

## ON THE CALCULATION OF LANTHANIDE SYSTEMS. THE SPECTRAL PARAMETERS OF PRASEODYMIUM TRIVALENT ION

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**Abstract.** In this work, taking the Pr(III) ion as a suitable case study, the authors test the capacity of a series of Gaussian Type Orbitals (GTOs) basis sets to account for the atomic spectra of lanthanide ions. An extended relevance of this assessment can be found in modeling the luminescence of lanthanide-based materials. It was selected the Pr(III) case because it shows a rather rich collection of experimental data, emerging from the  $f^2$  and  $fd$  configurations. The energy barycenters of spectral multiplets can be equated analytically in terms of the so-called Slater-Condon parameters. By multi-configurational *ab initio* procedures, with basis sets from existing GTO repositories, the calculated  $f \rightarrow f$  transitions are moderately higher than the experimental values, while the relative energies of  $f \rightarrow d$  states undergo both under- and over-estimation. The GTO shortcomings, that are impacting the accuracy, were debated, the critical perspective spreading the seeds of future development.

**Keywords:** lanthanide ion, luminescence, spectral term, Slater-Condon parameter, *ab initio* calculation.

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### Introduction

The electronic structure of lanthanide compounds is a difficult and tricky subject because, as the authors showed in their early pioneering contributions [1-3] the  $f$  shell of  $\text{Ln}^{3+}$  ions in compounds adopts a non-*aufbau* situation, carrying unpaired electrons placed at lower energy than doubly occupied orbitals belonging to the ligands. Because of this situation, the routine computation methods are not working. Our strategy [1-3] consisted in going directly to multi-configurational wave-function theory (WFT) [4] procedures, with guess orbitals prepared from fragments: naked lanthanide ions and the remainder of the molecule. Applications made with this strategy were proven to be surprisingly successful in explaining and reproducing the magnetic properties of lanthanide compounds [1-3]. Another barrier against the routine treatment of lanthanide compounds is the fact that the quite popular Density Functional Theory (DFT) [5] procedures are, in principle, not allowed for lanthanide compounds, since most of  $\text{Ln}^{3+}$  ions show degenerate ground states, offending then basic DFT theorems, demanding strictly non-degenerate fundamental states [6]. However, with a certain care, one may design numeric experiments based on DFT calculations, enabling the extraction of the parameters needed in the simulation of spectral properties [7-14].

In particular, our research was focused on states implied in the luminescence of doped lanthanide systems, with application in domestic lighting appliances [15].

To underpin the extended relevance of the rather pedantic assessments debated in this work, it must be pointed out the use of lanthanide-based materials as phosphors (from Greek *phosphoros* = light bearer), alleviating the emission of LED (light-emitting diodes) devices [16]. As is known, the LEDs are emitting usually at high energies, near violet and ultraviolet [17,18], so the phosphors are helping, with components of yellow-red radiation, to compose a white-light spectrum [19-22]. The process of obtaining low-energy radiation implies, in the case of lanthanide ions, a high-energy  $f \rightarrow d$  orbital transition, induced by the LED emission, followed by step-wise decay in a photon cascade, *via* intermediate excited states [23].

Combining our previous experience in WFT [1-3] or DFT [7-14] techniques and phenomenological spectral models [24], it occurred to us that the computational account of optical properties may be less accurate, in comparison with the surprisingly good simulation of magnetic quantities [1-3]. This situation prompted us to perform an extensive assessment of the performance of WFT methods on the platform of various Gaussian

Type Orbitals (GTOs) available in modern databases. It must be noted that the actual calculation methods, both in the WFT and DFT branches, are deeply based on GTO as basis sets [25,26], *i.e.*, as building blocks of atomic orbitals. The quasi-totality of electronic structure codes, including the most popular ones, such as Gaussian [27], Gamess [28], or Orca [29] are working with GTO bases. It was selected as a case study the triple positive praseodymium ion, Pr(III), because it offers a rich record of experimental data.

### Computational details

The calculations were done with the GAMESS suite [28], in the frame of the Complete Active Space Self Consistent Field (CASSCF) method, using an active space with 12 orbitals (comprising the  $4f$  and  $5d$  atomic shells) and two electrons (corresponding to the  $f^2$  and  $fd$  configurations). The various used basis sets are detailed in the main text. The analytic derivations leading to the resolution of spectral terms as functions of Slater-Condon integrals were helped by Mathematica™ computer algebra code [30,31].

### Results and discussion

For the sake of completeness, here it will be presented the theoretical backgrounds of the performed analysis, reconsidering the experimental data themselves. The experimental data of free lanthanide atoms and ions are tabulated in early collections [32], being also available in nowadays internet databases [33]. The interest is in spectra emerging from  $f^n$  and  $f^{n-1}d$  configurations, the last type resulting from  $4f \rightarrow 5d$  orbital promotions. However, not all the triply ionized lanthanide ions have enough experimental data. For instance, Gd(III) shows only one excited state from the  $f^7$  configuration (out of the many possible, in principle) and no  $f^6d$  state. In turn, Pr(III) presents a rich record of terms with  $f^2$  and  $fd$  parentage, making it best suited for the aimed analysis. As is well known, the spectral terms follow a general  $^{2S+1}[L]_J$  labeling, as function of the orbital, spin, and spin-orbital quantum numbers,  $L$ ,  $S$  and  $J$ , respectively. The  $[L]$  notation stands for a letter symbol assigned to a given integer  $L$  (*e.g.*, S for  $L=0$ , P for  $L=1$ , and so on). Although the spin-orbit coupling is important in the physics and chemistry of lanthanides, it is convenient to eliminate it from the active

parameters of the present study. This can be realized by taking the barycenter of the  $J$  multiplets emerging from a given  $L$  and  $S$  (with  $J$  running from  $|L-S|$  to  $L+S$ ), by weighted summations, by Eq.(1).

$$E_{av}(L, S) = \frac{\sum_{J=|L-S|}^{L+S} (2J+1)E(L, S, J)}{\sum_{J=|L-S|}^{L+S} (2J+1)} \quad (1)$$

The experimental data on  $J$  multiplets of Pr(III) ion [33] and corresponding averages are shown in Table 1 for the  $f^2$  configuration and in Table 2 for the  $fd$  case. The Pr(III) also benefits from the simple equating of spectral term energies in terms of the so-called Slater-Condon integrals, the formulas being posted also in Tables 1 and 2, respectively. The Slater-Condon (SC) integrals [34,35] are used in the theory of atomic spectra, defined as function of the radial parts of atomic orbitals,  $R(r)$ . For two atomic shells,  $a$  and  $b$ , there are two types of SC parameters, classified along with an integer  $k$ :

$$F_k^{ab} = \int_{r_1=0}^{\infty} \int_{r_2=0}^{\infty} R_a(r_1)R_b(r_1)R_a(r_2)R_b(r_2) \frac{\min(r_1, r_2)^k}{\max(r_1, r_2)^{k+1}} r_1^2 r_2^2 dr_1 dr_2 \quad (2)$$

and

$$G_k^{ab} = \int_{r_1=0}^{\infty} \int_{r_2=0}^{\infty} R_a(r_1)R_b(r_1)R_a(r_2)R_b(r_2) \frac{\min(r_1, r_2)^k}{\max(r_1, r_2)^{k+1}} r_1^2 r_2^2 dr_1 dr_2 \quad (3)$$

where,  $r_1$  and  $r_2$  are the distances of the two electrons from the nucleus. Denoting by  $l_a$  and  $l_b$  the secondary quantum numbers of the involved shells, the  $k$  indices are running from 0 to  $\min(2l_a, 2l_b)$  in the case of  $F_k$  terms, while between  $|l_a-l_b|$  and  $l_a+l_b$  for the  $G_k$  ones. When  $a=b$ , namely for intra-shell case, the  $F_k$  and  $G_k$  types become identical, keeping only the first notation. Thus, the two-electron integrals describing Coulomb and exchange effects within  $f^2$  configuration can be presented by the following SC parameters:  $F_0^{ff}$ ,  $F_2^{ff}$ ,  $F_4^{ff}$  and  $F_6^{ff}$ . The  $fd$  configuration is accounted by the  $F_0^{fd}$ ,  $F_2^{fd}$  and  $F_4^{fd}$  parameters for the Coulomb part and by  $G_1^{fd}$ ,  $G_3^{fd}$  and  $G_5^{fd}$  for exchange. In principle, one may consider the intra-shell d-type series,  $F_0^{dd}$ ,  $F_2^{dd}$ ,  $F_4^{dd}$ , but since the  $d^2$  excited configuration is not achieved in Pr(III) ion, this part will be discarded. One must note that the  $F_0$  parameters are neglected from spectral problems, vanishing when the relative differences with respect to the ground state are performed.

Table 1

The list of spectral terms with  $f^2$  parentage, for  $\text{Pr}^{3+}$  ion.

$^{2S+1}[L]$	$J$	$E(L,S,J)$	$E_{av}(L,S)$	$\Delta E_{av}(L,S)$	Energy formulas
$^3H(f^2)$	4	0			
	5	2152.09	2446.4	0	0
	6	4389.09			
$^3F(f^2)$	2	4996.61			
	3	6415.24	6265.83	3819.43	$15F_2^{ff} + 18F_4^{ff} - 273F_6^{ff}$
	4	6854.75			
$^1G(f^2)$	4	9921.24	9921.24	7474.84	$-5F_2^{ff} + 148F_4^{ff} + 91F_6^{ff}$
$^1D(f^2)$	2	17334.39	17334.39	14887.99	$44F_2^{ff} - 48F_4^{ff} + 728F_6^{ff}$
$^3P(f^2)$	0	21389.81			
	1	22007.46	22579.47	20133.07	$70F_2^{ff} + 84F_4^{ff} - 1274F_6^{ff}$
	2	23160.61			
$^1I(f^2)$	6	22211.54	22211.54	19765.14	$50F_2^{ff} + 60F_4^{ff} + 14F_6^{ff}$
$^1S(f^2)$	-	-	-	-	$85F_2^{ff} + 249F_4^{ff} + 1729F_6^{ff}$

The columns with  $J$  and  $E(L,S,J)$  headers are experimental data for spin-orbit multiplets,  $^{2S+1}[L]_J$ .

The  $E_{av}(L,S)$  and  $\Delta E_{av}(L,S)$  columns contain weighted averages (see Eq.(1)) and their shift, with ground state in origin. The last column gives analytical energy formulas expressed through the Slater-Condon parameters.

The energy values are in  $\text{cm}^{-1}$ .

Table 2

The list of spectral terms with  $fd$  parentage, for  $\text{Pr}^{3+}$  ion.

$^{2S+1}[L]$	$J$	$E(L,S,J)$	$E_{av}(L,S)$	$\Delta E_{av}$	Energy formulas
$^1G(fd)$	4	61170.95	61170.95	58724.55	$\Delta U - 15F_2^{fd} - 22F_4^{fd} - 10G_1^{fd} + 35G_3^{fd} + 11G_5^{fd}$
$^3F(fd)$	2	61457.48			
	3	64123.54	64514.97	62068.57	$\Delta U - 11F_2^{fd} + 66F_4^{fd} - 6G_1^{fd} - 19G_3^{fd} - 55G_5^{fd}$
	4	66518.01			
$^3G(fd)$	3	63355.94			
	4	65639.95	65968.28	63521.88	$\Delta U - 15F_2^{fd} - 22F_4^{fd} + 10G_1^{fd} - 35G_3^{fd} - 11G_5^{fd}$
	5	67899.32			
$^3H(fd)$	4	63580.59			
	5	65239.39	65905.16	63458.76	$\Delta U + 10F_2^{fd} + 3F_4^{fd} - 15G_1^{fd} - 10G_3^{fd} - G_5^{fd}$
	6	68077.83			
$^1D(fd)$	2	65321.67	65321.67	62875.27	$\Delta U + 6F_2^{fd} - 99F_4^{fd} - 3G_1^{fd} - 42G_3^{fd} + 165G_5^{fd}$
$^3D(fd)$	1	66967.72			
	2	68411.51	68161.98	65715.58	$\Delta U + 6F_2^{fd} - 99F_4^{fd} + 3G_1^{fd} + 42G_3^{fd} - 165G_5^{fd}$
	3	68495.57			
$^3P(fd)$	1	70755.33			
	0	70842.93	71559.38	69112.98	$\Delta U + 24F_2^{fd} + 66F_4^{fd} - G_1^{fd} - 24G_3^{fd} - 330G_5^{fd}$
	2	72185.1			
$^1F(fd)$	3	71724.77	71724.77	69278.37	$\Delta U - 11F_2^{fd} + 66F_4^{fd} + 6G_1^{fd} + 19G_3^{fd} + 55G_5^{fd}$
$^1H(fd)$	5	75265.66	75265.66	72819.26	$\Delta U + 10F_2^{fd} + 3F_4^{fd} + 15G_1^{fd} + 10G_3^{fd} + G_5^{fd}$
$^1P(fd)$	1	78776.38	78776.38	76329.98	$\Delta U + 24F_2^{fd} + 66F_4^{fd} + G_1^{fd} + 24G_3^{fd} + 330G_5^{fd}$

The explanations are similar to the caption of previous table. The  $\Delta U$  is an overall shift, not discussed here.

The many-electron wavefunctions can be generally presented as configuration interaction (CI) problems, handling Hamiltonian matrix elements that, in the case of the atom [36], contain linear expressions of Slater-Condon integrals, standing for the inter-electron effects. There are also involved one-electron integrals, say  $h_f$  and  $h_d$ , for the case of d and f orbitals, which will not enter into the focus of the actual discussion.

It follows a somewhat pedantic derivation of the formulas outlined in Tables 1 and 2, obtainable with the details shown in the Supplementary Material and the strategy explained in the following. This is a shortcut that is affordable when a given spectral term appears only once in the list of electronic states. Thus, for the  $f^2$  case, the spectral terms are:  $^3H$ ,  $^3F$ ,  $^3P$ ,  $^1I$ ,  $^1G$ ,  $^1D$ , and  $^1S$ . Having no repeated couples of

quantum numbers means that no configuration interaction takes place, and then one does not have to solve the complete eigenvalues problems.

In turn, one may use an algebraic theorem [37] stating that the sum of eigenvalues in a Hamiltonian matrix equals the sum of diagonal matrix elements (Eq.(4)).

$$\sum_i E_i = \sum_i H_{ii} \quad (4)$$

The Hamiltonian matrices for a given couple of  $(L,S)$  quantum numbers are factored in blocks running on the  $L_z = \{-L, -L+1, \dots, 0, \dots, L-1, L\}$  and  $S_z = \{-S, \dots, S\}$  projections. States with different  $(L,S)$  definitions are found together in a Hamiltonian block having a certain  $(L_z, S_z)$  common set of projections. The energy of a term with  $(L,S)$  orbital and quantum numbers is repeated  $(2S+1)(2L+1)$  times (the term degeneracy), with the  $E_{L,S}$  quantity appearing as an eigenvalue in each subsequent  $(L_z, S_z)$  Hamiltonian block. In other words, considering only the positive projections, the eigenvalues of each  $(L_z, S_z)$  block are containing the energies of all  $E_{L,S}$  terms having  $L \geq L_z$  and  $S \geq S_z$ . For negative projections, one must reverse the sense of inequalities. One may devise a series of successive subtractions, yielding at the end the energies of  $E_{L,S}$  states, provide that each  $^{2S+1}[L]$  term appears only once in the whole list of atomic states.

The matrix element with the highest spin or orbital projection appears only in one configuration, with their values (or analytic expressions) equalling the energy of the term with maximal respective quantum numbers,  $L^{\max}$  or  $S^{\max}$ . Table 3 shows the summations obtainable from the eigenvalues of the Hamiltonian blocks of the  $f^2$  configuration. One may see that the individual energies of all the spectral terms can result from corresponding differences

between the cells of the table. For instance:  $E(^1G) = \sum_{i \in (L_z=4, S_z=0)} H_{ii} - \sum_{i \in (L_z=5, S_z=0)} H_{ii}$ . The point is that it was avoided solving the whole secular equations, being necessary only to equate the diagonal elements,  $H_{ii}$ , by virtue of Eq.(4). The evaluation of the diagonal elements is given in the Supplementary Material.

Thus, handling the content of Table 3, with the help of data from Supplementary Materials, the equations given in Table 1 for the  $f^2$  configuration can be obtained. The  $fd$  case from Table 2 can be handled in a similar way. It must be pointed out that, although certain term labels from  $f^2$  parentage are also found in the  $fd$  list (e.g.,  $^3F$ ), these do not enter in a configurational interaction, because of the different parity, acting as supplementary quantum number. The fit of experimental data handled in Tables 1 and 2 to the equations detailed in their right-side columns yields the following parameters:  $F_2^{ff} = 316.67 \text{ cm}^{-1}$ ,  $F_4^{ff} = 58.73 \text{ cm}^{-1}$ ,  $F_6^{ff} = 5.46 \text{ cm}^{-1}$ ,  $F_2^{fd} = 222.03 \text{ cm}^{-1}$ ,  $F_4^{fd} = 30.01 \text{ cm}^{-1}$ ,  $G_1^{fd} = 326.05 \text{ cm}^{-1}$ ,  $G_3^{fd} = 34.48 \text{ cm}^{-1}$ ,  $G_5^{fd} = 7.37 \text{ cm}^{-1}$ , and  $\Delta U = 54701.67 \text{ cm}^{-1}$ .

In the following, the authors will compare the experimental Slater-Condon parameters with those resulting from *ab initio* calculations performed with different basis sets. The data are presented in Table 4. The acronyms of basis sets are formed non-systematically, e.g., from the initials of the authors, like SBKJC (Stevens, Bash, Krauss, Jensen, Cundari), or from the descriptions of components, like ccptvzdk (correlation consistent triple-zeta Douglas-Kroll), or even by place names (Cologne, Sapporo). There is also no simple principle able to organize the bases in a certain hierarchy. The first lines (SBKJC, CRENBL) are bases with effective core potentials (ECP), mimicking the action of inner orbitals, while their true functions are removed. The other entries correspond to all-electrons treatment.

Table 3

**The sums of eigenvalues contained in each  $(L_z, S_z)$  Hamiltonian block, for the spectral terms resulted from the  $f^2$  configuration.**

$L_z \setminus S_z$	1	0	-1
6		$E(^1I)$	
5	$E(^3H)$	$E(^3H) + E(^1I)$	$E(^3H)$
4	$E(^3H)$	$E(^3H) + E(^1I) + E(^1G)$	$E(^3H)$
3	$E(^3H) + E(^3F)$	$E(^3H) + E(^3F) + E(^1I) + E(^1G)$	$E(^3H) + E(^3F)$
2	$E(^3H) + E(^3F)$	$E(^3H) + E(^3F) + E(^1I) + E(^1G) + E(^1D)$	$E(^3H) + E(^3F)$
1	$E(^3H) + E(^3F) + E(^3P)$	$E(^3H) + E(^3F) + E(^3P) + E(^1I) + E(^1G) + E(^1D)$	$E(^3H) + E(^3F) + E(^3P)$
0	$E(^3H) + E(^3F) + E(^3P)$	$E(^3H) + E(^3F) + E(^3P) + E(^1I) + E(^1G) + E(^1D) + E(^1S)$	$E(^3H) + E(^3F) + E(^3P)$
-1	$E(^3H) + E(^3F) + E(^3P)$	$E(^3H) + E(^3F) + E(^3P) + E(^1I) + E(^1G) + E(^1D)$	$E(^3H) + E(^3F) + E(^3P)$
-2	$E(^3H) + E(^3F)$	$E(^3H) + E(^3F) + E(^1I) + E(^1G) + E(^1D)$	$E(^3H) + E(^3F)$
-3	$E(^3H) + E(^3F)$	$E(^3H) + E(^3F) + E(^1I) + E(^1G)$	$E(^3H) + E(^3F)$
-4	$E(^3H)$	$E(^3H) + E(^1I) + E(^1G)$	$E(^3H)$
-5	$E(^3H)$	$E(^3H) + E(^1I)$	$E(^3H)$
-6		$E(^1I)$	

At first glance on Table 4, the overestimation of the  $F_2^{ff}$  parameter is visible in all cases, with a ratio computed/experimental  $\sim 1.43$ , on average. The calculated  $F_4^{ff}$  and  $F_6^{ff}$  parameters are closer to the experimental ones, with the respective averaged ratios of 1.22 and 1.07. A surprisingly good ratio, 1.04, is found for the  $F_2^{fd}$  inter-shell parameter. All the other parameters are rather strongly underestimated, with 0.80 for  $F_4^{fd}$ , 0.75 for  $G_1^{fd}$ , 0.87 for  $G_3^{fd}$  and 0.69 for  $G_5^{fd}$ .

Measuring the accuracies by the ratio of computed vs. experimental energies of the spectral terms, the series of the  $f \rightarrow f$  transitions undergo an overall overestimation of excited levels, with the  $E^{calc}/E^{exp} \sim 1.37$  averaged ratio. For the  $f \rightarrow d$  transitions, the relative gaps of the terms with respect to the lowest one ( $^1G$ ) were measured. In this way, it was discarded the incidence of the  $\Delta U$  term, which does not make the object of actual discussion. In this convention, the relative gaps on the  $fd$ -type multiplets depend only on the  $F_k^{fd}$  and  $G_k^{fd}$  inter-shell parameters. As average on all the states higher than  $^1G(fd)$ , the ratio of  $\Delta E^{calc}/\Delta E^{exp} \sim 1.3$  is, globally good:  $\sim 1.09$ . However, at a closer look, one may note that some states are underestimated, the average on sub-unitary ratios being 0.86, while the other ones are overestimated, the ratio on this subset being  $\sim 1.27$ , as mean value. The Supplementary Materials shows, in Figures S1 and S2 the computed spectral lines, in comparison with experimental references.

From a synoptic perspective, one may conclude the semiquantitative performance of the existing basis sets with respect to the reproduction of atomic spectra and their determining parameters. This may be a collateral consequence of the customary methodology for producing basis sets. The procedure consists of minimizing the total energy of a collection of systems, the neutral atom, and a few simple compounds incorporating the given atom [38-47].

A suggestion is that, in turn, stating as a criterion the good account of spectral states for the atom and its most important oxidation states may be a better way, closer to the first principles of action. Equivalently, the retrieval of Slater-Condon parameters closer to the experimental values can be set as an optimization target. The perspective of tuning a basis by calibrating the basic atomic parameters is inhibited in the calculation scaffolds of Gaussian-type orbitals because, in this frame, the integrals are expanded by factoring on Cartesian components,  $x$ ,  $y$ , and  $z$ , rather than dichotomizing in radial and angular coordinates. Then, the Gaussian-based calculation engines are ignoring the systematizing power, substantiated by spherical symmetry (*i.e.* the theoretical *corpus* defining the Slater-Condon integrals). However, as it is showed here, the SC parameters can be recovered indirectly and, in principle, chosen as pivots in the fine tuning of basis sets.

Table 4

**The Slater-Condon parameters resulted from computed CASSCF states of Pr(III) ion, using the basis sets whose acronyms and references are given on the first column. The values are in  $\text{cm}^{-1}$ .**

#	Basis/Parameters	$F_2^{ff}$	$F_4^{ff}$	$F_6^{ff}$	$F_2^{fd}$	$F_4^{fd}$	$G_1^{fd}$	$G_3^{fd}$	$G_5^{fd}$
0	Exp. (re-analyzed)	316.7	58.7	5.5	222.0	30.0	326.1	34.5	7.4
1	SBKJC [38]	439.9	56.5	6.0	237.2	17.7	570.4	36.8	5.2
2	CRENBL [39]	458.0	59.1	6.3	242.9	17.9	552.9	36.1	5.1
3	COLOGNE [40]	459.9	59.7	6.4	242.3	17.7	310.5	28.5	4.5
4	AHGBS5 [41]	467.3	60.6	6.4	237.0	17.2	301.8	27.9	4.4
5	CCPVDZDK3 [42]	508.4	66.6	7.1	252.5	18.1	276.8	27.1	4.4
6	CCPVTZDK3 [42]	504.5	65.9	7.0	240.6	17.1	271.8	26.3	4.2
7	CCPVDZX2C [42]	504.3	66.0	7.0	251.6	18.0	281.2	27.4	4.4
8	JORGE_ATZP [43]	501.3	65.4	7.0	224.4	15.7	248.6	23.8	3.8
9	JORGE_TZP [43]	503.4	65.7	7.0	241.6	17.1	264.7	25.5	4.1
10	JORGE_TZPKH [43]	508.5	66.6	7.1	239.7	16.8	254.5	24.7	4.0
11	SAPPORO_DKH3_DZP [44]	509.3	66.6	7.1	247.2	17.7	278.1	27.0	4.4
12	SAPPORO_DKH3_TZP [44]	500.6	65.3	7.0	238.6	17.0	273.0	26.3	4.2
13	SAPPORO_DKH3_QZP [44]	473.8	61.5	6.5	238.5	17.3	298.4	27.8	4.4
14	SARC2_QZV_DKH2 [45]	467.6	60.6	6.5	237.5	17.3	302.8	28.0	4.5
15	SARC2_QZVP_DKH2 [45]	467.6	60.6	6.5	237.5	17.3	302.8	28.0	4.5
16	SARC2_QZVP_ZORA [45]	467.2	60.6	6.4	237.5	17.3	303.2	28.0	4.5
17	SARC2_QZV_ZORA [45]	467.2	60.6	6.4	237.5	17.3	303.2	28.0	4.5
18	SARC_ZORA [46]	431.8	55.7	5.9	257.3	19.4	363.0	32.6	5.2
19	SARC_DKH2 [46]	431.9	55.7	5.9	257.6	19.4	363.1	32.6	5.2
20	UGBS [47]	465.5	60.2	6.4	277.5	20.6	362.0	33.7	5.4

Another caveat about the hidden drawbacks of GTOs lies in the architecture of their primitives. Thus, the atomic orbitals with a given secondary quantum number,  $l$ , are made of  $r^l \cdot \exp(-\zeta r^2)$  pieces, the set of  $\zeta$  being adjustable. Usually, it is believed that the shortcomings of GTOs consist in using the  $\exp(-\zeta r^2)$  exponential instead of the Slater-type one,  $\exp(-\zeta r)$ , expected to be more suitable for atoms, if recall the exact solutions for the hydrogen atom. A less observed weakness stays in the rigid nature of the pre-exponential factor,  $r^l$ , for a given  $l$  shell. Thus, the  $4f$  orbitals are made only by  $r^3 \cdot \exp(-\zeta r^2)$  primitives, which is qualitatively reasonable considering the node-less hydrogenic  $4f$  orbital,  $r^3 \cdot \exp(-Zr/3)$ , and also that, intuitively, the mixing of higher  $5f$  or  $6f$  functions is not expected in the chemistry of lanthanides. On the other hand, the  $6d$  shell, of interest for the exposed problems, is expanded only with the  $r^2$  factor, lacking useful degrees of freedom in the construction of the wavefunction. By comparison, in the code called Amsterdam Density Functional (ADF) [48], one of the few packages based on Slater-type orbitals, the construction of  $d$  orbitals includes  $r^2$ ,  $r^3$  and  $r^4$  factors, the higher powers being necessary ingredients for specific features of outer orbits. Such intrinsic limitations of GTO frame, inherited from the early ages of computational chemistry, are probably impeding the performance of basis sets, particularly in special instances such as the excited states of heavy elements.

Here, the GTO principles for the less perfect account of Slater-Condon parameters are criticized because, at least in the debated particular case, the accuracy in their retrieval is directly related with the construction of the basis set. One may counter-opine that improvements are possible with extended methods, such as larger active spaces or second-order perturbations [49,50]. This may be true, as technical realism, but yet disputable at the conceptual level, because what is expected from the post-CASSCF perturbation correction is the gain in the so-called correlation effects, coming from the interaction of the many configurations expected in the enlarged account. However, one may advocate that the Pr(III) ion, in its  $f^2$  and  $f^1 d^1$  orbital configurations, is almost free of correlation effects. More concretely, the states encountered in a large energy domain, in the range of  $10^5$  Hartree, span different orbital and spin quantum numbers, *i.e.*, a situation precluding their mutual configuration interaction. Therefore, whatever attainable

correction may be spurious, because, as a matter of principle, in the absence of configuration interactions over a large energy window, a good result should be expected in the CASSCF mode. The authors are in disfavour of second-order post-CASSCF increments [49,50], because these are prone to arbitrary conventions and do not obey the self-consistency principles. Conceptually, the CASSCF techniques are the perfect choice to describe optical and magnetic properties of lanthanide compounds, transparently accounting the many-electron nature of wavefunctions.

## Conclusions

Taking the case of Pr(III) ion as a fortunate situation where rich experimental data on spectral terms are available and, at the same time, their theoretical expressions can be obtained analytically, the authors assess the performance of various basis sets in accounting for the  $f \rightarrow f$  and  $f \rightarrow d$  transitions. The incidence of spin-orbit coupling is eliminated by corresponding weighted averages. A pedantic derivation of the spectral term energies, as function of Slater-Condon parameters, is given. It was applied a shortcut that avoids the resolution of the complete eigenvalue problem, using only the diagonal elements of the Hamiltonian matrix.

The CASSCF calculations with two electrons in the space of twelve orbitals from  $4f$  and  $5d$  sets are performed with a series of twenty GTO basis sets, forming the quasi-totality of available data. The performance in retrieving the computed spectral terms (in comparison to the experiment) is satisfactory, but the authors suggest the hidden GTO drawbacks that may impede a better match. A conceptual strategy for improving the GTO methodology is outlined. It is impossible to apply the suggested hints here, because this would imply a prohibitive technical effort. However, we put the issue on the table, as a matter of critical debate and as an announcement about our further commitment on this issue.

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## Supplementary information

Supplementary data are available free of charge at <http://cjm.ichem.md> as PDF file.

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