

Supporting Information:

**Ab Initio Non-Covalent Crystal Field Theory for
Lanthanide Complexes: A Multiconfigurational
Non-Orthogonal Group Functions Approach**

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Spin partitioning

Some simplification can be done nothing that \mathbf{S} is block diagonal in the spin coordinates. Then, \mathbf{S}^{-1} is explicitly given by:

$$\mathbf{S}^{-1} = \begin{pmatrix} \mathbf{S}_{\alpha\alpha}^{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_{\beta\beta}^{-1} \end{pmatrix} \quad (\text{S1})$$

and the term in the right-hand side of eq. (49) in the main text reads:

$$\langle \phi_i | h | \phi_j \rangle \text{cof}[\mathbf{S}](ij) = \delta_{\eta_i \eta_j} \langle \chi_i | h | \chi_j \rangle \text{cof}[\mathbf{S}](ij) \quad (\text{S2})$$

where χ_i/η_i is the spatial/spin part of ϕ_i , and:

$$\text{cof}[\mathbf{S}](ij) = \begin{cases} \text{cof}[\mathbf{S}_{\alpha\alpha}](ij) \det(\mathbf{S}_{\beta\beta}) & \text{if } \eta_i = \eta_j = \alpha \\ \text{cof}[\mathbf{S}_{\beta\beta}](ij) \det(\mathbf{S}_{\alpha\alpha}) & \text{if } \eta_i = \eta_j = \beta \end{cases} \quad (\text{S3})$$

The matrix partitioning presented in eq. (53) is now applied to $\mathbf{S}_{\alpha\alpha}$ and $\mathbf{S}_{\beta\beta}$ blocks. In a similar way, the term in the right-hand side of eq. (50) reads:

$$\langle \phi_i \phi_k | g | \phi_j \phi_l \rangle \text{cof}[\mathbf{S}](ij|kl) = \delta_{\eta_i \eta_j} \delta_{\eta_k \eta_l} \langle \chi_i \chi_k | g | \chi_j \chi_l \rangle \text{cof}[\mathbf{S}](ij|kl) \quad (\text{S5})$$

with:

$$\text{cof}[\mathbf{S}](ij|kl) = \begin{cases} \text{cof}[\mathbf{S}_{\alpha\alpha}](ij|kl) \det(\mathbf{S}_{\beta\beta}) & \text{if } \eta_i = \eta_j = \eta_k = \eta_l = \alpha \\ \text{cof}[\mathbf{S}_{\beta\beta}](ij|kl) \det(\mathbf{S}_{\alpha\alpha}) & \text{if } \eta_i = \eta_j = \eta_k = \eta_l = \beta \\ \text{cof}[\mathbf{S}_{\alpha\alpha}](ij) \text{cof}[\mathbf{S}_{\beta\beta}](kl) & \text{if } \eta_i = \eta_j = \alpha, \text{ and } \eta_k = \eta_l = \beta \\ \text{cof}[\mathbf{S}_{\beta\beta}](ij) \text{cof}[\mathbf{S}_{\alpha\alpha}](kl) & \text{if } \eta_i = \eta_j = \beta, \text{ and } \eta_k = \eta_l = \alpha \end{cases} \quad (\text{S6})$$

Note that in the last two cases the second-order cofactor reduces to the product of two first-order cofactors.

Cholesky representation

A strategy that allows for a significant speed up in the computations is the use of the Cholesky representation of the two-electron repulsion integrals (ERI). Within this representation, the ERIs are defined as:

$$\langle \chi_i \chi_k | g | \chi_j \chi_l \rangle = \sum_J L_{ij}^J L_{kl}^J \quad (\text{S10})$$

where L_{ij}^J is a component of the J -th Cholesky vector \mathbf{L}^J . Partitioning both $\mathbf{S}_{\alpha\alpha}$ and $\mathbf{S}_{\beta\beta}$ blocks as shown in eq.(53), and defining the three matrices:

$$\mathbf{T}^J = \mathbf{L}^J \mathbf{T} \quad \mathbf{W}^J = \mathbf{L}^J \mathbf{W} \quad \mathbf{K}^J = \mathbf{Y}' \mathbf{L}^J \mathbf{X}' \quad (\text{S11})$$

eq. (S5) can be written for the case $\eta_i = \eta_j = \eta_k = \eta_l = \alpha$ as (similar development for the case $\eta_i = \eta_j = \eta_k = \eta_l = \beta$):

$$\begin{aligned} & \sum_{\substack{i < k \\ i, k \in \alpha}} \sum_{\substack{j < l \\ j, l \in \alpha}} \left[\langle \phi_i \phi_k | g | \phi_j \phi_l \rangle - \langle \phi_i \phi_k | g | \phi_l \phi_j \rangle \right] \text{cof}[\mathbf{S}](ij|kl) \\ &= \det(\mathbf{S}_{\beta\beta}) \det(\mathbf{A}) \sum_J \left\{ \det(\mathbf{Z}) \sum_{i < k} (T_{ii}^J T_{kk}^J - T_{ik}^J T_{ki}^J) \right. \\ & \quad + \sum_{i < k} (T_{ii}^J W_{kk}^J - T_{ik}^J W_{ki}^J + W_{ii}^J T_{kk}^J - W_{ik}^J T_{ki}^J) \\ & \quad \left. + \sum_{p < r} \sum_{q < s} \text{cof}[\mathbf{Z}](qp|sr) (K_{qp}^J K_{sr}^J - K_{qr}^J K_{sp}^J) \right\} \quad (\text{S12}) \end{aligned}$$

We made use of the following simplifications:

$$\begin{aligned} & \sum_{i < k} \sum_{j < l} (L_{ij}^J L_{kl}^J - L_{il}^J L_{kj}^J) (T_{ji} T_{lk} - T_{li} T_{jk}) \\ &= \frac{1}{2} \sum_{i < k} \sum_{j < l} (L_{ij}^J L_{kl}^J - L_{il}^J L_{kj}^J) (T_{ji} T_{lk} - T_{li} T_{jk}) \\ &= \frac{1}{2} \sum_{i < k} \sum_{j < l} (L_{ij}^J T_{ji} L_{kl}^J T_{lk} - L_{ij}^J T_{jk} L_{kl}^J T_{li} + L_{il}^J T_{li} L_{kj}^J T_{jk} - L_{il}^J T_{lk} L_{kj}^J T_{ji}) \\ &= \sum_{i < k} (T_{ii}^J T_{kk}^J - T_{ik}^J T_{ki}^J) \quad (\text{S13}) \end{aligned}$$

$$\begin{aligned} & \sum_{i < k} \sum_{j < l} (L_{ij}^J L_{kl}^J - L_{il}^J L_{kj}^J) (T_{ji} W_{lk} - T_{li} W_{jk} + W_{ji} T_{lk} - W_{li} T_{jk}) \\ &= \frac{1}{2} \sum_{i < k} \sum_{j < l} (L_{ij}^J L_{kl}^J - L_{il}^J L_{kj}^J) (T_{ji} W_{lk} - T_{li} W_{jk} + W_{ji} T_{lk} - W_{li} T_{jk}) \\ &= \frac{1}{2} \sum_{i < k} \sum_{j < l} (L_{ij}^J T_{ji} L_{kl}^J W_{lk} - L_{ij}^J W_{jk} L_{kl}^J T_{li} + L_{ij}^J W_{ji} L_{kl}^J T_{lk} - L_{ij}^J T_{jk} L_{kj}^J T_{jk} \\ & \quad - L_{il}^J W_{lk} L_{kj}^J T_{jk} + L_{il}^J T_{li} L_{kj}^J W_{jk} - L_{il}^J T_{lk} L_{kj}^J W_{ji} + L_{il}^J W_{li} L_{kj}^J T_{jk}) \\ &= \sum_{i < k} (T_{ii}^J W_{kk}^J - T_{ik}^J W_{ki}^J + W_{ii}^J T_{kk}^J - W_{ik}^J T_{ki}^J) \quad (\text{S14}) \end{aligned}$$

$$\begin{aligned}
& \frac{1}{2} \sum_{i \neq k} \sum_{j \neq l} L_{ij}^J L_{kl}^J \sum_{p < r} \sum_{q < s} \text{cof}[\mathbf{Z}](qp|sr) (X_{jp} X_{lr} - X_{jr} X_{lp}) (Y_{qi} Y_{sk} - Y_{si} Y_{qk}) \\
&= \frac{1}{2} \sum_{p < r} \sum_{q < s} \text{cof}[\mathbf{Z}](qp|sr) \sum_{ik} \sum_{jl} \left(Y_{qi} L_{ij}^J X_{jp} Y_{sk} L_{kl}^J X_{lr} - Y_{si} L_{ij}^J X_{jp} Y_{qk} L_{kl}^J X_{lr} \right. \\
&\quad \left. + Y_{si} L_{ij}^J X_{jr} Y_{qk} L_{kl}^J X_{lp} - Y_{qi} L_{ij}^J X_{jr} Y_{sk} L_{kl}^J X_{lp} \right) \\
&= \sum_{p < r} \sum_{q < s} \text{cof}[\mathbf{Z}](qp|sr) \left(K_{qp}^J K_{sr}^J - K_{qr}^J K_{sp}^J \right) \tag{S15}
\end{aligned}$$

For the case $\eta_i = \eta_j = \alpha$ and $\eta_k = \eta_l = \beta$ we have (similar development for the case $\eta_i = \eta_j = \beta$, and $\eta_k = \eta_l = \alpha$):

$$\begin{aligned}
& \sum_{i < k} \sum_{j < l} \left[\langle \phi_i \phi_k | g | \phi_j \phi_l \rangle - \langle \phi_i \phi_k | g | \phi_l \phi_j \rangle \right] \text{cof}[\mathbf{S}](ij|kl) \\
&= \sum_{ij \in \alpha} \sum_{kl \in \beta} \langle \chi_i \chi_k | g | \chi_j \chi_l \rangle \text{cof}[\mathbf{S}](ij) \text{cof}[\mathbf{S}](kl) \\
&= \sum_J \left[\sum_{ij} L_{ij}^J \text{cof}[\mathbf{S}_{\alpha\alpha}](ij) \right] \left[\sum_{kl} L_{kl}^J \text{cof}[\mathbf{S}_{\beta\beta}](kl) \right] \\
&= \sum_J \text{Tr}(\mathbf{T}_{\alpha\alpha}^J + \mathbf{W}_{\alpha\alpha}^J) \cdot \text{Tr}(\mathbf{T}_{\beta\beta}^J + \mathbf{W}_{\beta\beta}^J) \tag{S16}
\end{aligned}$$

where $\text{Tr}(\mathbf{T})$ is the trace of the matrix \mathbf{T} .

Magnetic moment and g -tensor

The γ cartesian component of the magnetic moment operator μ_γ is defined in terms of the γ components of the total orbital-angular momentum $\mathcal{L}_\gamma = \sum_i^{N_{\text{TOT}}} l_\gamma(i)$ and the total spin-angular momentum $\mathcal{S}_\gamma = \sum_i^{N_{\text{TOT}}} s_\gamma(i)$ as:

$$\mu_\gamma = -(\mathcal{L}_\gamma + g_e \mathcal{S}_\gamma) \tag{S17}$$

where is g_e the electron spin g -factor. The expectation values of the orbital-angular momentum on the product functions basis set is then given by:

$$\langle \Psi_n | \mathcal{L}_\gamma | \Psi_{n'} \rangle = \sum_{ij}^{N_{\text{TOT}}} \langle \phi_i | l_\gamma | \phi_j \rangle \text{cof}[\mathbf{S}](ij) \tag{S18}$$

It is easy to see that the z component of the total spin-angular momentum is given by:

$$\langle \Psi_n | \mathcal{S}_z | \Psi_{n'} \rangle = \frac{M_S}{2} \det(\mathbf{S}) \tag{S19}$$

where $M_S = (N_\alpha^{\text{TOT}} - N_\beta^{\text{TOT}})$. For the development of the equations for the x and y components it is more convenient to make use of the spin ladder operators:

$$s_x(i) = \frac{s_+(i) + s_-(i)}{2} \quad (\text{S20})$$

$$s_y(i) = i \frac{s_-(i) - s_+(i)}{2} \quad (\text{S21})$$

$s_+(i)$ operator flips the spin of the orbital $\phi_i = \chi_i \eta_i$ in $\Psi_{n'}$ from β to α , or it destroys $\Psi_{n'}$ if $\eta_i = \alpha$, or $s_+(i) | \Psi_{n'} \rangle = 0$. Similarly, $s_-(i)$ flips η_i from α to β . $s_+(i)$ acting on a product function leads to:

$$\begin{aligned} \langle \Psi_n | s_+(i) | \Psi_{n'} \rangle &= \langle \Psi_n | \Psi_{n'} [\chi_i \beta \rightarrow \chi_i \alpha] \rangle \\ &= \det(\mathbf{S}') \end{aligned} \quad (\text{S22})$$

where $\mathbf{S}' = \mathbf{S}[\chi_i \beta \rightarrow \chi_i \alpha]$. Note that if ϕ_i is an inactive orbital $\det(\mathbf{S}') = 0$, due to the presence of two identical columns. By the use of eq. (S20) and (S21), \mathcal{S}_x and \mathcal{S}_y on the product functions basis are given by:

$$\langle \Psi_n | \mathcal{S}_x | \Psi_{n'} \rangle = \frac{1}{2} \sum_i^{N_{\text{act}}} \langle \Psi_n | s_+(i) + s_-(i) | \Psi_{n'} \rangle \quad (\text{S23})$$

$$\langle \Psi_n | \mathcal{S}_y | \Psi_{n'} \rangle = \frac{i}{2} \sum_i^{N_{\text{act}}} \langle \Psi_n | s_-(i) - s_+(i) | \Psi_{n'} \rangle \quad (\text{S24})$$

Finally, the explicit form of the g -tensor for the system are calculated as the eigenvalues of the \mathbf{G} matrix, defined by:

$$G_{\gamma,\delta} = \sum_{ij} \langle \Phi_i | \mu_\gamma | \Phi_j \rangle \langle \Phi_j | \mu_\delta | \Phi_i \rangle \quad (\text{S25})$$

Statistics

Table S1: Mean μ and standard deviation σ for the % errors affecting the energies within the ground spin-orbit multiplet 7F_6 of different Tb(III) complexes estimated using the different methods presented in this work versus the results calculated at CAHF/CASCI-SO level on the whole systems.

	FAIMP1		FAIMP2		FAIMP3		NOGF1		NOGF2		NOGF3	
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
acac3-2h2o	-37.5	15.0	-39.7	13.5	-5.9	11.4	-28.8	6.9	-19.7	16.6	+16.2	8.0
acac3-dpq	-70.1	5.2	-49.8	6.7	-30.6	7.9	-35.6	8.5	-11.7	6.6	+3.5	6.3
acac3-dppz	-63.6	5.7	-57.4	5.5	-23.1	8.1	-58.7	12.6	-14.8	11.3	+13.1	9.6
acac3-phen	-73.4	3.2	-48.4	3.0	-22.2	6.5	-48.2	5.4	-8.8	3.9	+15.3	6.0
pc2-	-67.8	15.1	-47.2	9.7	-40.3	11.9	-15.7	4.4	-0.6	6.8	+5.4	3.1
paah2-2no3-meoh	-71.4	3.7	-30.4	9.7	+8.2	17.7	-39.1	9.0	+7.6	9.0	+44.1	16.2
tta3-bipy	-79.6	5.8	-66.0	2.9	-38.7	7.0	-76.3	9.8	-16.9	5.2	+11.3	8.3
tta3-phen	-74.4	4.5	-54.4	3.9	-34.8	6.5	-49.6	7.9	-11.8	4.2	+7.3	5.4
tfpb3-dppz	-77.9	6.3	-59.4	6.5	-42.4	9.0	-53.2	12.2	-14.3	10.8	+2.6	10.8
hfac3-glyme	-79.3	4.8	-55.6	6.1	-32.4	7.9	-66.8	10.1	-12.9	6.8	+10.5	8.4

Table S2: Mean μ and standard deviation σ for the % errors affecting the energies within the ground spin-orbit multiplet ${}^6H_{15/2}$ of different Dy(III) complexes estimated using the different methods presented in this work versus the results calculated at CAHF/CASCI-SO level on the whole systems.

	FAIMP1		FAIMP2		FAIMP3		NOGF1		NOGF2		NOGF3	
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
acac3-2h2o	-70.7	3.6	-58.9	10.3	-44.4	10.2	-60.2	12.2	-20.1	8.5	-3.3	6.8
acac3-dpq	-68.8	5.1	-54.2	3.5	-39.0	5.2	-45.6	7.9	-20.9	6.5	-4.2	7.5
acac3-dppz	-77.0	3.4	-65.9	4.3	-47.8	5.6	-57.4	8.9	-25.0	5.2	-6.3	6.0
acac3-phen	-76.9	1.9	-57.4	2.2	-40.4	3.9	-49.5	5.3	-20.1	5.0	-2.6	5.8
pc2-	+31.0	86.8	-4.2	37.0	+5.4	44.9	-28.3	27.2	-8.9	18.7	-4.9	18.8
trensai	-68.1	19.1	-63.2	5.0	-40.8	11.2	-10.9	13.5	-14.3	11.7	+2.2	15.7
paah2-2no3-meoh	-79.7	5.8	-48.6	1.2	-24.6	2.3	-53.5	4.2	-6.6	4.5	+17.4	5.8
tta3-bipy	-72.1	8.4	-64.3	5.9	-40.8	11.6	-61.8	3.7	-27.4	5.4	-7.9	9.7
tta3-phen	-70.5	6.0	-59.3	4.6	-39.4	8.4	-64.4	11.4	-24.8	7.2	-4.4	8.4
tfpb3-dppz	-74.5	7.8	-66.0	4.5	-49.0	7.5	-62.7	7.1	-30.6	6.3	-14.5	6.5
hfac3-glyme	-70.8	3.6	-59.2	2.9	-40.5	6.1	-56.9	4.8	-26.1	6.9	-8.4	8.3

Table S3: Mean μ and standard deviation σ for the % errors affecting the energies within the ground spin-orbit multiplet 5I_8 of different Ho(III) complexes estimated using the different methods presented in this work versus the results calculated at CAHF/CASCI-SO level on the whole systems.

	FAIMP1		FAIMP2		FAIMP3		NOGF1		NOGF2		NOGF3	
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
acac3-2h2o	-66.2	10.8	-71.4	7.6	-66.0	11.3	-43.3	14.6	-23.2	2.9	-17.6	8.5
acac3-dpq	-68.5	4.4	-73.7	3.9	-67.8	4.8	-41.3	5.2	-20.7	5.9	-12.3	9.2
acac3-dppz	-74.8	4.7	-76.7	2.3	-68.2	2.5	-51.5	5.1	-27.1	4.2	-18.3	6.4
pc2-	-11.8	37.9	+1.2	48.0	+3.2	49.6	+29.7	102.9	-30.5	16.1	-26.4	15.6
paah2-2no3-meoh	-77.1	3.1	-71.9	3.9	-60.0	5.8	-53.7	3.1	-20.4	7.7	-8.6	12.5
tta3-bipy	-80.8	6.7	-79.5	2.9	-70.3	3.8	-56.5	3.0	-28.4	3.3	-19.8	5.1
tta3-phen	-71.5	3.8	-77.1	3.8	-68.7	4.0	-52.6	3.2	-26.8	2.9	-18.6	5.6
tfpb3-dppz	-69.0	5.6	-78.5	5.0	-49.5	3.1	-49.5	3.1	-14.5	19.0	-25.4	5.3

Table S4: Mean μ and standard deviation σ for the % errors affecting the energies within the ground spin-orbit multiplet $^4I_{15/2}$ of different Er(III) complexes estimated using the different methods presented in this work versus the results calculated at CAHF/CASCI-SO level on the whole systems.

	FAIMP1		FAIMP2		FAIMP3		NOGF1		NOGF2		NOGF3	
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
acac3-2h2o	-51.7	13.0	-32.3	14.6	-19.7	17.1	-44.8	6.0	-12.3	10.0	-0.3	16.9
acac3-dpq	-53.1	14.5	-46.6	18.4	-42.4	14.4	-27.6	18.6	-7.9	24.1	+1.0	30.4
acac3-dppz	-43.2	25.7	-54.6	15.8	-46.2	15.4	-43.5	5.3	-27.2	6.5	-17.6	10.6
acac3-phen	-61.5	7.3	-56.5	12.1	-44.7	12.0	-39.7	9.5	-14.7	19.7	+0.1	32.1
trensal	-54.9	23.7	-62.4	14.2	-43.9	22.4	-38.1	18.0	-21.7	21.8	-21.8	21.7
paah2-2no3-meoh	-80.8	4.9	-77.4	3.0	-67.5	4.2	-52.0	2.2	-32.0	3.3	-26.4	5.2
tta3-bipy	-69.9	9.0	-67.1	9.1	-62.9	5.1	-48.3	5.0	-34.4	5.9	-25.3	7.4
tta3-phen	-63.4	6.5	-40.8	34.0	-38.6	25.3	-37.8	13.2	-14.2	16.8	-2.8	25.4
tfpb3-dppz	-59.1	10.3	-35.1	49.1	-37.8	39.8	-36.3	18.2	-18.9	13.5	-25.6	8.4
hfac3-glyme	-67.2	8.9	-35.5	40.9	-28.5	39.3	-44.5	7.1	-19.1	15.5	-6.7	22.6