

#### LFDFT – a practical tool for coordination chemistry

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○ SCM team





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#### Content

#### Introduction

- Ligand-field method and DFT (how do we obtain non-empirical parameters?)
- Some examples for application
  - Luminescence of lanthanide complexes: 4f -> 4f
  - Luminescence of lanthanide complexes: 4f -> 5d
  - XAS spectra: lanthanide 3d -> 4f, transition metal 2p -> 3d
- Future developments
  - Intensities of lanthanide 4f -> 4f and transition metal 3d -> 3d transitions
  - Pre-edge energy region of transition metal K-edge XAS: 1s -> 3d
  - Resonant X-ray Inelastic Scattering (RIXS): actinide 3d -> 5f + 4f-> 3d

Demo

#### Introduction



#### Why LFDFT?



- Coordination compounds: metal ion + ligands
- The electronic structure results with open-shell electrons
- Standard DFT method does not work (near-degeneracy correlation and multiplet structure)

#### **Ligand-field Model**



The multi-electronic effective Hamiltonian



3d-3d transitions: M. Atanasov, C. Daul and C. Rauzy, *Struct. Bonding* **2004**, *106*, 97. 4f-5d transitions: H. Ramanantoanina, M. Shanoun, A. Barbiero, M. Ferbinteanu and F. Cimpoesu, *Phys. Chem. Chem. Phys.*, **2015**, *17*, 18547 XAS: H. Ramanantoanina, *Phys. Chem. Chem. Phys.*, **2017**, *19*, 32481

#### **Ligand-field Model**



Inter-electron repulsion

$$H_{ER} = \sum_{k} W^{k}(nl, nl) \varphi_{k}(nl, nl)$$
Coefficients
Slater integrals

Spin-orbit coupling

$$H_{SO} = \sum_{i} \zeta_{n_{i}l_{i}}(r_{i}) (l_{i} \cdot s_{i})$$
  
Coefficients

Spin-orbit coupling constant

Ligand-field interaction

$$H_{LF} = \sum_{k} \sum_{q} B_{q}^{k} (nl, nl) C_{q}^{(k)}$$
Coefficients

Ligand-field parameters

3d-3d transitions: M. Atanasov, C. Daul and C. Rauzy, *Struct. Bonding* **2004**, *106*, 97. 4f-5d transitions: H. Ramanantoanina, M. Shanoun, A. Barbiero, M. Ferbinteanu and F. Cimpoesu, *Phys. Chem. Chem. Phys.*, **2015**, *17*, 18547 XAS: H. Ramanantoanina, *Phys. Chem. Chem. Phys.*, **2017**, *19*, 32481

#### **Ligand-field Model**



Inter-electron repulsionSpin-orbit coupling $H_{ER} = \sum_{k} W^k(nl,nl) \varphi_k(nl,nl)$ <br/>Coefficients $H_{SO} = \sum_{i} \zeta_{n_i l_i}(r_i) (l_i \cdot s_i)$ <br/>CoefficientsSlater integralsSpin-orbit coupling constant

Ligand-field interaction

 $H_{LF} = \sum_{k} \sum_{q} B_{q}^{k}(nl, nl) C_{q}^{(k)}$ Coefficients Ligand-field parameters

Coefficients for a given configuration are stored in /amshome/atomicdata

Parameters have to be calculated from first principles



Single Point DFT calculation (select the active subspace)

Important Keywords

Symmetry NOSYM

IrrepOccupations
 A (average of configuration)
End



Single Point DFT calculation (select the active subspace)

Important Keywords

Symmetry NOSYM

IrrepOccupations A (average of configuration) End To represent the electron configuration at hand:

For 3d<sup>n</sup>, 5 MOs with predominant 3d character are occupied with n/5 electrons

For 4f<sup>n</sup>, 7 MOs with predominant 4f character are occupied with n/7 electrons



**Practical example** 



#### MnF<sub>2</sub>, crystal structure



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5 MOs with nearly atomic characters are occupied with fractional electrons (Mn config. 3d<sup>5</sup>)



The matrix elements of the ligand-field potential are extracted from the MO energies and eigenfunctions

The ligand-field potential parameterizes the Hamiltonian term  $H_{LF}$ 

	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>z2</sub>	3d <sub>yz</sub>	3d <sub>x2-y2</sub>	Δ
<i>t</i> <sub>2g</sub> (#1)						$c_g$
t <sub>2g</sub> (#2)						
e <sub>g</sub> (#1)						
t <sub>2g</sub> (#3)						+
e <sub>g</sub> (#2)						<b>ı</b> 2g



The matrix elements of the ligand-field potential is a matrix with 5 by 5 elements

	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>z2</sub>	3d <sub>yz</sub>	3 <i>d</i> <sub>x2-y2</sub>
<i>t</i> <sub>2g</sub> (#1)	-0.4000	0.0000	0.0000	0.0000	0.0000
<i>t</i> <sub>2g</sub> (#2)	0.0000	-0.4000	0.0000	0.0000	0.0000
e <sub>g</sub> (#1)	0.0000	0.0000	0.6000	0.0000	0.0000
<i>t</i> <sub>2g</sub> (#3)	0.0000	0.0000	0.0000	-0.4000	0.0000
e <sub>g</sub> (#2)	0.0000	0.0000	0.0000	0.0000	0.6000





	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>z2</sub>	3d <sub>yz</sub>	3 <i>d</i> <sub>x2-y2</sub>
<i>t</i> <sub>2g</sub> (#1)	-0.4000	0.0000	0.0000	0.0000	0.0000
t <sub>2g</sub> (#2)	0.0000	-0.4000	0.0000	0.0000	0.0000
e <sub>g</sub> (#1)	0.0000	0.0000	0.6000	0.0000	0.0000
t <sub>2g</sub> (#3)	0.0000	0.0000	0.0000	-0.4000	0.0000
e <sub>g</sub> (#2)	0.0000	0.0000	0.0000	0.0000	0.6000





The Slater integrals and spin-orbit coupling constants are derived from the radial functions

These integrals parameterize the Hamiltonian term  $H_{ER}$  and  $H_{SO}$ 



 $R_{3d, atomic}$ 

r.R<sub>3d, eg</sub>



The Slater integrals and spin-orbit coupling constants are derived from the radial functions

These integrals parameterize the Hamiltonian term  $H_{ER}$  and  $H_{SO}$ 

*r.R*<sub>3d, t2g</sub>

2

*r* [Å]

3

Δ

5

The dashed blue line represents an average radial function

$$R_{nl,av} = \frac{1}{2l+1} \sum_{i}^{2l+1} R_{nl,i}$$

1.0

0.8

0.6

0.4

0.2

0.0

r.R<sub>3d</sub>



- $(MnX_6)^{4-}$ , with X = F<sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup>
- Slater Integrals and spin-orbit coupling from radial functions

$$F^{k}(3d, 3d) = \int_{0}^{\infty} \int_{0}^{\infty} \frac{r_{<}^{k}}{r_{>}^{k+1}} R_{3d}^{2}(r_{1}) R_{3d}^{2}(r_{2}) r_{1}^{2} r_{2}^{2} dr_{1} dr_{2}$$



F.M.F. de Groot et al, J. Electron Spectrosc. Relat. Phenom. 2021, 249, 147061

### • $(MnX_6)^{4-}$ , with X = F<sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup>

Slater Integrals and spin-orbit coupling from radial functions

$$F^{k}(3d, 3d) = \int_{0}^{\infty} \int_{0}^{\infty} \frac{r_{<}^{k}}{r_{>}^{k+1}} R_{3d}^{2}(r_{1}) R_{3d}^{2}(r_{2}) r_{1}^{2} r_{2}^{2} dr_{1} dr_{2}$$

Reduction of the Slater integrals = Nephelauxetic effect == covalency



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#### How do we obtain the parameters?





#### **Examples for Application**













Neodymium 60

Nd

144.2



Lasers Ο Ο

Gadolinium 64

Gd

157.3





**Biomedical Analyses and Imaging** 

J.-C. Bünzli, Chem. Rev., 2010, 110, 2729; J. Dreiser, J. Phys.: Condens. Matter, 2015, 27, 183203

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Lighting technology

Luminescence properties *versus* trivalent lanthanide ions

Based on  $4f^n - 4f^{n*}$  transitions, the spectral energy range of the visible light is entirely covered.



But, these transitions are formally forbidden

Also, the 4f electrons have core-like properties. Therefore the luminescence is not really

affected by chemical environments by the lanthanide center





Eu(NO<sub>3</sub>)<sub>3</sub>(phenanthroline)<sub>2</sub>

 The central Eu<sup>3+</sup> ion is mainly in a ground 4f<sup>6</sup> electron configuration (Ground-state in Russel-Saunders <sup>7</sup>F)

• The spin-orbit coupling split this ground state into 7 components  ${}^{7}F_{0} + {}^{7}F_{1} + {}^{7}F_{2} + {}^{7}F_{3} + {}^{7}F_{4} + {}^{7}F_{5} + {}^{7}F_{6}$ 

 The ligand-field interaction splits the atomic multiplets the atomic multiplet terms.

Exp. Data available (good to validate the method)

H. Ramanantoanina, Computation 2022, 10, 70



 $Eu^{3+} 4f^6 \rightarrow 4f^6$ 



 $Eu(NO_3)_3$ (phenanthroline)<sub>2</sub>

Leve	Levels		LFDFT				Percent Error			
State	Ι	PBE	B3LYP	PBE0	KMLYP		(1)	(2)	(3)	(4)
$^{7}F_{0}$	А	0	0	0	0	0	-	-	-	-
$^{7}F_{1}$	А	214	261	273	349	295	-27.46	-11.53	-7.46	18.31
	В	393	396	392	368	367	7.08	7.90	6.81	0.27
	В	700	523	498	389	444	57.66	17.79	12.16	-12.39
<sup>7</sup> F <sub>2</sub>	В	946	971	974	986	947	-0.11	2.53	2.85	4.12
	В	1020	975	980	1022	981	3.98	-0.61	-0.10	4.18
	А	1047	1117	1108	1023	1016	3.05	9.94	9.06	0.69
	А	1288	1134	1109	1027	1080	19.26	5.00	2.69	-4.91
	А	1323	1135	1112	1039	1111	19.08	2.16	0.09	-6.48
<sup>7</sup> F <sub>3</sub>	В	1882	1884	1874	1839		-	-	-	-
	А	1909	1894	1882	1852		-	-	-	-
	В	1952	1919	1905	1859	1808	7.96	6.14	5.37	2.82
	А	2011	1926	1910	1865	1846	8.94	4.33	3.47	1.03
	В	2027	1932	1913	1870	1857	9.15	4.04	3.02	0.70
	В	2032	1932	1921	1873	1893	7.34	2.06	1.48	-1.06
_	А	2137	1985	1962	1874		-	-	-	-
${}^{7}F_{4}$	В	2244	2742	2764	2771	2587	-13.26	5.99	6.84	7.11
	А	2473	2812	2818	2780	2603	-4.99	8.03	8.26	6.80
	А	2698	2834	2834	2799	2633	2.47	7.63	7.63	6.30
	В	2790	2890	2876	2801	2648	5.36	9.14	8.61	5.78
	А	2866	2897	2885	2812	2735	4.79	5.92	5.48	2.82
	А	2945	2913	2888	2838	2872	2.54	1.43	0.56	-1.18
	А	3072	2915	2898	2843	2946	4.28	-1.05	-1.63	-3.50
	В	3179	2983	2945	2850	2967	7.15	0.54	-0.74	-3.94
_	В	3245	2987	2950	2886	3086	5.15	-3.21	-4.41	-6.48
$^{5}D_{0}$	А	16,081	16,517	16,535	16,874	17,241	-6.73	-4.20	-4.09	-2.13
<sup>5</sup> D <sub>1</sub>	А	17,705	18,128	18,143	18,485	18,945	-6.55	-4.31	-4.23	-2.43
	В	17,716	18,164	18,176	18,488		-	-	-	-
	В	17,806	18,199	18,206	18,493		-	-	-	-

H. Ramanantoanina, Computation 2022, 10, 70



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	${}^{7}F_{1}$	А	214	261	273	349	295	-27.46	-11.53	-7.46	18.31
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	<sup>5</sup> D <sub>1</sub>	А	17,705	18,128	18,143	18,485	18,945	-6.55	-4.31	-4.23	-2.43
		В	17,716	18,164	18,176	18,488		-	-	-	-
-		В	17,806	18,199	18,206	18,493		-	-	-	-

H. Ramanantoanina, Computation 2022, 10, 70





Eu<sup>2+</sup> 4f<sup>7</sup> -> 4f<sup>6</sup> 5d<sup>1</sup>



The molecular  $Eu(\eta^9-C_9H_9)_2$  complex possesses high symmetry  $D_{9h}$  structure.



H. Ramanantoanina, L. Merzoud, J. T. Muya, H. Chermette and C. Daul, J. Phys. Chem. A 2020, 124, 152

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 $Eu^{2+} 4f^7 \rightarrow 4f^6 5d^1$ 



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The molecular  $Eu(\eta^9-C_9H_9)_2$  complex possesses high symmetry  $D_{9h}$  structure.



30030 single determinants H. Ramanantoanina et al, J. Phys. Chem. A 2020, 124, 152











С

Calculated excitation spectra versus DFT functional



- Multiple transitions in the 4f 5d excitation process, governed by the two-electron repulsion and 5d ligand-field splitting.
- Good agreement with the experiments, in particular for the PBE results.

H. Ramanantoanina, L. Merzoud, J. T. Muya, H. Chermette and C. Daul, J. Phys. Chem. A 2020, 124, 152

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#### X-ray Absorption Spectroscopy



## X-rays X-rays 3d<sub>5/2</sub> 3d<sub>3/2</sub>

Ground state config.: 4f<sup>n</sup> XAS excited state config.: 3d<sup>9</sup> 4f<sup>n+1</sup>



#### **Mechanism of the XAS process**

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H. Ramanantoanina, Chem. Commun.. 2019, 55, 2988



X-ray Absorption Spectroscopy

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#### **Future developments**



#### f-f intensities

In collaboration with Cristian Celis-Barros (Florida)





T. Poe, S. Molinari, M. Beltran-Leiva, C. Celis-Barros, H. Ramanantoanina and T. Albrecht-Schönzart, Inorg. Chem. 2021, 60, 15196

#### **Transition metal K-edge XAS**





D. Trummer, K. Searles, A. Algasov, S. Guda, A. Soldatov, H. Ramanantoanina, O. Sofonova, A. Guda, and C. Copéret, *J. Am. Chem. Soc.* **2021**, *143*, 7326

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#### **Transition metal K-edge XAS**



Transition metal - Oh symmetry Theory,  $3d^{n} \rightarrow 1s^{1} 3d^{n+1}$  (pre-edge energy region) ∃ T<sub>d</sub> symmetry multiplets 1E V.1×0.5 Vormalized Intensity IV.3×0.5 dipole + quadrupole transitions Possible 3d/4p mix Quadrupole transitions 5988 5990 5992 5994 Energy, eV Relative Energy, eV Relative Energy, eV No 3d/4p mix D. Trummer, K. Searles, A. Algasov, S. Guda, A. Soldatov, H. Ramanantoanina,

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O. Sofonova, A. Guda, and C. Copéret, J. Am. Chem. Soc. 2021, 143, 7326

#### **Resonant Inelastic X-ray Scattering**



#### **Mechanism of the RIXS process**



In collaboration with Tonya Vitova (Karlsruhe)



#### **Resonant Inelastic X-ray Scattering**

![](_page_43_Picture_1.jpeg)

![](_page_43_Figure_2.jpeg)

#### Acknowledgment

![](_page_44_Picture_1.jpeg)

More than 20 years of development of LFDFT (2000 – now) Special thanks to all the collaborators

![](_page_44_Picture_3.jpeg)

![](_page_44_Figure_4.jpeg)

![](_page_45_Picture_0.jpeg)

![](_page_45_Picture_1.jpeg)

- Part 0: AMSGUI, build molecular complex (e.g. Mn(5-crown ether)2+) with Mn 3d^5
- Part 1: Ground state configuration Mn 3d^5: LFDFT without and with spin-orbit coupling.
- Part 2: Mn L2,3-edge XAS: XAS excited state configuration Mn 2p^5 3d^6 and electric-dipole transitions 3d^5 -> 2p^5 3d^6.
- Part 3: Mn L2,3-edge XMCD: XAS with magnetic field