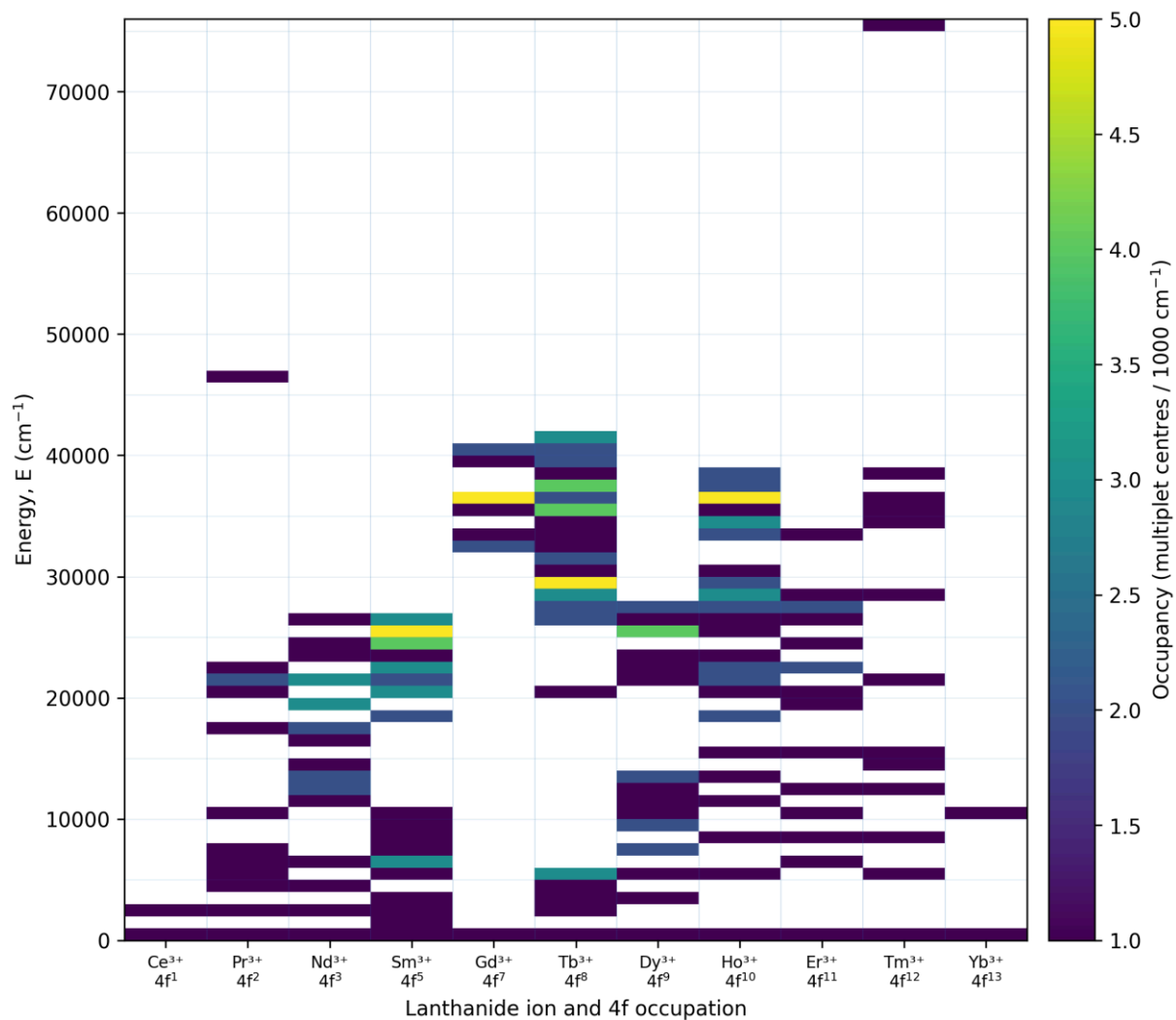


Figure 2. Shell-resolved spectral occupancy analysis of Ln^{3+} energy-only manifolds. The occupancy function $O(E, n)$ describes the distribution of multiplet-centre energies as a function of both energy and $4f^n$ occupation after removal of spectroscopic state identities. The representation corresponds to the first collective organisation level of the reduced manifold, preserving information about how the spectral-energy space is populated without using term assignments, angular-momentum labels or transition identities. The non-uniform occupancy pattern indicates that the energy-only manifolds retain structured information rather than reducing to a featureless distribution of states.

Additional descriptors are therefore required to determine whether specific electronic configurations leave identifiable signatures in the collective representation after a further stage of information compression.

This motivates the transition from energy-resolved manifold descriptions to scalar quantities that quantify complementary properties of the distribution, including energetic displacement, spectral dispersion, occupation density and information content.

3.3. Entropy and Compactness Reveal Collective Manifold Structure

The spectral occupancy analysis demonstrates that the coarse-grained manifolds retain a non-random organisation. However, occupancy alone describes where electronic states are located and does not quantify how the available spectral space is used by each $4f^n$ configuration.

To investigate this aspect, a set of complementary global descriptors was analysed: spectral entropy S , manifold compactness C , mean manifold energy μ_E , and spectral

dispersion σ_E . These quantities probe different projections of the same physical object: the collective organisation of the energy-only spectral manifold.

The spectral entropy measures the degree of energetic spreading of the manifold using an information-based description of the occupation probability distribution [19,20]. Low entropy values correspond to configurations where the multiplet states occupy a more restricted set of energy regions, whereas higher entropy values indicate a broader distribution of states across the available energy space.

The compactness parameter C , defined in Equation (13) as an operational descriptor of manifold state density, provides complementary information by relating the number of accessible multiplet states to the total spectral extension of the manifold. It therefore measures whether the electronic states are concentrated within a limited energy window or distributed over a broader range.

In contrast, the energetic descriptors describe the position and extension of the manifold in energy space. The mean manifold energy μ_E , defined in Equation (10), was evaluated for each Ln^{3+} ion as a collective coordinate of the complete multiplet distribution. Although this quantity represents a strong reduction in the original spectroscopic information, its evolution provides direct information on how the energetic centre of the manifold changes during progressive filling of the $4f$ shell. This result is particularly relevant because μ_E is calculated without using electronic term assignments, degeneracies, transition strengths or selection rules. It therefore represents a purely collective coordinate describing the energetic centre of the complete multiplet distribution. The evolution of μ_E shows that progressive occupation of the $4f$ shell not only modifies the number or density of accessible states; instead, electron filling is accompanied by a displacement of the complete spectral manifold within the energy landscape.

The spectral dispersion σ_E , defined in Equation (11), provides the complementary energetic measure by quantifying the spread of the multiplet energies around the mean manifold energy. Together, μ_E and σ_E show whether shell filling modifies the energetic location and width of the manifold, while S and C describe how states occupy the available spectral space.

The evolution of these energetic descriptors shows that progressive occupation of the $4f$ shell not only modifies the number of accessible multiplet states; instead, shell filling is accompanied by changes in the position and extension of the complete spectral manifold within the energy landscape. This behaviour indicates that the energetic organisation of the lanthanide series is not determined only by isolated levels or selected optical transitions, but is reflected in the collective properties of the full set of multiplet states.

Among the observed trends, the half-filled-shell configuration $\text{Gd}^{3+} (4f^7)$ exhibits distinctive behaviour relative to neighbouring configurations. The $4f^7$ configuration is electronically distinguished by its half-filled-shell character and associated symmetry [3,4,13,23]; the present results suggest that this characteristic also leaves a measurable signature in the global organisation of the energy-only manifold. This observation motivates a stricter validation test to determine whether the $4f^7$ signature can be recovered without prior knowledge of its electronic identity.

Importantly, none of these descriptors uses spectroscopic labels, transition probabilities, selection rules or angular-momentum information. These descriptors are calculated exclusively from the geometry of the energy distribution, providing an independent test of whether electronic shell information survives the reduction from labelled multiplets to an unlabelled manifold.

The evolution of these descriptors across the lanthanide series reveals that the collective organisation of the manifold is strongly influenced by the occupation of the $4f$ shell. However, the different descriptors do not provide identical information. Entropy

and compactness are primarily sensitive to how efficiently the available spectral space is populated, whereas μ_E and σ_E describe the energetic reorganisation of the manifold.

Remarkably, the most pronounced deviations are associated with the electronically distinguished configurations $4f^1$, $4f^7$, $4f^{13}$.

These correspond respectively to the single-electron limit Ce^{3+} , the half-filled-shell configuration Gd^{3+} and the nearly closed-shell limit Yb^{3+} [1–4,13,23].

This result is important because these configurations were not introduced as targets during descriptor calculation. Their appearance across different manifold descriptors suggests that shell filling influences several independent aspects of the energy distribution, rather than a single selected parameter.

Therefore, the observed behaviour indicates that the influence of shell filling is not restricted to selected multiplets or specific transitions. Instead, it affects the global arrangement of the electronic-state distribution.

The recovery of these characteristic configurations from intentionally reduced information demonstrates that part of the electronic-structure hierarchy is encoded at the collective manifold level rather than exclusively in individual quantum-state assignments. The corresponding descriptor evolutions are shown in Figure 3, where entropy, compactness, mean manifold energy and spectral dispersion provide complementary projections of the same energy-only manifold.

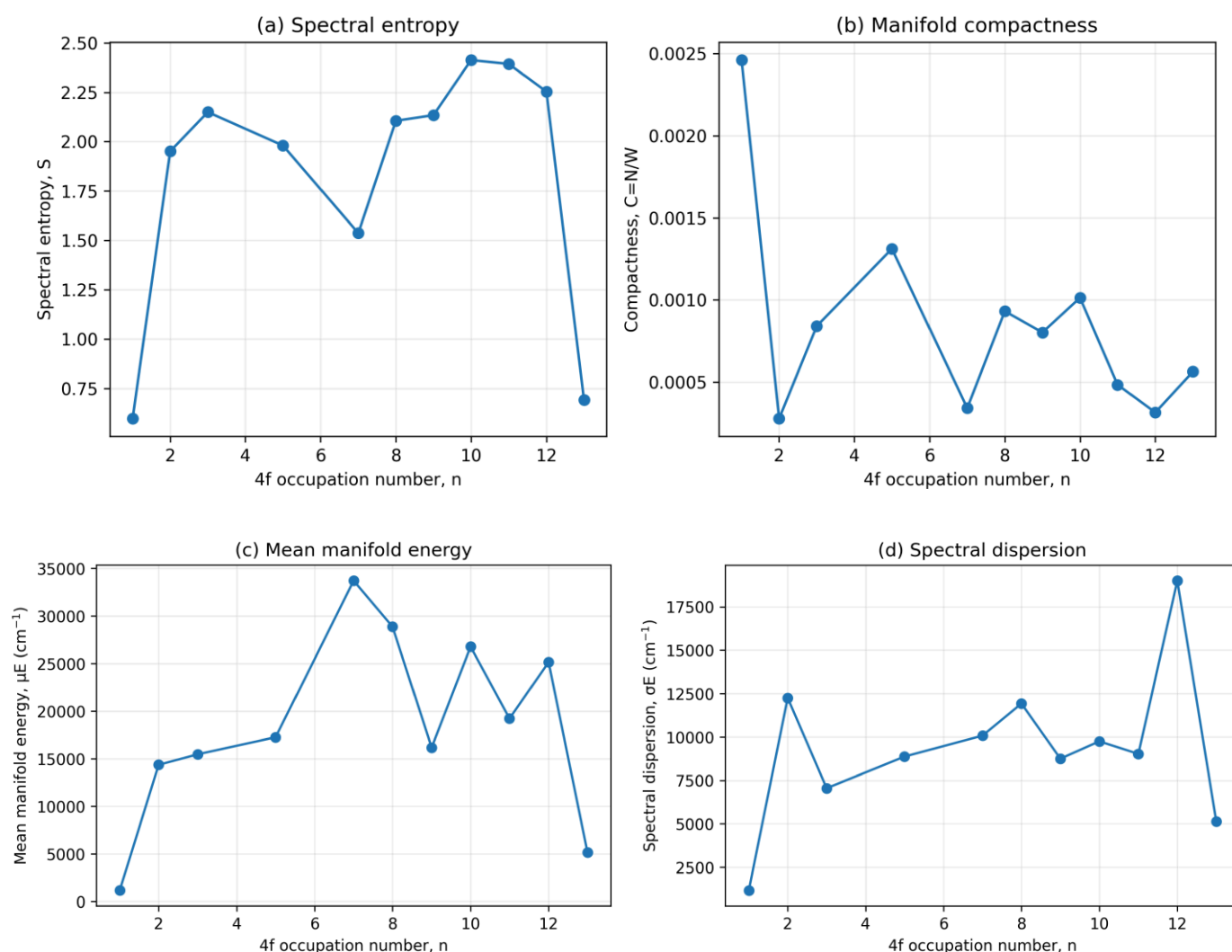


Figure 3. Collective descriptors of the Ln^{3+} energy-only spectral manifolds: (a) Spectral entropy S , describing the distribution of multiplet centres across the accessible energy space. (b) Manifold

compactness $C = N/W$, representing the density of states within the spectral extension of each ion. (c) Mean manifold energy μ_E , describing the collective energetic displacement of the complete distribution. (d) Spectral dispersion σ_E , quantifying the energetic spreading of the manifold. All the descriptors were calculated after removal of spectroscopic term labels, angular-momentum information and transition assignments. The evolution across the $4f^n$ series reveals distinct behaviour associated with the shell-edge configurations Ce^{3+} ($4f^1$) and Yb^{3+} ($4f^{13}$), and with the half-filled-shell configuration Gd^{3+} ($4f^7$). The persistence of these features after information reduction indicates that signatures of the $4f$ electronic architecture are encoded in the collective organisation of the spectral-energy manifold.

3.4. Blind Recovery of the Half-Filled-Shell Configuration

The previous analyses show that several independent manifold descriptors identify the electronically distinguished regions of the lanthanide series. However, since the special role of the half-filled shell is well established in atomic physics and rare-earth spectroscopy [3,4,13,23], an important question remains:

Does the manifold analysis genuinely recover this configuration, or is the interpretation imposed after inspection of the data?

This question is particularly relevant because the descriptors discussed above were calculated after a strong reduction in the original spectroscopic information. Term assignments, angular-momentum labels and transition identities were removed, and only the collective properties of the energy-only manifolds were retained.

To address this point, a blind reconstruction test was performed. The Gd^{3+} ion, corresponding to the half-filled $4f^7$ configuration, was removed from the dataset before constructing the reference evolution of the spectral manifold. The remaining lanthanide ions were then used to define the expected trend of the collective energy coordinate.

The mean manifold energy μ_E was selected for this reconstruction test because, among the descriptors analysed above, it provides a single collective coordinate describing the global energetic displacement of each manifold.

This procedure eliminates prior knowledge of the half-filled-shell position during the reconstruction step. The test therefore evaluates whether the collective manifold organisation itself contains sufficient information to identify the missing electronic configuration.

Only after this reference behaviour was established was the Gd^{3+} manifold reintroduced.

The deviation from the predicted manifold evolution was calculated using the residual R_n defined in Equation (16), where $\mu_E^{ref}(n)$ represents the reference trend obtained without including the tested configuration.

The residual analysis shows that Gd^{3+} produces the strongest positive deviation of the entire series:

$$R_{Gd} \approx 1.1 \times 10^4 \text{ cm}^{-1}$$

The magnitude of this deviation indicates that the half-filled-shell signature is not confined to selected electronic states but is also reflected in a detectable displacement of the complete spectral manifold.

Thus, within the adopted reconstruction procedure, the half-filled-shell configuration is recovered from the collective organisation of the spectral manifold rather than imposed through prior knowledge of atomic structure.

The significance of this result is not that Gd^{3+} is electronically distinguished—this is already well established from Hund's rules and conventional atomic theory [3,4,23]. Instead, the important observation is that the signature of this half-filled-shell character survives after removing the microscopic information normally used to identify it.

The half-filled-shell character is therefore not only encoded in specific quantum numbers or selected electronic states. The present analysis shows that it also leaves a measurable fingerprint in the global distribution of the multiplet manifold.

This result complements the multi-descriptor analysis presented above: while S , C , μ_E , and σ_E reveal different aspects of manifold organisation, the blind reconstruction test demonstrates that one of the most fundamental electronic configurations of the lanthanide series can be recovered without explicitly introducing its spectroscopic identity.

As an additional control, randomised shell-order tests suppressed the systematic descriptor evolution observed along the physical $4f^n$ sequence, supporting the interpretation that the recovered signatures are associated with shell filling rather than with the numerical distribution of descriptor values alone.

This blind recovery provides internal validation of the manifold-based approach by showing that information deliberately removed at the level of individual spectroscopic labels is partially retained in the collective organisation of the energy landscape. The blind reconstruction and the corresponding residual analysis are shown in Figure 4.

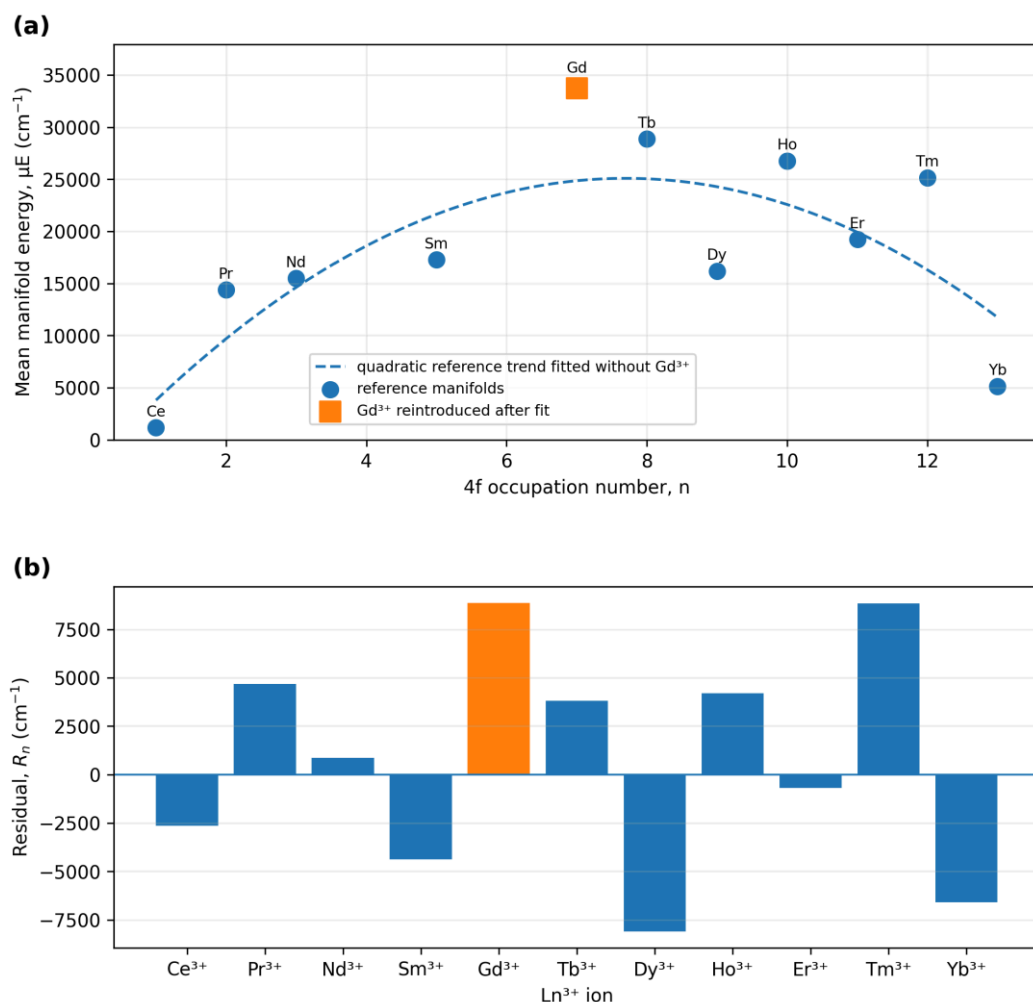


Figure 4. Blind recovery of the half-filled-shell configuration from manifold-level analysis: (a) Reconstruction of the mean manifold-energy evolution after excluding Gd^{3+} ($4f^7$) from the reference trend. The dashed curve represents the reference behaviour obtained from the remaining Ln^{3+} manifolds, while Gd^{3+} is reintroduced only after the reconstruction step. (b) Residual analysis using $R_n = \mu_E(n) - \mu_E^{\text{ref}}(n)$, where $\mu_E^{\text{ref}}(n)$ corresponds to the Gd^{3+} -excluded reference trend. The half-filled-shell configuration exhibits the largest positive residual, demonstrating that the $4f^7$ signature is recovered from the collective energy distribution without using term labels, angular-momentum information or transition assignments.

3.5. Distributed Encoding of 4f Electronic Information

A key outcome of the present analysis is that the identification of the electronically distinguished configurations does not depend on a single selected descriptor.

This point is important because a single global quantity could, in principle, emphasise only a particular mathematical property of the dataset rather than reflect a physical characteristic of the underlying electronic structure.

Recent multiparametric analyses of lanthanide spectra have shown that different derived quantities may emphasise complementary aspects of the same spectroscopic dataset [23]. In the present analysis, the mean manifold energy μ_E reflects the collective energetic displacement of the manifold, while the spectral dispersion σ_E describes its energetic extension. In contrast, entropy S and compactness C describe how states are organised and concentrated within the available spectral window.

A comparison between descriptors shows that the shell-edge and half-filled-shell configurations produce simultaneous signatures across multiple distinct and complementary representations of the manifold.

To visualise this distributed response, each descriptor was converted into a normalised fingerprint coordinate $Z_X(n)$, allowing the relative contributions of entropy, compactness, mean energy and spectral dispersion to be compared on the same scale (Figure 5).

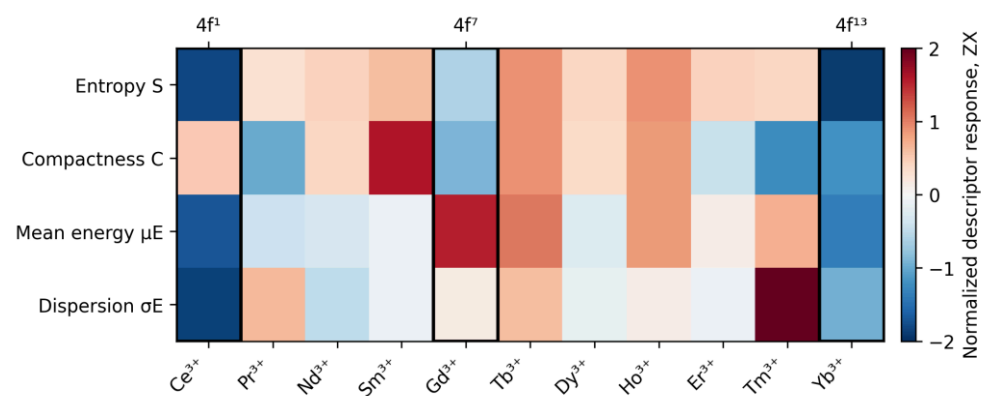


Figure 5. Multi-descriptor fingerprints of lanthanide energy-only manifolds. Normalised descriptor responses $Z_X(n)$ for spectral entropy S , compactness C , mean manifold energy μ_E , and spectral dispersion σ_E . The fingerprint representation highlights that the characteristic configurations Ce^{3+} ($4f^1$), Gd^{3+} ($4f^7$) and Yb^{3+} ($4f^{13}$) are expressed through distributed changes across multiple collective descriptors rather than through a single isolated parameter.

The convergent response across these descriptors supports the interpretation that the observed behaviour is not an artefact of a single mathematical definition but reflects the organisation of the spectral manifold itself.

The descriptors therefore provide complementary projections of the same underlying energy landscape. The electronically distinguished configurations of the lanthanide series are not expressed only through shifts in the energetic centre of the manifold, but also through changes in state distribution, compactness and spectral spreading.

Together, these results indicate that the relevant information is distributed across different aspects of the spectral manifold.

This distributed character is central to the interpretation proposed here.

The electronically distinguished character of Ce^{3+} , Gd^{3+} and Yb^{3+} within the $4f^n$ sequence is well established [1–4,13,23]. If the consequences of these electronic configurations were confined exclusively to isolated multiplets, removing state identities would be expected to suppress their recognition in the reduced representation. Instead, their signatures

remain detectable after coarse-graining, indicating that the consequences of the $4f$ -shell architecture are also expressed through collective properties of the complete manifold.

In this sense, the spectral manifold acts as an intermediate level of description between individual quantum states and global electronic trends: it does not replace conventional atomic-structure analysis but reveals which aspects of that structure remain accessible after systematic information reduction.

Therefore, the lanthanide spectral manifold can be treated as a collective representation that retains recoverable global information about electronic shell structure, rather than simply as a catalogue of individual energy levels.

The descriptor fingerprints of the intermediate $4f^n$ configurations provide additional information on the collective organisation of the lanthanide manifolds. These ions occupy the central region of the shell-filling sequence, where Coulomb interactions, spin-orbit coupling, configuration-dependent term multiplicities and crystal-field perturbations act simultaneously without producing a single dominant electronic constraint comparable to the shell-edge or half-filled-shell cases. Local variations in entropy, compactness, mean manifold energy or spectral dispersion therefore reflect the response of the retained manifold to this combined electronic organisation.

Within this framework, the common upper energy boundary adopted in the present analysis provides a consistent operational definition of the analysed manifold across the investigated lanthanide series. Consequently, descriptors depending on spectral occupation or manifold extension may show sensitivity to the finite range of retained multiplet centres, particularly for intermediate ions. These variations should therefore be interpreted as collective responses of the retained manifold rather than as unique microscopic assignments.

The methodology is best suited to testing whether electronic shell information survives controlled spectroscopic information reduction and to identifying robust collective deviations within a consistently defined multiplet-centre dataset. Detailed microscopic attribution of intermediate non-singular $4f^n$ configurations remains linked to conventional assigned spectroscopy, including Hamiltonian analysis, crystal-field modelling and related level-by-level approaches.

4. Conclusions

Lanthanide spectroscopy is traditionally interpreted through assigned multiplets, transition probabilities and crystal-field interactions. In this work, we examined a complementary representation by treating the experimentally established $\text{Ln}^{3+}:\text{LaF}_3$ multiplet-centre energies as collective spectral manifolds after removing term labels, transition assignments and angular-momentum information.

The analysed energy-only manifolds retain structured organisation across the lanthanide series. Spectral entropy, compactness, mean manifold energy and spectral dispersion reveal distinctive responses associated with Ce^{3+} ($4f^1$), Gd^{3+} ($4f^7$) and Yb^{3+} ($4f^{13}$), even though no explicit information about Hund's rules, term identities or shell symmetry is introduced into the descriptor calculations.

The blind reconstruction test of Gd^{3+} provides the strongest internal validation of this interpretation. When the $4f^7$ configuration is excluded from the reference trend and subsequently reintroduced, it emerges as the dominant positive deviation of the mean manifold-energy coordinate. This shows that the half-filled-shell signature is not confined to explicit spectroscopic labels or selected multiplets, but remains detectable in the collective energy distribution.

Together, the results indicate that $4f$ electronic shell information is distributed across several complementary properties of the complete manifold, including state occupation, compactness, energetic displacement and spectral spreading. The lanthanide spectral

manifold can therefore be treated as a physically informative collective representation, complementary to conventional level-by-level spectroscopy.

The present analysis is intentionally restricted to the internally consistent $\text{Ln}^{3+}:\text{LaF}_3$ multiplet-centre dataset. This choice allows the descriptor methodology to be evaluated using a homogeneous experimental reference across the investigated lanthanide series, without combining shell-filling effects with host-dependent barycentre shifts, different crystal-field environments or differences in dataset completeness. The conclusions should therefore be understood as manifold-level signatures recovered within this consistently defined LaF_3 reference system, rather than as a demonstration of cross-host invariance.

The methodology proposed here adds a collective diagnostic layer to conventional lanthanide spectroscopy. By treating the multiplet-centre distribution as a physical manifold, it provides a complementary framework for investigating how electronic shell information is preserved after systematic reduction in microscopic spectroscopic labels. Extending this framework to high-lying $4f^n-15d$ configurations, strongly host-dependent manifolds or incomplete experimental series represents a natural continuation of the present work and will require the development of dedicated manifold representations adapted to those physical situations.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/photonics13070658/s1>. Table S1: Extracted $\text{Ln}^{3+}:\text{LaF}_3$ multiplet-centre energy dataset; Table S2: Calculated spectral-manifold descriptors; Table S3: Shell-resolved occupancy matrices; Table S4: Blind reconstruction analysis of the half-filled-shell configuration; Table S5: Normalised descriptor responses.

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Data Availability Statement: The spectroscopic energy dataset extracted from the literature and the calculated descriptors required to reproduce the results are provided as Supplementary Materials.

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