



Wave-functions overlap in stoichiometric lanthanide laser crystals



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ABSTRACT

Two-center overlap integrals (TCOIs), $\langle 4f|4f \rangle$ of symmetry types σ , π , δ , φ , $\langle 2s|4f \rangle$, $\langle 2p|4f \rangle_{\sigma}$, and $\langle 2p|4f \rangle_{\pi}$, have been computed for 11 stoichiometric lasing lanthanide compounds: $\text{PrP}_4\text{O}_{15}$, $\text{NdP}_5\text{O}_{14}$, $\text{NdLiP}_4\text{O}_{12}$, $\text{NdAl}_3(\text{BO}_3)_4$, $\text{NdNa}_5(\text{WO}_4)_4$, $\text{NdK}_3(\text{PO}_4)_2$, $\text{NdKP}_4\text{O}_{12}$, HoF_3 , $\text{Ho}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, and $\text{ErP}_5\text{O}_{14}$. Four-term (4-t) and six-term (6-t) SCF Slater-type orbitals have been employed for Ln^{3+} at mean distances Ln^{3+} – Ln^{3+} and Ln^{3+} –ligand. Different results for ion pair overlap have been obtained by using 4-t or 6-t wave functions of Pr^{3+} and Nd^{3+} . The TCOIs have been correlated with measured lifetimes of laser transitions of Pr^{3+} , Nd^{3+} , Ho^{3+} , and Er^{3+} in the mentioned crystals.

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1. Introduction

Insulating crystals of lanthanide compounds amplifying light after optical pumping, often by LEDs, have been defined as stoichiometric lasers. The active medium of these minilasers is a complex lanthanide borate, fluoride, garnet, phosphate, or tungstate. Their structural and laser properties have been compiled in review articles or book chapters [1–3]; more recent applications are relevant to microchip laser systems for data storage and integrated optical communications [4]. Unlike the doped crystals, the lanthanide ions constitute sublattices in the mentioned compounds and are naturally separated at large distances by poly-oxoanions AlO_6^{9-} , BO_3^{3-} , PO_4^{3-} , and WO_4^{2-} , etc. thus minimizing to certain extent the depletion of the population inversion. Neodymium compounds are the most studied in this group since the 4f energy-level scheme of Nd^{3+} ion is favorable for lasing at room temperature, basically through the transitions $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ (1.06 μm) and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ (1.32 μm). Pr^{3+} radiative levels are $^3\text{P}_0$, $^1\text{D}_2$, and $^1\text{G}_4$. All levels below 20,000 cm^{-1} for Ho^{3+} and Er^{3+} are radiative. A partial energy-level diagram with laser transitions of Pr^{3+} , Nd^{3+} , Ho^{3+} , and Er^{3+} in stoichiometric compounds can be found e.g. in [1].

The Ln^{3+} –ligand overlap, $\langle 2\nu|4f \rangle$, where $\nu = s, p\sigma$, or $p\pi$, is among the basic tools in discussing the spectroscopic properties of triply ionized lanthanides in dielectric crystals. These TCOIs have been included in numerous studies towards various problems, for example, overlap and covalent bonding effects on the optical properties of rare earths [5], superposition model in lanthanide

crystal fields [6], rare earth crystal fields [7,8], shielding factors [9], and non-radiative transition probabilities [10,11], etc.

The Ln^{3+} – Ln^{3+} interactions result in energy transfer by multipole, exchange, and superexchange mechanisms. The energy transfer gives rise to concentration quenching, fluorescence quenching by non-radiative transition(s), sensibilization through radiative transition(s), and migration of resonant excitation [2].

Compared with the TCOIs $\langle 2\nu|4f \rangle$, the application of $\langle 4f|4f \rangle$ is very scarce: non-radiative transitions in Eu^{3+} complexes [11], indirect magnetic exchange interactions in orthorhombic lanthanide aluminates [12]. The main reason for this situation is due to the difference in the order of magnitude: ordinarily, $\langle 2\nu|4f \rangle \approx 10^{-2}$, whereas $\langle 4f|4f \rangle \approx 10^{-4}$ or lower. The proportion in turn is based on the fact that the Ln^{3+} –ligand separation is shorter than that of Ln^{3+} – Ln^{3+} , on the exponential decrease of the TCOIs with the internuclear distance, as well as on the inneratomic character of the 4f wave function.

Since the TCOIs are necessary for the evaluation of multicenter integrals, different calculational techniques have been proposed recently applicable to Slater-type orbitals (STOs) [13–15] or to other functions [16]. To the best of our knowledge, except in analyzing the Hartree–Fock wave functions exemplified by $\langle 3\nu|4f \rangle$ TCOIs for Nd^{3+} – Cl^- [17], no other studies have included the use of six-basis STOs for four lowest terms of Nd^{3+} [18].

Malta [11] has presented a variation of 4f–4f overlap vs. distance in Eu^{3+} complexes but without specifying lanthanide wave function, mode of overlap, i.e. the symmetry type σ , π , etc., and the actual Eu^{3+} – Eu^{3+} distance(s). It has been noted in the same paper, however, that for distances Ln^{3+} – Ln^{3+} exceeding 4 Å (≈ 7.6 a.u.) the applied mechanism of non-radiative transitions is unacceptable. Therefore, the extent of overlapping with participation

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of 4f wave functions in stoichiometric lanthanide laser crystals needs a more detailed evaluation.

The aim of this work is to apply the model of wave-functions overlap to pairs $\text{Ln}^{3+}-\text{Ln}^{3+}$ and $\text{Ln}^{3+}-\text{ligand (L)}$ in the title lanthanide compounds and to relate its effect to ion-ion interactions and certain laser characteristics.

2. Method

A TCOf of STOs χ_a and χ_b located at centers a and b respectively are expressed as:

$$\int dr d\theta d\varphi \chi_a(r, \theta, \varphi) \chi_b(r, \theta, \varphi) = \chi_a \chi_b \quad (1)$$

where (r, θ, φ) are spherical coordinates in respect to the origin.

The TCOfs in this work have been computed by routine based on the procedure proposed by Lofthus [19]. The principal quantum numbers and the respective polynomials in [19] have been raised by operator differentiation to obtain those for $\langle 2s|4f \rangle$, $\langle 2p|4f \rangle_\sigma$, $\langle 2p|4f \rangle_\pi$, and $\langle 4f|4f \rangle_\kappa$, where κ stands for σ , π , δ , or φ . This technique is applicable to pairs of unnormalized STOs which in the case of radial 4f orbitals are expansions in the form:

$$R_{4f}(r) = r^3 \sum_{i=1}^k C_i \exp(-\zeta_i r) \quad (2)$$

where C_i and ζ_i designate coefficients and exponents, respectively. The following types of analytical SCF STOs have been used in the computations of the TCOfs in this work: four-term (4-t) wave functions of Freeman and Watson [20] for Pr^{3+} , Nd^{3+} and Er^{3+} or those of Sovers [21] for Ho^{3+} ; wave functions of the same type for oxygen (2-) sitting in a well of (+2) charge as reported by Watson [22] and for fluorine (-) [23]. Analytical six-term (6-t) SCF wave functions for the lowest states of Nd^{3+} , namely 4I , 4F , 4G , and 4D [18], and for the ground state of Pr^{3+} [24] have been converted into their unnormalized form by means of the following notation [25]:

$$\begin{aligned} \varphi_{i\lambda\alpha} &= \sum \chi_{i\lambda\alpha} C_{i\lambda p} \chi_{p\lambda\alpha}(r, \theta, \varphi) \\ &= R_{i\lambda p}(r) Y_{i\lambda\alpha}(\theta, \varphi), \chi_{p\lambda\alpha}(r, \theta, \varphi) \\ &= R_{i\lambda p}(r) Y_{i\lambda\alpha}(\theta, \varphi) \end{aligned} \quad (3)$$

$$R_{i\lambda p}(r) = \left[(2\zeta_{i\lambda p})^{n+1/2} \right] / \left[(2n!)^{1/2} \right] r^{n-1} \exp(-\zeta_{i\lambda p} r). \quad (4)$$

Comparing C_i from Eq. (2), $C_{i\lambda p}$ from Eq. (3), and considering Eq. (4), the following relationship between both types of expansion coefficients can be obtained:

$$C_i = C_{i\lambda p} \left[(2\zeta_{i\lambda p})^{n+1/2} \right] / \left[(2n!)^{1/2} \right], \quad (5)$$

where $n=4$ for 4f orbitals.

The computed values of TCOfs have been rounded off to the third decimal figure in the tables below; such presentation of the accuracy is usual for overlap with participation of 4f STOs [5,17].

3. Results and discussion

The necessary distances $\text{Ln}^{3+}-\text{Ln}^{3+}$ and $\text{Ln}^{3+}-\text{L}$ for the computations of the TCOfs in this work are presented in the first two tables below as average values of those reported in crystal structure studies except for $\text{PrP}_5\text{O}_{14}$ and $\text{ErP}_5\text{O}_{14}$ where minimal $\text{Ln}^{3+}-\text{Ln}^{3+}$ distances have been employed. The ligands are almost exclusively O^{2-} ions; F^- ions are present in the case of HoF_3 only. All compounds are listed in order of increasing the distances $\text{Ln}^{3+}-\text{L}$

Table 1

Mean distances (in a.u.), TCOfs ($/10^{-2}$) $\text{Ln}^{3+}-\text{L}$ with 4-t wave functions for Pr^{3+} , Nd^{3+} , and Er^{3+} [20], 4-t expansions for Ho^{3+} [21], and 6-t for Pr^{3+} [24].

Compound	Ref. ($\text{Ln}^{3+}-\text{L}$)	Mean ($\text{Ln}^{3+}-\text{L}$ / a.u.)	$\langle 2s 4f \rangle$	$\langle 2p 4f \rangle_\sigma$	$\langle 2p 4f \rangle_\pi$	$\Sigma \langle 2\mu 4f \rangle$
HoF_3	[26]	4.420	0.884	1.389	0.858	3.131
$\text{Er}_3\text{Al}_5\text{O}_{12}$	[27]	4.4728	0.876	1.333	0.879	3.088
$\text{Ho}_3\text{Al}_5\text{O}_{12}$	[28]	4.4768	0.985	1.425	0.957	3.367
$\text{NdAl}_3(\text{BO}_3)_4$	[29]	4.4805	2.021	2.230	1.845	6.096
$\text{NdK}_3(\text{PO}_4)_2$	[30]	4.6166	1.765	2.134	1.631	5.530
$\text{NdP}_5\text{O}_{14}$	[31]	4.6242	1.763	2.124	1.619	5.506
$\text{ErP}_5\text{O}_{14}$	[32]	4.6282	0.770	1.184	0.746	2.700
$\text{NdNa}_5(\text{WO}_4)_4$	[33]	4.6487	1.722	2.096	1.584	5.402
$\text{NdKP}_4\text{O}_{12}$	[34,35]	4.6487	1.722	2.096	1.584	5.402
$\text{PrP}_5\text{O}_{14}$, 4-t	[36,37]	4.6506	1.950	1.965	1.731	5.646
$\text{PrP}_5\text{O}_{14}$, 6-t		4.6506	1.985	2.320	1.815	6.120
$\text{NdLiP}_4\text{O}_{12}$	[38]	4.6525	1.715	2.091	1.578	5.384

* 1 a.u. = 0.529177×10^{-10} m

and $\text{Ln}^{3+}-\text{Ln}^{3+}$ in Table 1 and Table 2, respectively.

TCOfs between wave functions of lanthanide (3+) and O^{2-} or F^- ions are presented in Table 1. STOs of Ln^{3+} contain 4-t SCF wave functions or 4-t and 6-t ones for Pr^{3+} in praseodymium pentaphosphate. It is evident from the same table that all values decrease in magnitude in the following order: (i) $\langle 2p|4f \rangle_\sigma > \langle 2s|4f \rangle > \langle 2p|4f \rangle_\pi$ which is the usual inequality direction; (ii) with increasing the lanthanide–ligand distance for one and the same ion, i.e. wave function; (iii) from Pr^{3+} to Er^{3+} due to decreasing the lanthanide (3+) ion radius, e.g. compare the values for HoAG and ErAG . It should be also noted that all values of these TCOfs are not large, about 1–2%.

It is expected that the forbidden 4f–4f optical transitions in the title compounds exhibit electric dipole oscillator strengths originating from interactions with the ligands (O^{2-} or F^-) 2p – wave functions [2]. It has been found for $\text{PrP}_5\text{O}_{14}$ [39, 40] that the interaction radius of effective concentration quenching for the radiative level 3P_0 is approximately equal to 14 a.u.; it has been also proposed that dipole–dipole interactions are dominant in this type of quenching.

In Fig. 1, the dependence of squared overlap ($2p\sigma + 2p\pi$) – 4f is plotted as a function of the distance $\text{Nd}^{3+}-\text{O}^{2-}$. Although linear, the mentioned plot confirms the overlap model in which the actual dependence is exponential since $\langle 2p|4f \rangle^2 \propto \exp(-2\delta R)$. The resulting linear graph could be explained by small relative changes

Table 2

TCOfs $\text{Nd}^{3+}-\text{O}^{2-}$ with six-basis wave functions for certain terms of Nd^{3+} [18] and sums of TCOfs over $\langle 2\mu|$ (last column), all values $/10^{-2}$

Compound	O^{2-} orbitals	$ ^4I\rangle$	$ ^4F\rangle$	$ ^4G\rangle$	$ ^4D\rangle$	$\Sigma \langle 2\mu ^{2S+1}L\rangle$
$\text{NdAl}_3(\text{BO}_3)_4$		1.850	2.119	1.195	2.140	7.304
		1.938	2.031	2.035	2.250	8.254
		1.714	1.764	1.785	2.038	7.301
$\text{NdK}_3(\text{PO}_4)_2$		1.662	1.604	1.750	2.191	7.207
		1.823	1.892	1.864	1.916	7.495
		1.533	1.572	1.585	1.794	6.484
$\text{NdP}_5\text{O}_{14}$		1.651	1.530	2.007	1.845	7.033
		1.782	1.875	1.856	1.952	7.465
		1.519	1.560	1.575	1.799	6.453
$\text{NdNa}_5(\text{WO}_4)_4$		1.615	1.479	1.476	1.783	6.353
		1.762	1.856	1.844	1.924	7.386
		1.488	1.529	1.547	1.758	6.322
$\text{NdKP}_4\text{O}_{12}$		1.615	1.479	1.476	1.783	6.353
		1.762	1.856	1.844	1.924	7.386
		1.488	1.529	1.547	1.758	6.322
$\text{NdLiP}_4\text{O}_{12}$		1.551	1.572	1.268	1.812	6.203
		1.760	1.850	1.850	1.966	7.426
		1.481	1.524	1.544	1.758	6.307

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