Extension of Judd-Ofelt theory: Application on Eu^{3+}, Nd^{3+} and Er^{3+}

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Dijon, France

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- Introduction and motivation
- Judd-Ofelt theory
- Calculations
  - JO extension
  - Free-ion calculations
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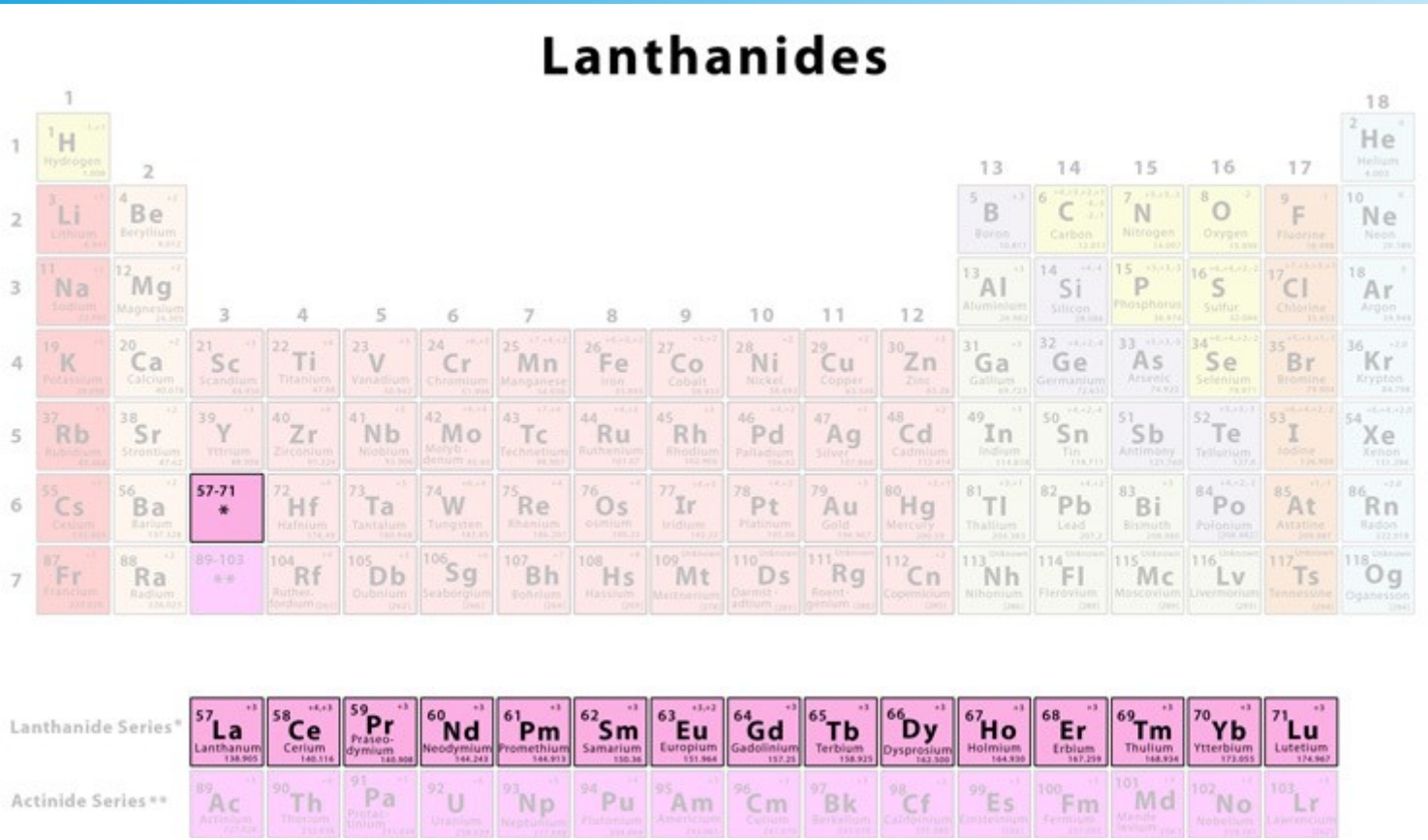

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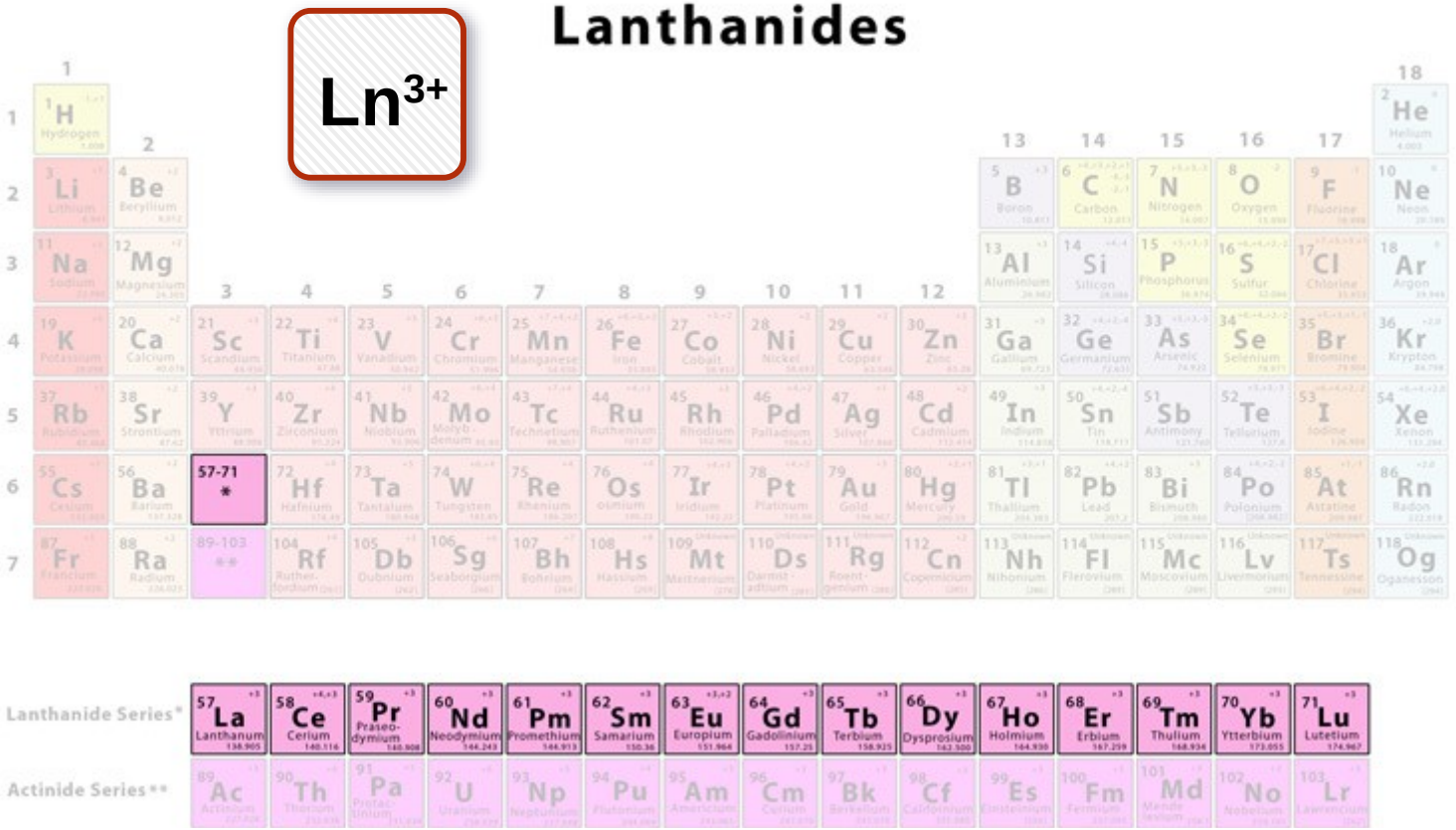

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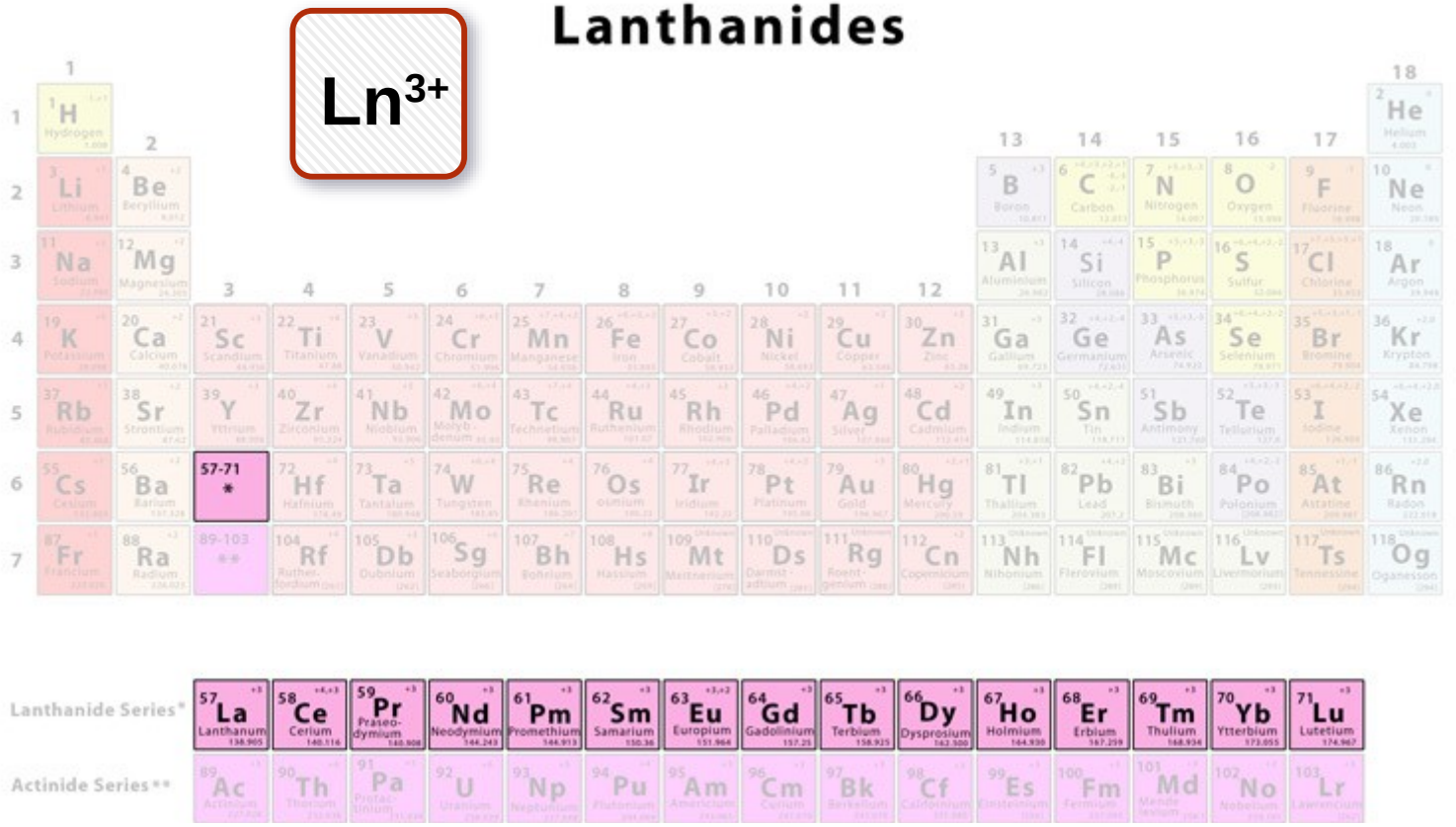

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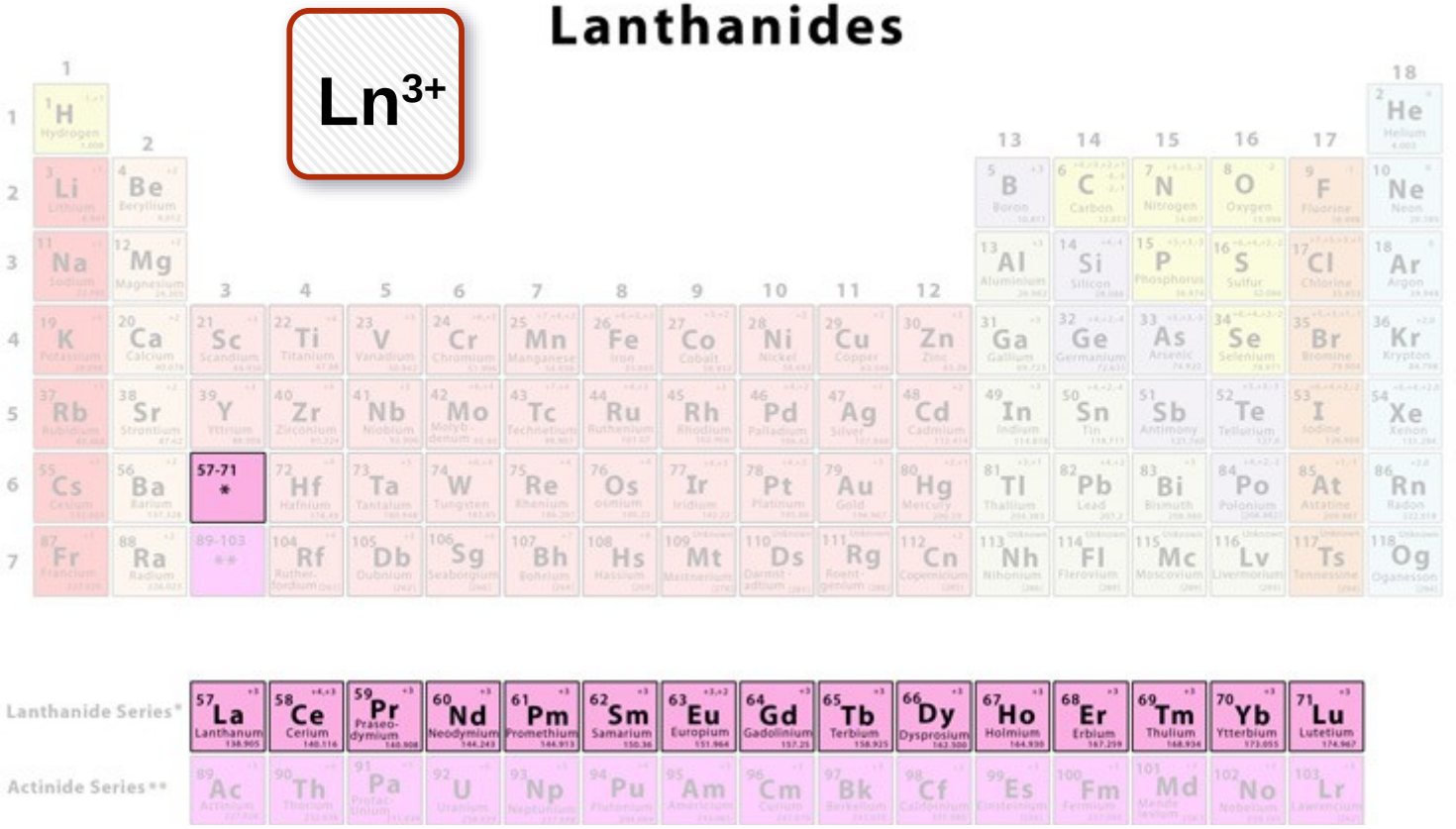

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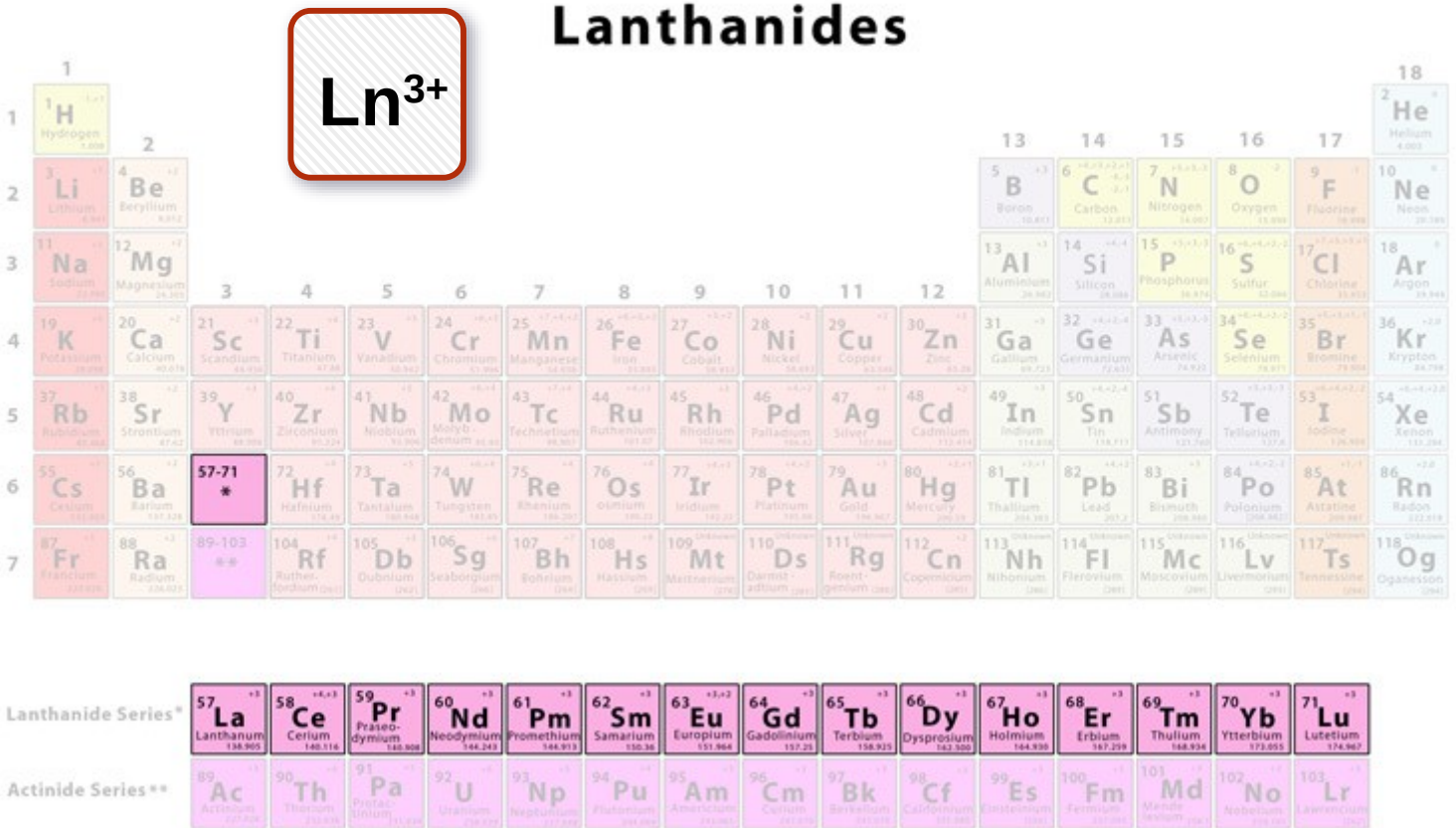

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- ✔ energy spectrum
- ✔ transition probabilities
- ✔ radial matrix elements

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Solids doped with Eu^{3+} : Judd-Ofelt theory

- Interpretation of the **intensities of absorption and emissions lines** of crystals and glasses doped with Ln^{3+}

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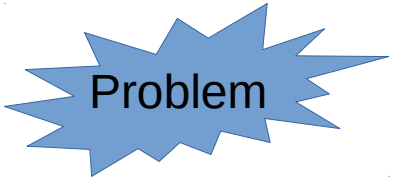

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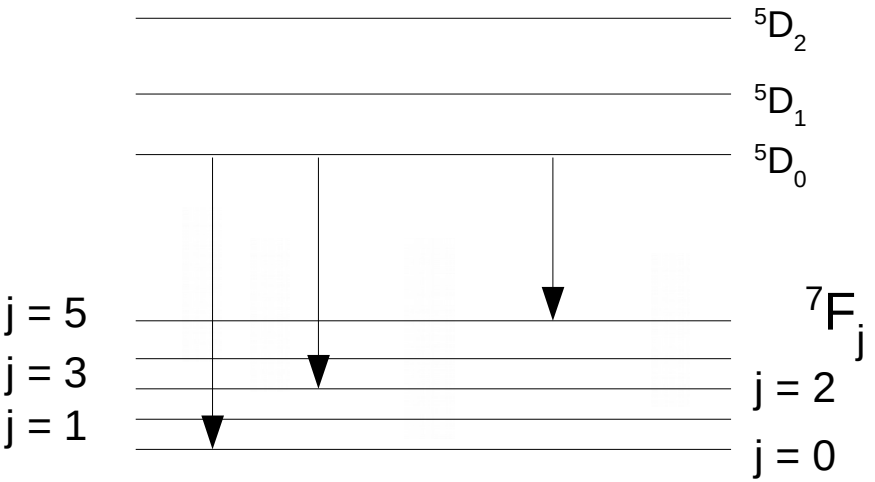

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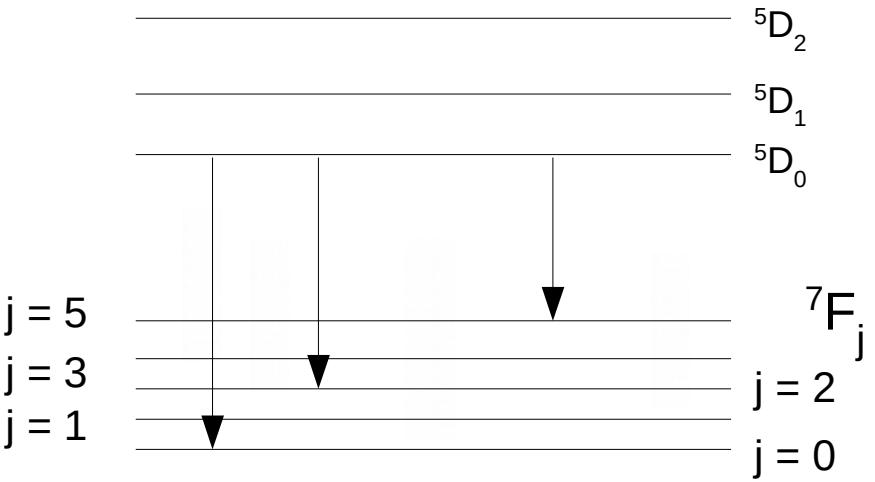

Pr^{3+}

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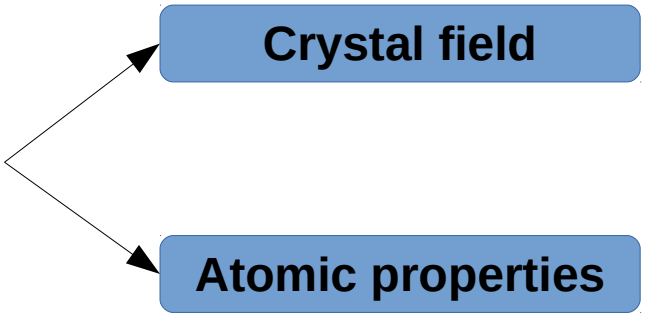

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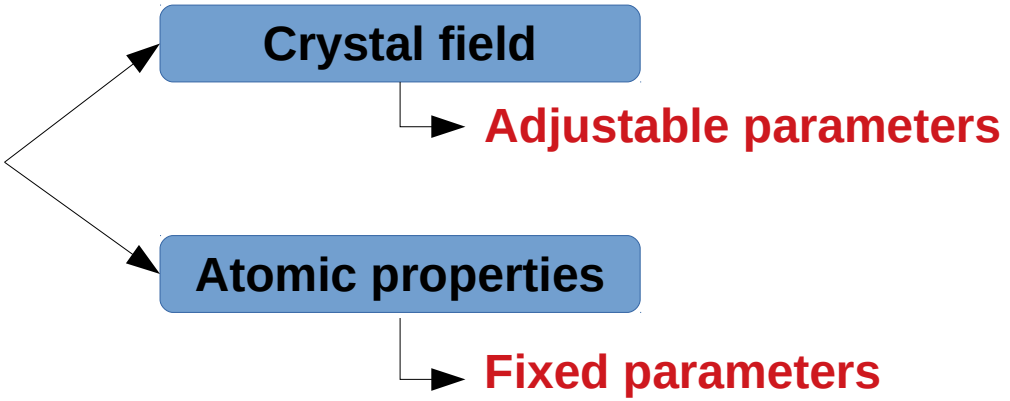

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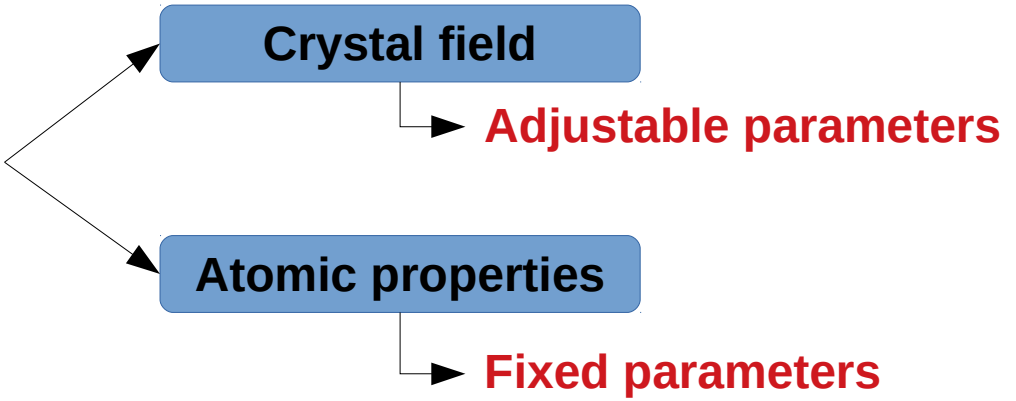

Radial matrix elements

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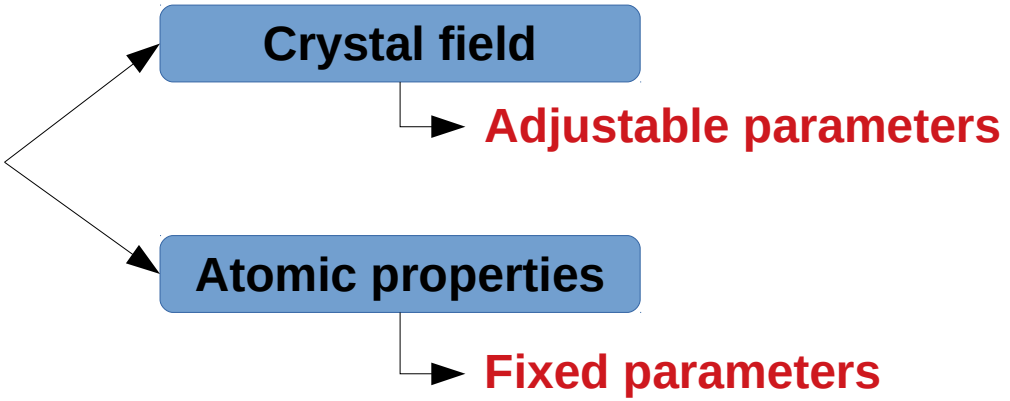

Radial matrix elements

$\langle n'l' \| r^k \| nl \rangle$

k = 1	k = 3	k = 5
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Eu^{3+}

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- relaxing of some of the strong assumptions of standard JO theory
- simple interpretation of the transitions that are forbidden in standard JO theory

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transition amplitude → 2nd order contribution bare influence of CF + 3rd order contribution influence of CF and excited SO

Line strengths calculations

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Crystal-field parameters : A_{kq}

- Oscillator strengths: $$f_{12,\mathrm{ED}} = \frac{2m_e a_0^2 (E_2 - E_1)}{3\hbar^2 (2J_1 + 1)} S_{\mathrm{ED}} \frac{(n_r^2 + 2)/9}{n_r}$$

Extension calculations

FORTRAN program

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experimental details
on transitions

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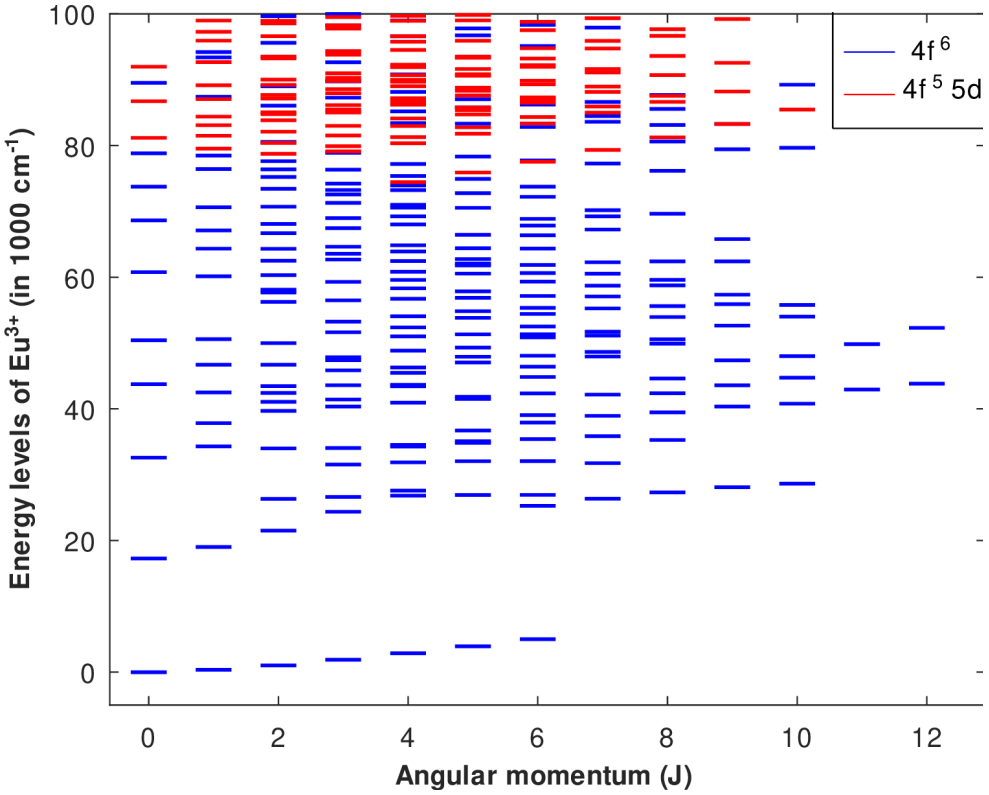

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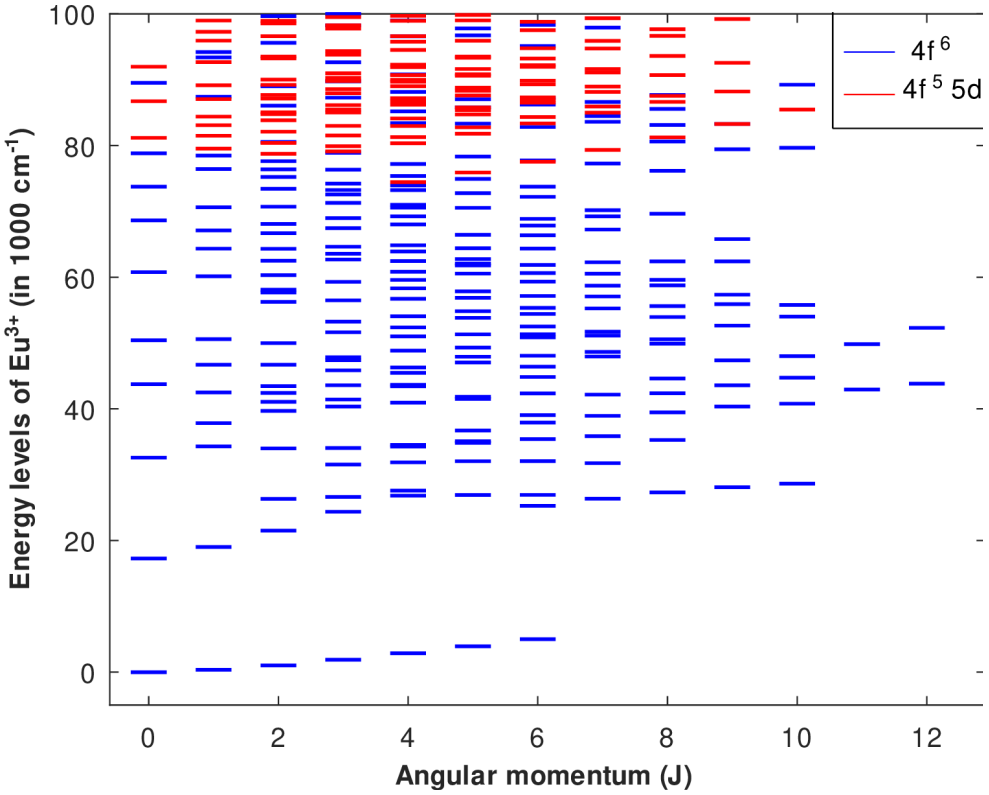

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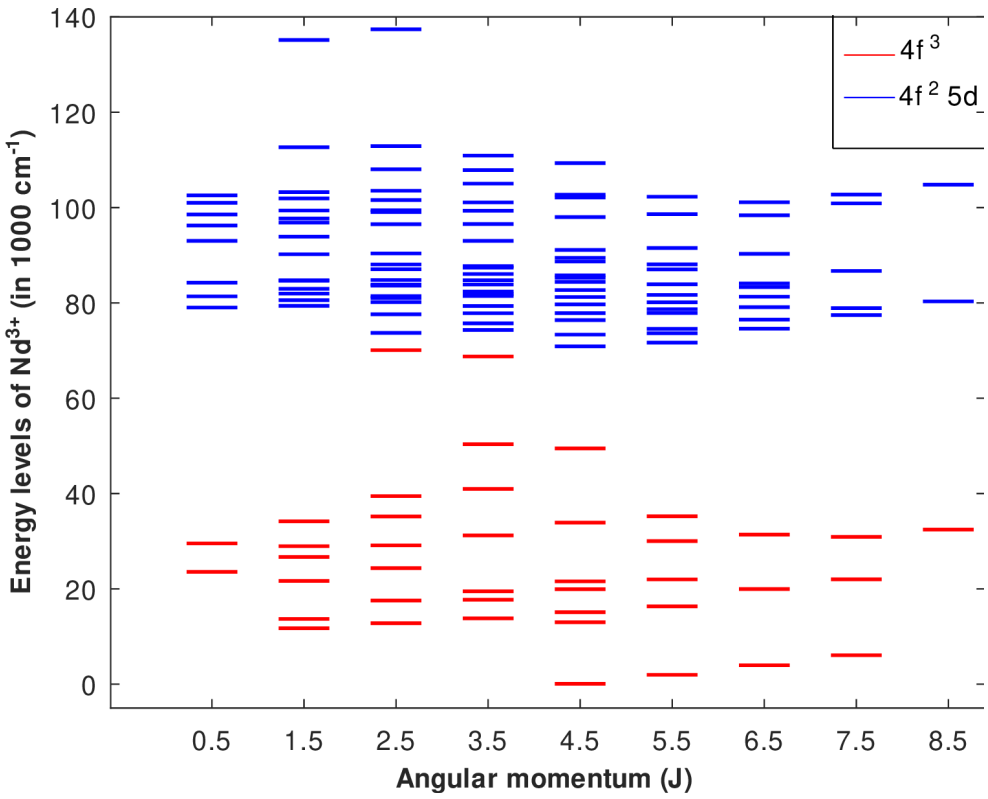

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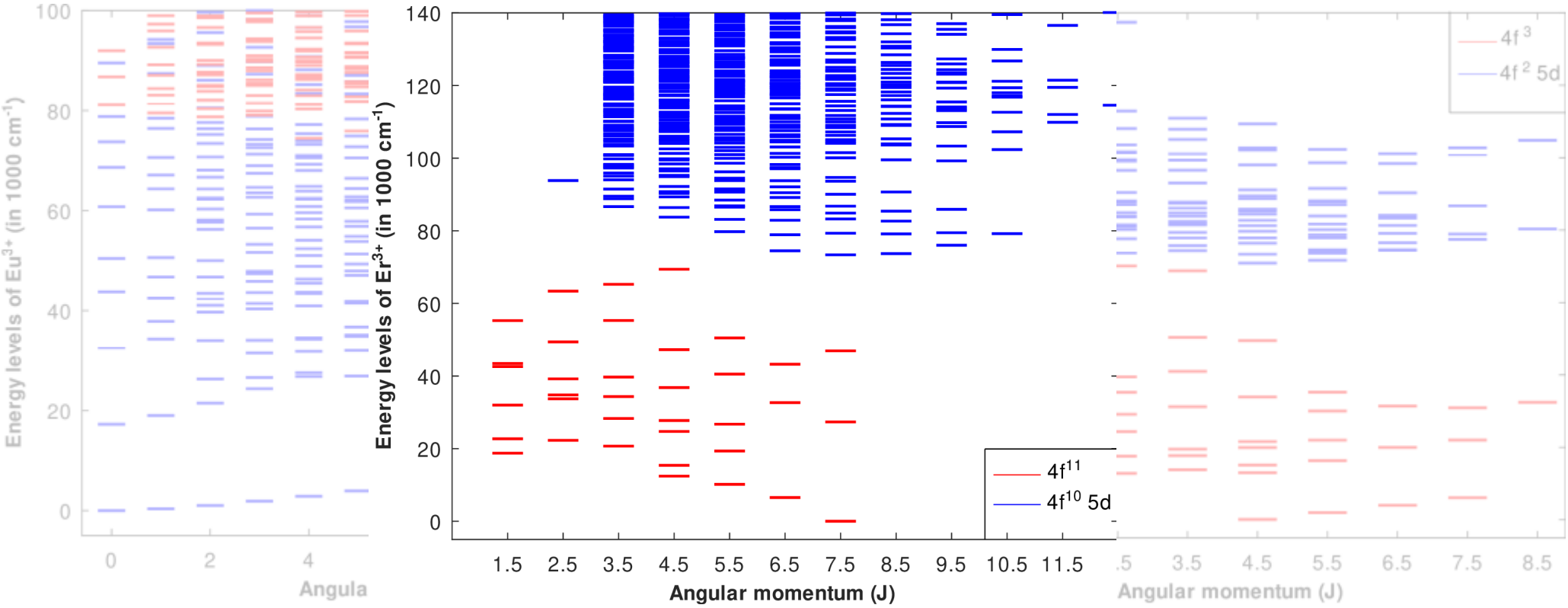

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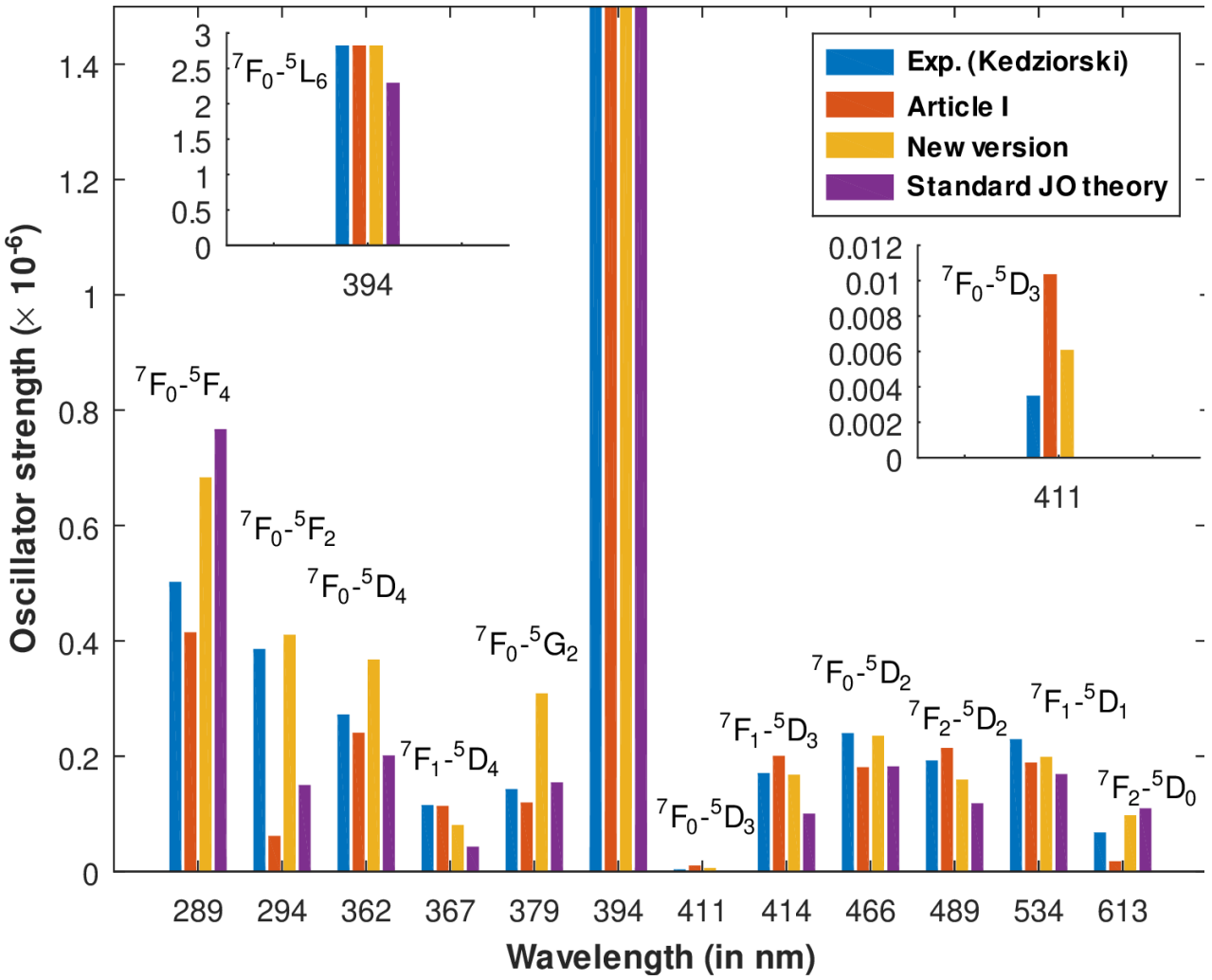

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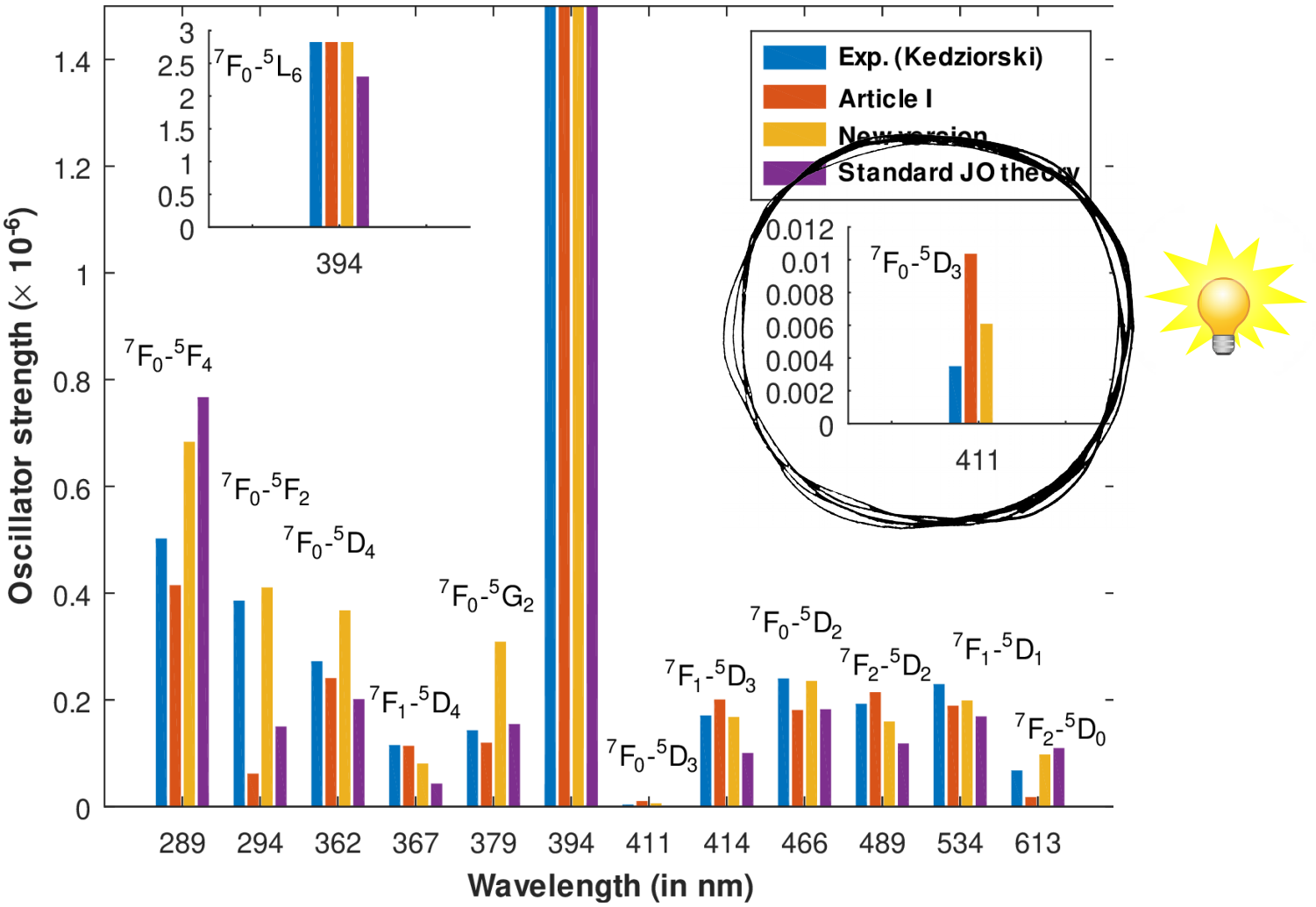

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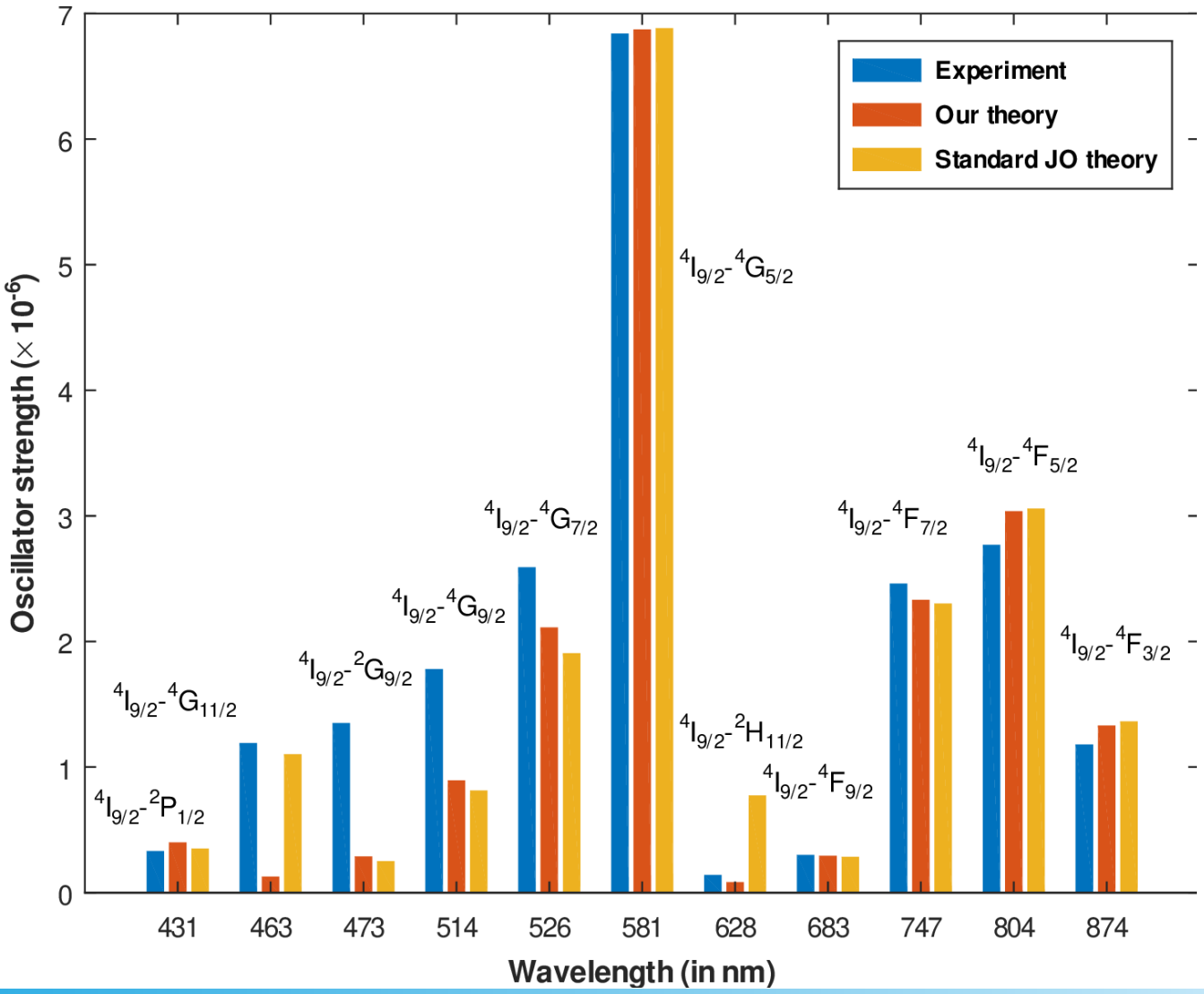

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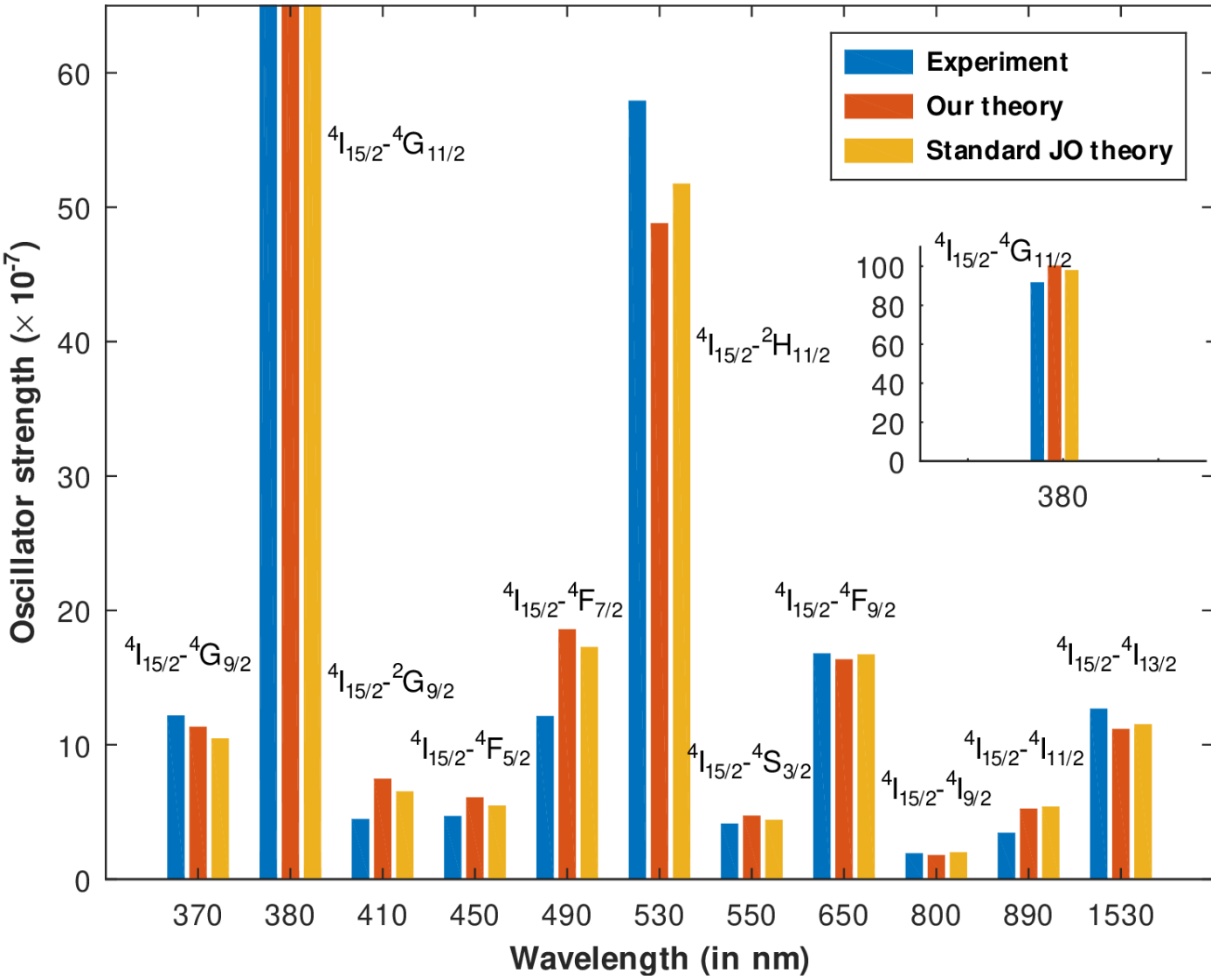

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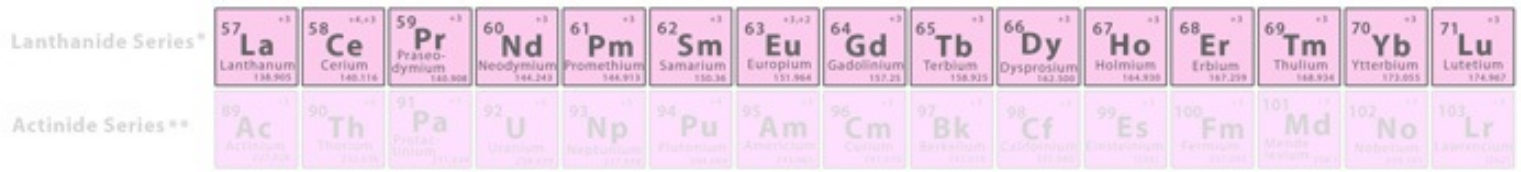
Future improvements

- Account for different light polarizations and free-ion sublevels, or for overlapping transitions.

Hovhannesyan, G., Boudon, V., & Lepers, M. (2022). *Transition intensities of trivalent lanthanide ions in solids: Extending the Judd-Ofelt theory*. Journal of Luminescence, 241, 118456.

Thank you for your attention !



Methodology

Semi empirical method = ***ab initio*** + **least square**

First step

- P_{nl} with HFR method
- Energy parameters

Second step

- Setting up energy matrices
- Diagonalization
- Eigenvalues and eigenvectors

Third step

- Least-square fitting

$$s = \left[\frac{\sum_i (E_i - T_i)^2}{N_{\mathrm{lev}} - N_{\mathrm{par}}} \right]^{\frac{1}{2}}$$

Description of calculations

Multipolar expansion of the crystal-field potential: $V_{\mathrm{CF}} = \sum_{kq} A_{kq} P_q^{(k)}$

k = 1, 3, 5

ED transition amplitude:

4f $^{w-1}$ 5d

$$D_{12} = \sum_t \left[\frac{\langle \Psi_1^0 | V_{\mathrm{CF}} | \Psi_t^0 \rangle \langle \Psi_t^0 | P_p^{(1)} | \Psi_2^0 \rangle}{E_1 - E_t} + \frac{\langle \Psi_1^0 | P_p^{(1)} | \Psi_t^0 \rangle \langle \Psi_t^0 | V_{\mathrm{CF}} | \Psi_2^0 \rangle}{E_2 - E_t} \right.$$

$$+ \sum_u \left\{ \frac{\langle \Psi_1^0 | V_{\mathrm{CF}} | \Psi_t^0 \rangle \langle \Psi_t^0 | H_{\mathrm{SO}} | \Psi_u^0 \rangle \langle \Psi_u^0 | P_p^{(1)} | \Psi_2^0 \rangle}{(E_1 - E_t)^2} \right.$$

4f $^{w-1}$ 5d

$$\left. \left. + \frac{\langle \Psi_1^0 | P_p^{(1)} | \Psi_t^0 \rangle \langle \Psi_t^0 | H_{\mathrm{SO}} | \Psi_u^0 \rangle \langle \Psi_u^0 | V_{\mathrm{CF}} | \Psi_2^0 \rangle}{(E_2 - E_u)^2} \right\} \right]$$

Unperturbed levels:
free-ion levels:

$$|\Psi_i^0\rangle = \sum_{\alpha_i L_i S_i} c_{\alpha_i L_i S_i} \left| n\ell^w \, \alpha_i L_i S_i J_i M_i \right\rangle$$

Results on JO parameters

Eu^{3+}

	X_1 (10^{-4} a.u.)	Ω_2 (10^{-20} cm^2)		X_3 (10^{-5} a.u.)	Ω_4 (10^{-20} cm^2)		X_5 (10^{-8} a.u.)	Ω_6 (10^{-20} cm^2)	
		Our	Rep.		Our	Rep.		Our	Rep.
Babu	1.816	18.73	17.96	1.898	12.58	11.92	6.882	2.253	2.13
Kedziorski	0.7887	6.991	-	0.1317	8.326	-	0.1008	4.940	-

Nd^{3+}

	X_1 (10^{-6} a.u.)	Ω_2 (10^{-20} cm^2)		X_3 (10^{-6} a.u.)	Ω_4 (10^{-20} cm^2)		X_5 (10^{-8} a.u.)	Ω_6 (10^{-20} cm^2)	
		Our	Rep.		Our	Rep.		Our	Rep.
Zhang	1.801	1.208	1.883	3.302	5.637	4.441	5.489	7.571	2.956
Chanthima	5.035	1.547	1.09	1.859	2.850	1.97	1.702	2.388	3.37

Er^{3+}

	X_1 (10^{-5} a.u.)	Ω_2 (10^{-20} cm^2)		X_3 (10^{-6} a.u.)	Ω_4 (10^{-20} cm^2)		X_5 (10^{-7} a.u.)	Ω_6 (10^{-20} cm^2)	
		Our	Rep.		Our	Rep.		Our	Rep.
Liu	6.060	0.8085	0.89 ± 0.16	-1.444	0.06749	0.16 ± 0.10	2.417	6.143	1.85 ± 0.25
Piao	19.17	2.792	2.46	11.97	0.8883	1.24	2.387	0.9541	0.51