

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

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

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Motivation

Lanthanides

1											13	14	15	16	17	18		
1	¹ H Hydrogen 1.008																² He Helium 4.003	
2	³ Li Lithium 6.941	⁴ Be Beryllium 9.012											⁵ B Boron 10.811	⁶ C Carbon 12.011	⁷ N Nitrogen 14.007	⁸ O Oxygen 15.999	⁹ F Fluorine 18.998	¹⁰ Ne Neon 20.180
3	¹¹ Na Sodium 22.990	¹² Mg Magnesium 24.305											¹³ Al Aluminum 26.982	¹⁴ Si Silicon 28.086	¹⁵ P Phosphorus 30.974	¹⁶ S Sulfur 32.065	¹⁷ Cl Chlorine 35.453	¹⁸ Ar Argon 39.948
4	¹⁹ K Potassium 39.098	²⁰ Ca Calcium 40.078	²¹ Sc Scandium 44.956	²² Ti Titanium 47.88	²³ V Vanadium 50.942	²⁴ Cr Chromium 51.996	²⁵ Mn Manganese 54.938	²⁶ Fe Iron 55.845	²⁷ Co Cobalt 58.933	²⁸ Ni Nickel 58.693	²⁹ Cu Copper 63.546	³⁰ Zn Zinc 65.38	³¹ Ga Gallium 69.723	³² Ge Germanium 72.631	³³ As Arsenic 74.922	³⁴ Se Selenium 78.971	³⁵ Br Bromine 79.904	³⁶ Kr Krypton 83.798
5	³⁷ Rb Rubidium 85.468	³⁸ Sr Strontium 87.62	³⁹ Y Yttrium 88.906	⁴⁰ Zr Zirconium 90.224	⁴¹ Nb Niobium 92.906	⁴² Mo Molybdenum 95.94	⁴³ Tc Technetium 98.906	⁴⁴ Ru Ruthenium 101.07	⁴⁵ Rh Rhodium 102.905	⁴⁶ Pd Palladium 106.42	⁴⁷ Ag Silver 107.868	⁴⁸ Cd Cadmium 112.414	⁴⁹ In Indium 114.818	⁵⁰ Sn Tin 118.710	⁵¹ Sb Antimony 121.757	⁵² Te Tellurium 127.6	⁵³ I Iodine 126.905	⁵⁴ Xe Xenon 131.294
6	⁵⁵ Cs Cesium 132.905	⁵⁶ Ba Barium 137.327	57-71 *	⁷² Hf Hafnium 178.49	⁷³ Ta Tantalum 180.948	⁷⁴ W Tungsten 183.85	⁷⁵ Re Rhenium 186.207	⁷⁶ Os Osmium 190.23	⁷⁷ Ir Iridium 192.22	⁷⁸ Pt Platinum 195.08	⁷⁹ Au Gold 196.967	⁸⁰ Hg Mercury 200.59	⁸¹ Tl Thallium 204.383	⁸² Pb Lead 207.2	⁸³ Bi Bismuth 208.980	⁸⁴ Po Polonium 209	⁸⁵ At Astatine 209	⁸⁶ Rn Radon 222
7	⁸⁷ Fr Francium 223	⁸⁸ Ra Radium 226	89-103	¹⁰⁴ Rf Rutherfordium 261	¹⁰⁵ Db Dubnium 262	¹⁰⁶ Sg Seaborgium 263	¹⁰⁷ Bh Bohrium 264	¹⁰⁸ Hs Hassium 265	¹⁰⁹ Mt Meitnerium 266	¹¹⁰ Ds Darmstadtium 267	¹¹¹ Rg Roentgenium 268	¹¹² Cn Copernicium 269	¹¹³ Nh Nihonium 270	¹¹⁴ Fl Flerovium 271	¹¹⁵ Mc Moscovium 272	¹¹⁶ Lv Livermorium 273	¹¹⁷ Ts Tennessine 274	¹¹⁸ Og Oganesson 276

Lanthanide Series*	⁵⁷ La Lanthanum 138.905	⁵⁸ Ce Cerium 140.116	⁵⁹ Pr Praseodymium 140.908	⁶⁰ Nd Neodymium 144.242	⁶¹ Pm Promethium 144.913	⁶² Sm Samarium 150.36	⁶³ Eu Europium 151.964	⁶⁴ Gd Gadolinium 157.25	⁶⁵ Tb Terbium 158.925	⁶⁶ Dy Dysprosium 162.500	⁶⁷ Ho Holmium 164.930	⁶⁸ Er Erbium 167.259	⁶⁹ Tm Thulium 168.934	⁷⁰ Yb Ytterbium 173.055	⁷¹ Lu Lutetium 174.967
Actinide Series**	⁸⁹ Ac Actinium 227	⁹⁰ Th Thorium 232.038	⁹¹ Pa Protactinium 231.036	⁹² U Uranium 238.029	⁹³ Np Neptunium 237.048	⁹⁴ Pu Plutonium 244.064	⁹⁵ Am Americium 243.061	⁹⁶ Cm Curium 247.070	⁹⁷ Bk Berkelium 247.070	⁹⁸ Cf Californium 251.080	⁹⁹ Es Einsteinium 252.083	¹⁰⁰ Fm Fermium 257.103	¹⁰¹ Md Mendelevium 258.106	¹⁰² No Nobelium 259.108	¹⁰³ Lr Lawrencium 260.105

Motivation

Lanthanides

Ln^{3+}

The periodic table shows elements from Hydrogen (1) to Oganesson (118). The lanthanide series (elements 57-71) and actinide series (elements 89-103) are highlighted in pink. A box labeled Ln^{3+} is positioned above the lanthanide series.

Lanthanide Series*

57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
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Actinide Series**

89 Ac Actinium 227.033	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium 252.083	100 Fm Fermium 257.103	101 Md Mendelevium 258.106	102 No Nobelium 259.108	103 Lr Lawrencium 260.109
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Motivation

Lanthanides

The image shows a periodic table with a callout box containing Ln^{3+} . Below the main table are two rows of elements: the Lanthanide Series (57-71) and the Actinide Series (89-103).

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H Hydrogen 1.008	2 He Helium 4.003																	
2 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	
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7 Fr Francium 223	88 Ra Radium 226	89-103 ** Actinides	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 264	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Ds Darmstadtium 267	111 Rg Roentgenium 268	112 Cn Copernicium 269	113 Nh Nihonium 270	114 Fl Flerovium 271	115 Mc Moscovium 272	116 Lv Livermorium 273	117 Ts Tennessine 274	118 Og Oganesson 276	

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- ✓ Rechargeable hybrid batteries
- ✓ Organic electronics
- ✓ Wind- and solar-energy conversion

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																		Lanthanide Series*																								
																		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71										
																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu										
																		Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium										
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																		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr										
																		Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium										
																		227.03	232.04	231.04	238.03	237.05	244.06	243.06	247.07	247.07	251.08	252.08	257.10	258.10	261.10	261.10										

- ✓ Rechargeable hybrid batteries
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- ✓ Bio-analyses, imaging
- ✓ Optical fiber amplifiers
- ✓ Lasers

Motivation

Lanthanides

The image shows a periodic table with a callout box containing Ln^{3+} . Below the main table are two rows of elements: the Lanthanide Series (La to Lu) and the Actinide Series (Ac to Lr).

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
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- ✓ Rechargeable hybrid batteries
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Nd:YAG

EDFA

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Introduction: Ln^{3+} in solids

Electronic configuration: $[\text{Xe}] 4f^w$

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$w = 3$ for Nd^{3+}

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Ion-crystal
interaction

$\sim 100 \text{ cm}^{-1}$

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Spin-orbit
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Columbic
interaction

$\sim 10000 \text{ cm}^{-1}$

Introduction: Ln^{3+} in solids

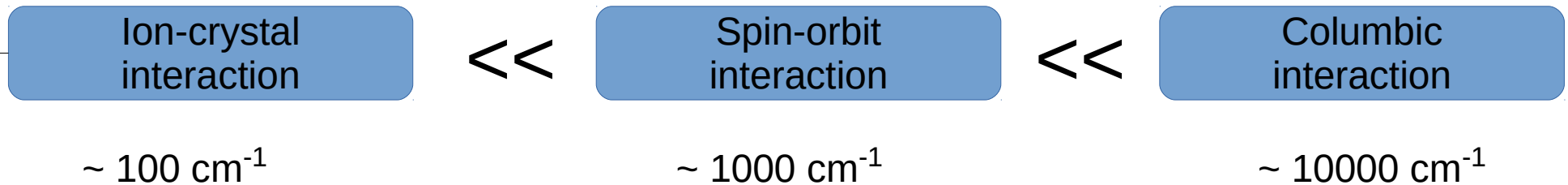
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- To use perturbation theory to describe the ion-crystal system
- To use the quantum numbers of free ion to describe the levels

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\ll

Spin-orbit
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$\sim 1000 \text{ cm}^{-1}$

\ll

Columbic
interaction

$\sim 10000 \text{ cm}^{-1}$


- To use perturbation theory to describe the ion-crystal system
- To use the quantum numbers of free ion to describe the levels

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

- Introduction and motivation
- **Judd-Ofelt theory**
- Calculations
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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+}


- 
- Judd, B. R. (1962). Optical absorption intensities of rare-earth ions. *Physical review*, 127(3), 750.
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- Interpretation of the **intensities of absorption and emissions lines** of crystals and glasses doped with Ln^{3+}

Selection Rules

Problem

	S	L	J (No $0 \leftrightarrow 0$)	Induced by crystal
Electric Dipole	$\Delta S = 0$	$\Delta L \leq 6$	$\Delta J \leq 6$ $\Delta J = 2, 4, 6$ (J or $J' = 0$)	Yes

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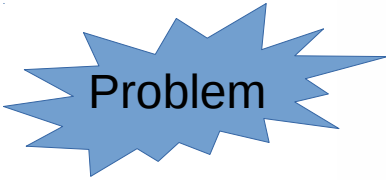
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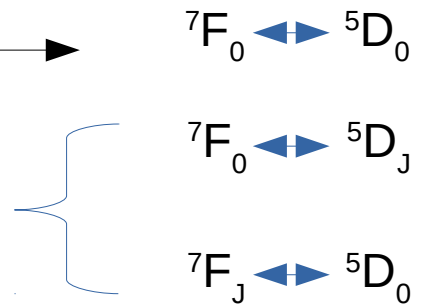
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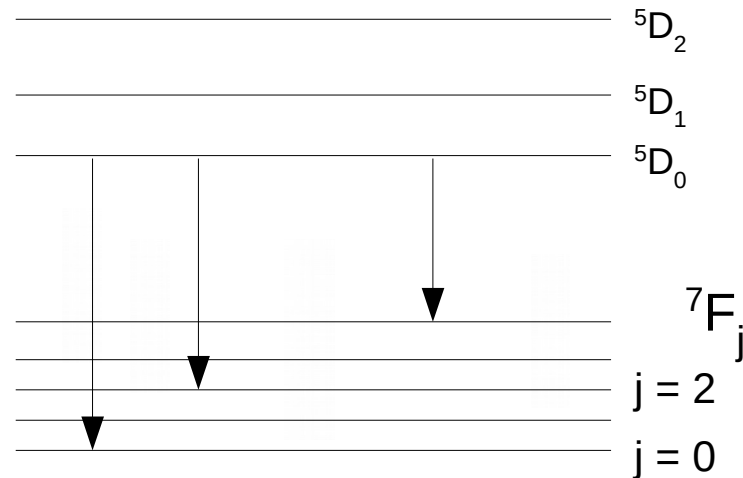
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Eu^{3+}

with J odd



$j = 5$
 $j = 3$
 $j = 1$



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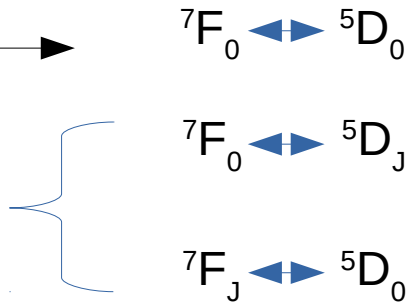
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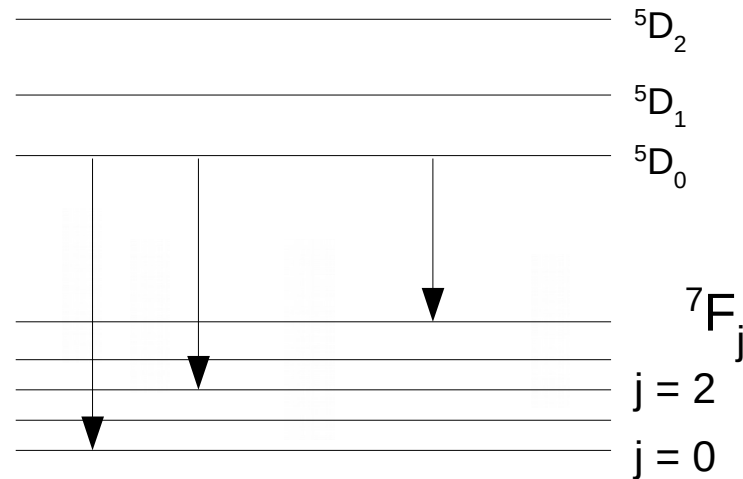
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Pr^{3+}

Sm^{3+}

Tb^{3+}

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Extension of JO theory

Standard JO → least square fitting with 3 parameters

Extension of JO theory

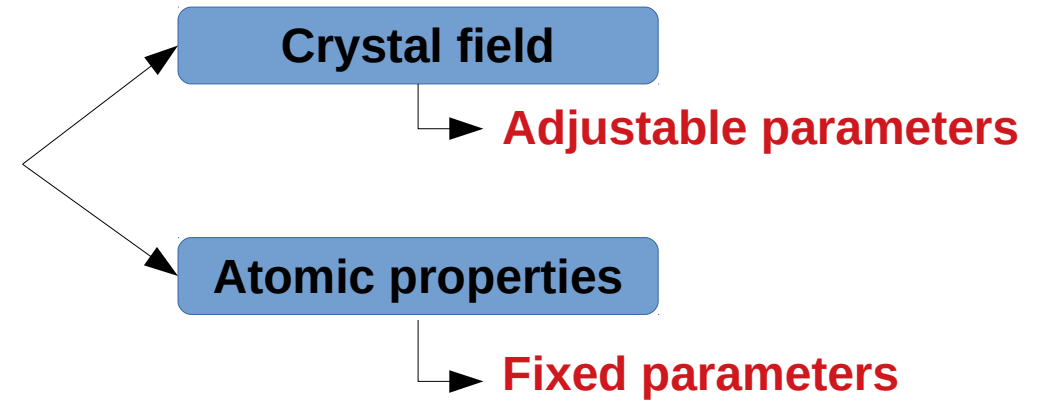
Standard JO → least square fitting with 3 parameters

Crystal field

Atomic properties

Extension of JO theory

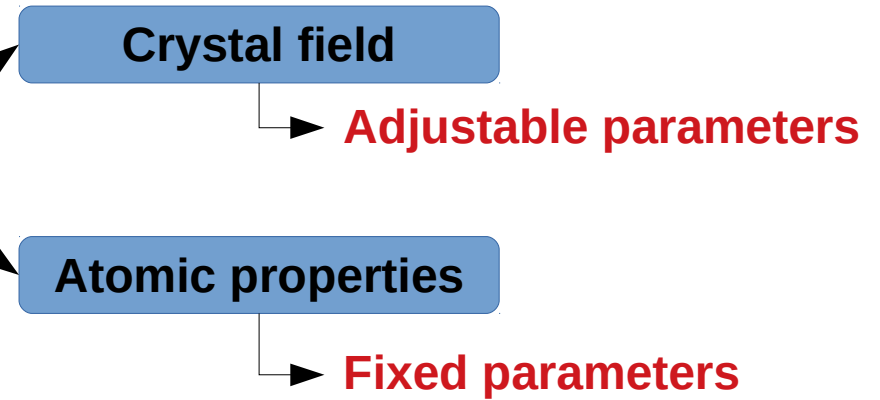
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Extension of JO theory

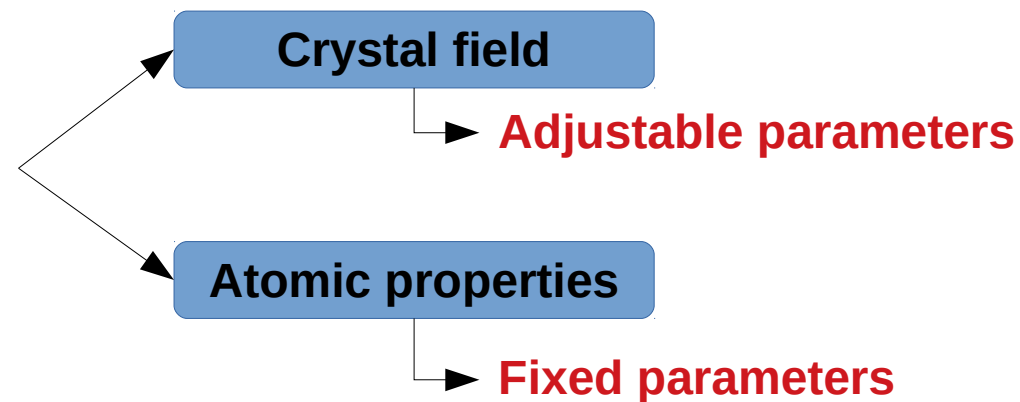
Standard JO → least square fitting with 3 parameters

Radial matrix elements



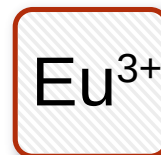
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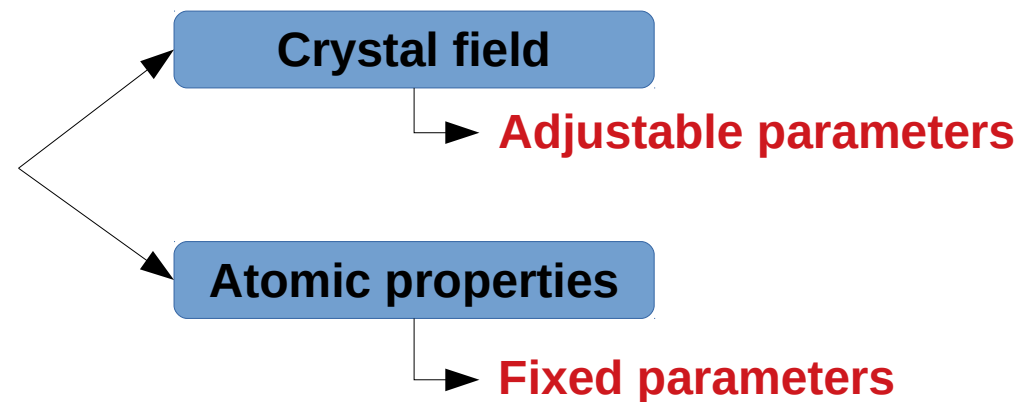
Radial matrix elements

$\langle n'l' r^k nl \rangle$	k = 1	k = 3	k = 5
	1.13062	-3.22134	21.72715



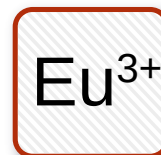
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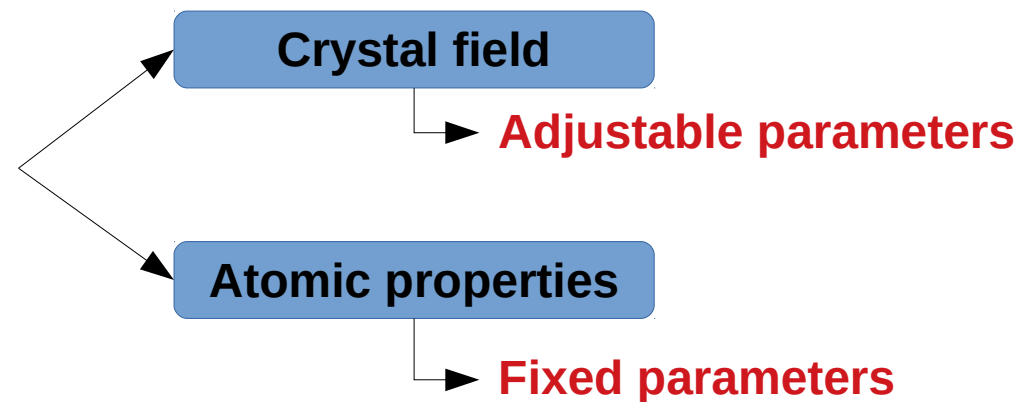
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- relaxing of some of the strong assumptions of standard JO theory

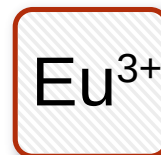
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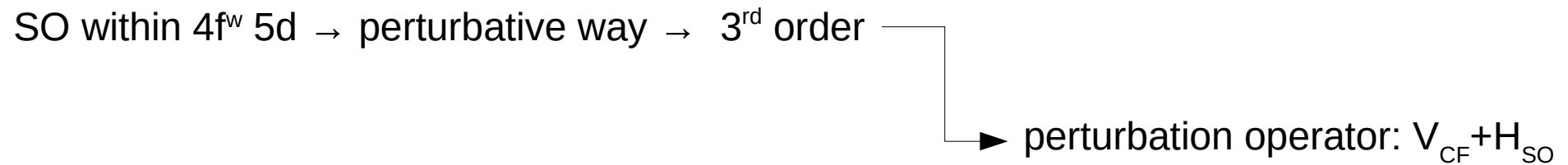
- relaxing of some of the strong assumptions of standard JO theory
- simple interpretation of the transitions that are forbidden in standard JO theory

Extension

SO within 4f^w 5d → perturbative way → 3rd order

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SO within $4f^w 5d$ → perturbative way → 3rd order



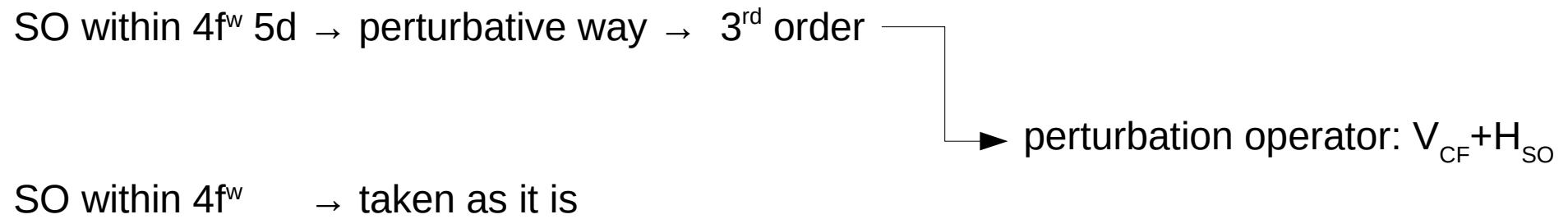
▶ perturbation operator: $V_{CF} + H_{SO}$

Extension

SO within $4f^w$ $5d$ → perturbative way → 3rd order

SO within $4f^w$ → taken as it is

→ perturbation operator: $V_{CF} + H_{SO}$



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▶ perturbation operator: $V_{CF} + H_{SO}$

SO within $4f^w$ → taken as it is

all eigenvector components

wavelength-dependence of
the refractive index

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▶ perturbation operator: $V_{CF} + H_{SO}$

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all eigenvector components

wavelength-dependence of the refractive index

$$n_r^2(\lambda) = n_0^2 + \frac{A\lambda^2}{\lambda^2 - B}$$

Extension

SO within $4f^w$ $5d$ → perturbative way → 3rd order

▶ perturbation operator: $V_{CF} + H_{SO}$

SO within $4f^w$ → taken as it is

all eigenvector components

wavelength-dependence of the refractive index

$$n_r^2(\lambda) = n_0^2 + \frac{A\lambda^2}{\lambda^2 - B}$$

transition amplitude



2nd order contribution
bare influence of CF



3rd order contribution
influence of CF and excited SO

Line strengths calculations

- Electric dipole moment  Line strengths

Line strengths calculations

- Electric dipole moment \rightarrow Line strengths

$$S_{\text{ED}} = \sum_{M1, M2, p} D_{12} = C_1 X_1 + C_3 X_3 + C_5 X_5, \quad \text{where} \quad X_k = \sum_{q=-k}^{+k} \frac{|A_{kq}|^2}{2k+1}$$

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Crystal-field parameters : A_{kq}

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

Extension calculations

FORTRAN program

Extension calculations

FORTRAN program



experimental details
on transitions

Extension calculations

FORTRAN program



experimental details
on transitions



theoretical line
strengths

Extension calculations

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experimental details
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theoretical line
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least-squares fitting
on line strengths

Extension calculations

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we can calculate line strengths of any given transition

Extension calculations

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

Free-ion calculations

Free-ion calculation

Free-ion calculations

Free-ion calculation

=

ab initio

+

least square

Free-ion calculations

Free-ion calculation

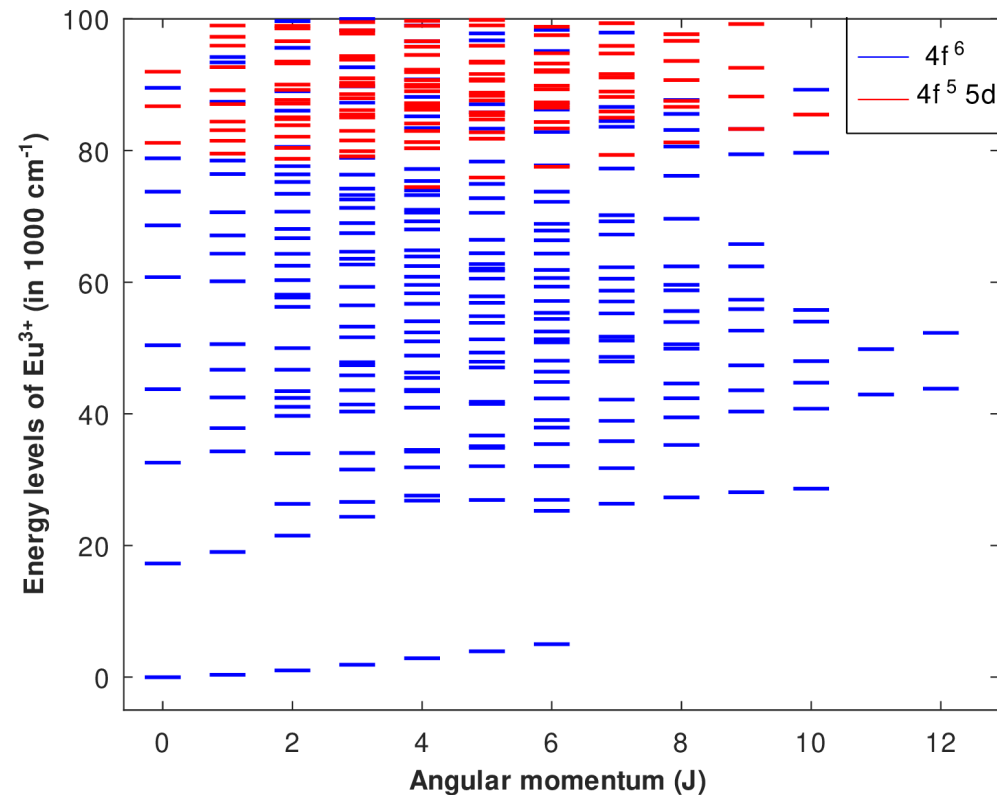


ab initio



least square

Eu^{3+}



Free-ion calculations

Free-ion calculation



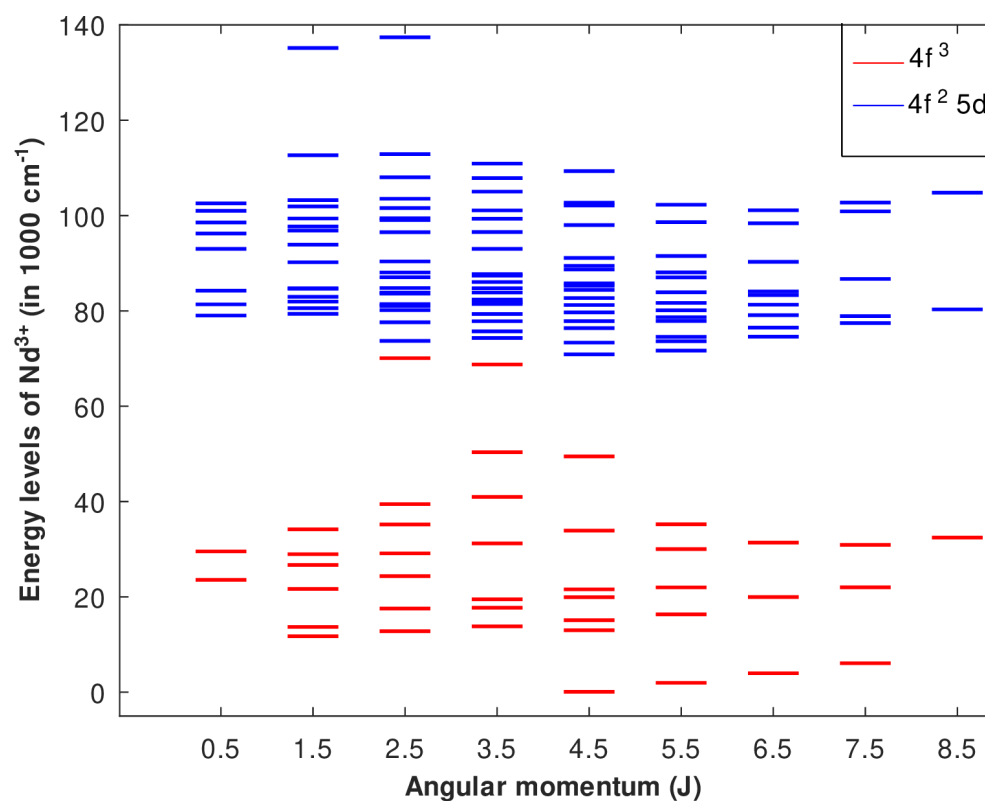
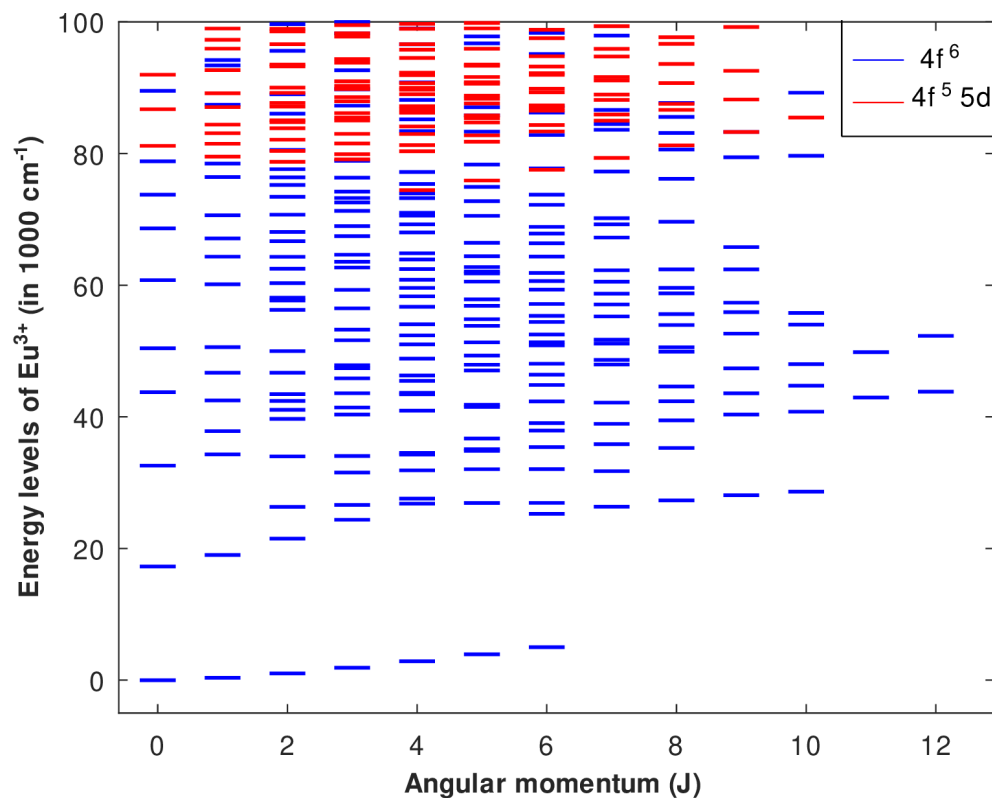
ab initio



least square

Eu^{3+}

Nd^{3+}



Free-ion calculations

Free-ion calculation

=

ab initio

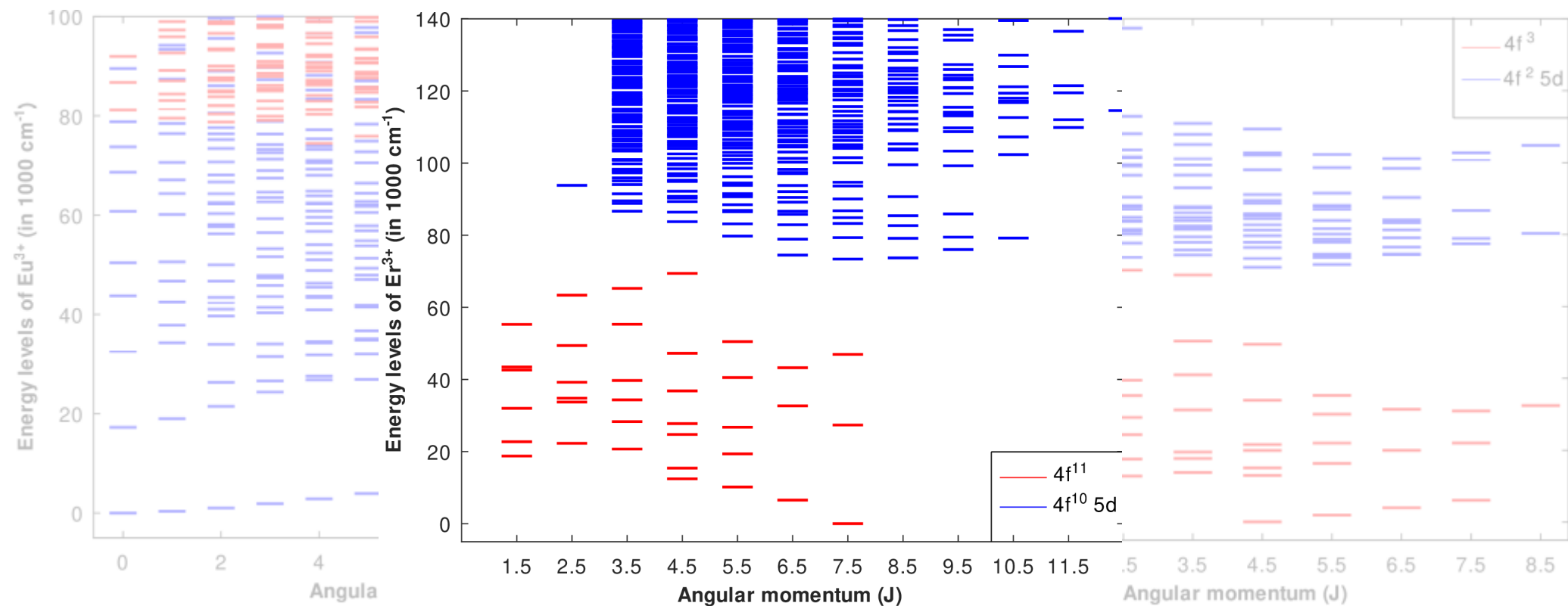
+

least square

Eu^{3+}

Er^{3+}

Nd^{3+}



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Results on Eu^{3+}

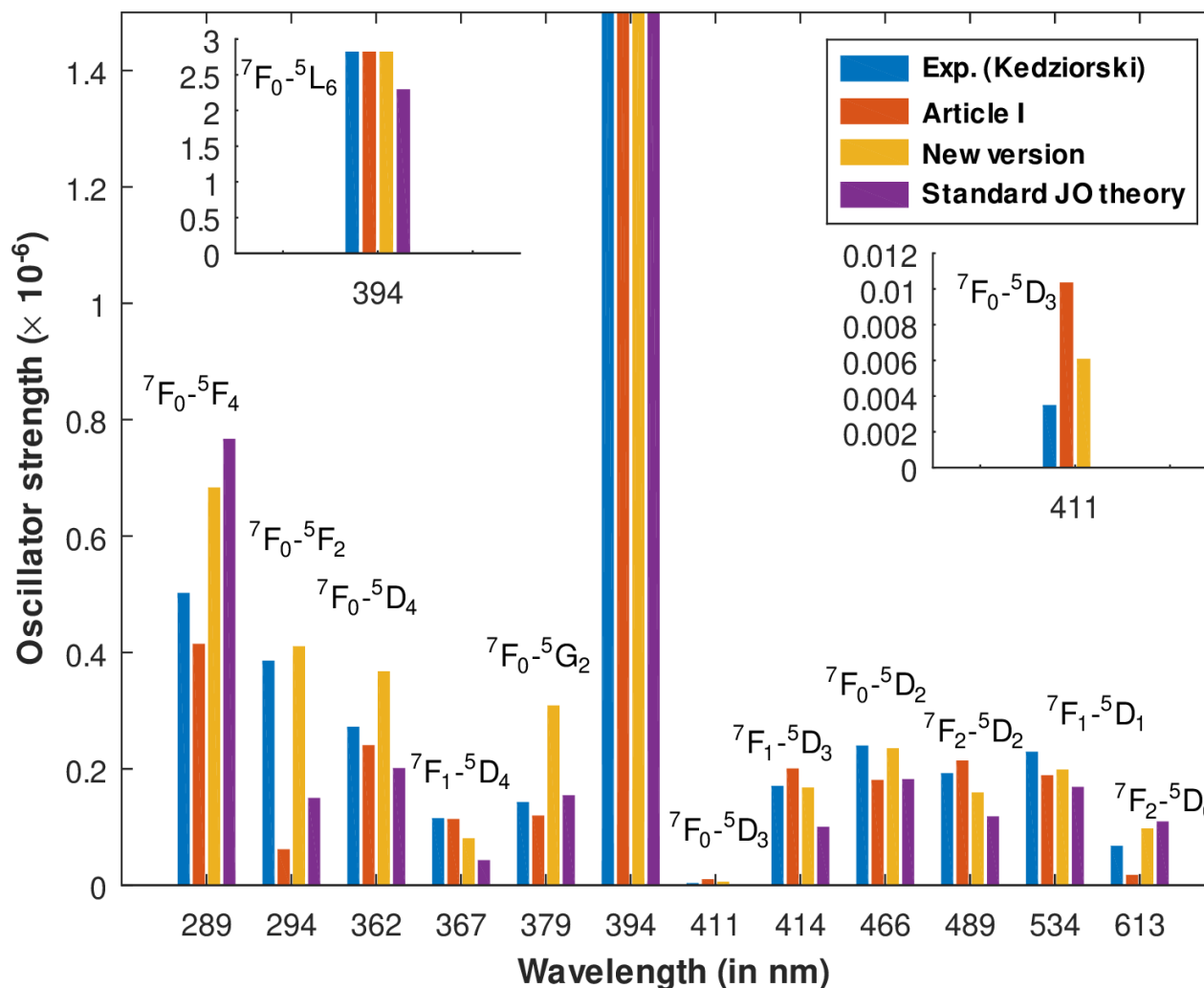
Kedzioski *et al.*:
 Eu^{3+} in acetate crystal



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

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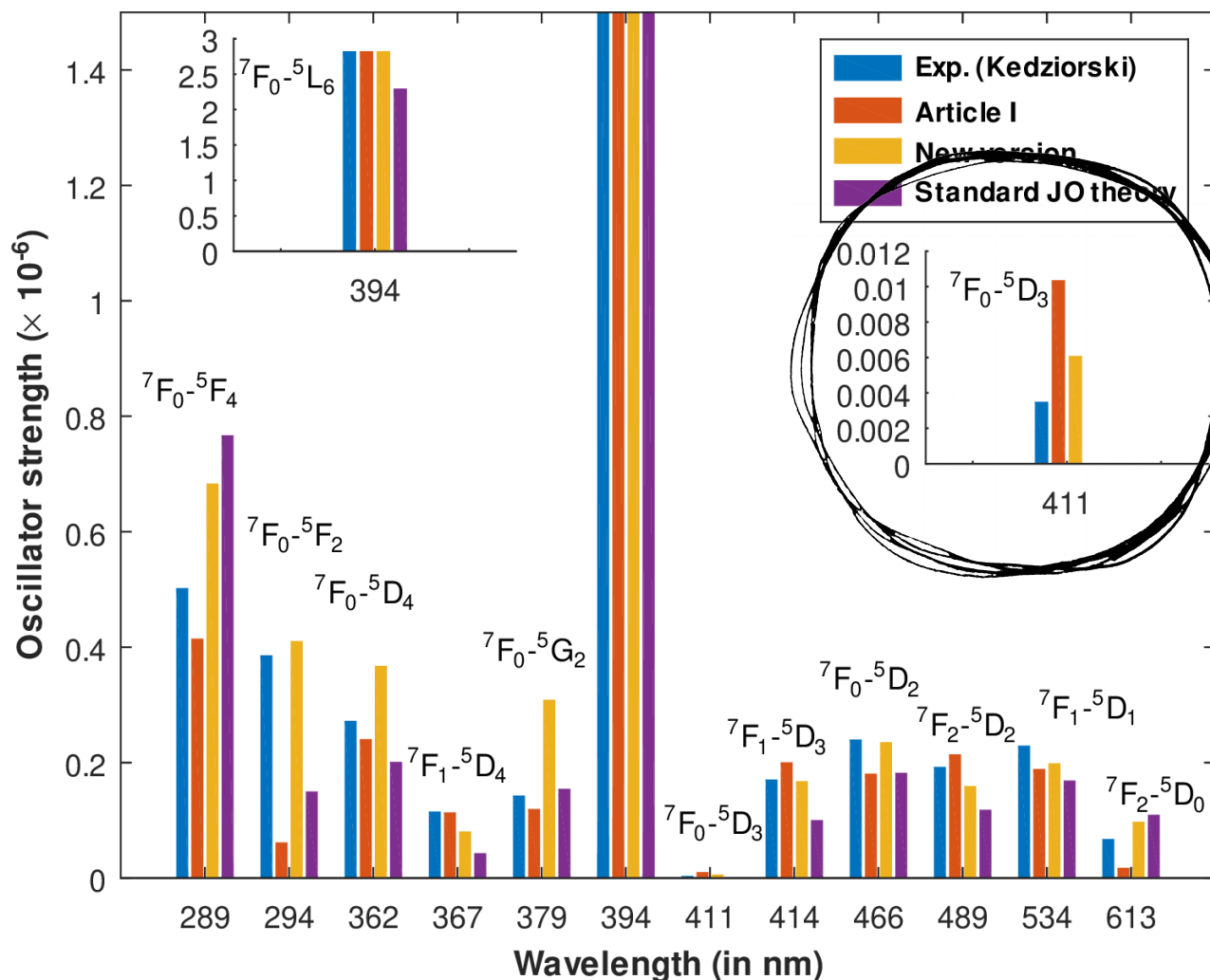
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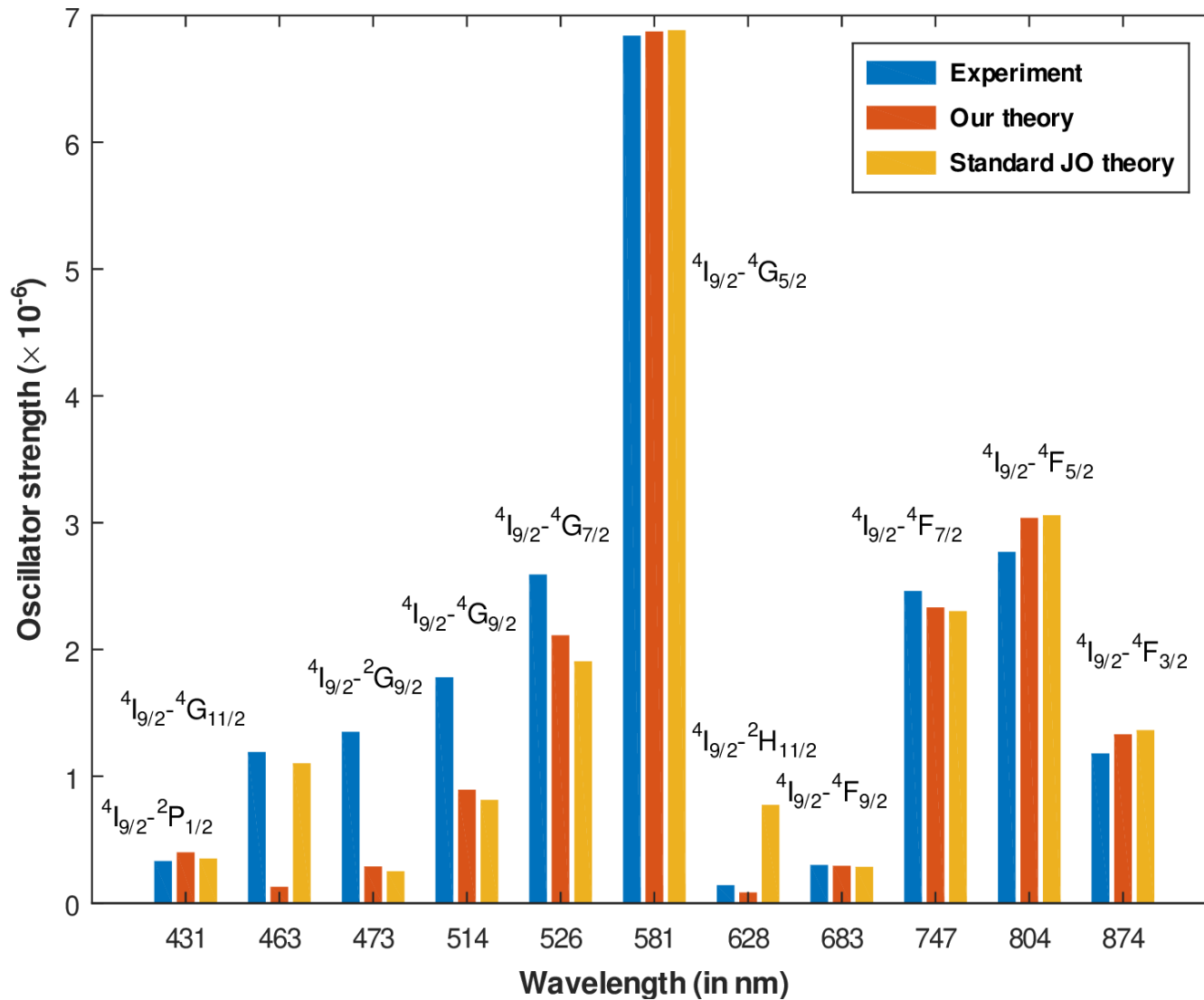
Results on Nd³⁺

Chanthima *et al.*:

Nd³⁺ in CaO-BaO-P₂O₅

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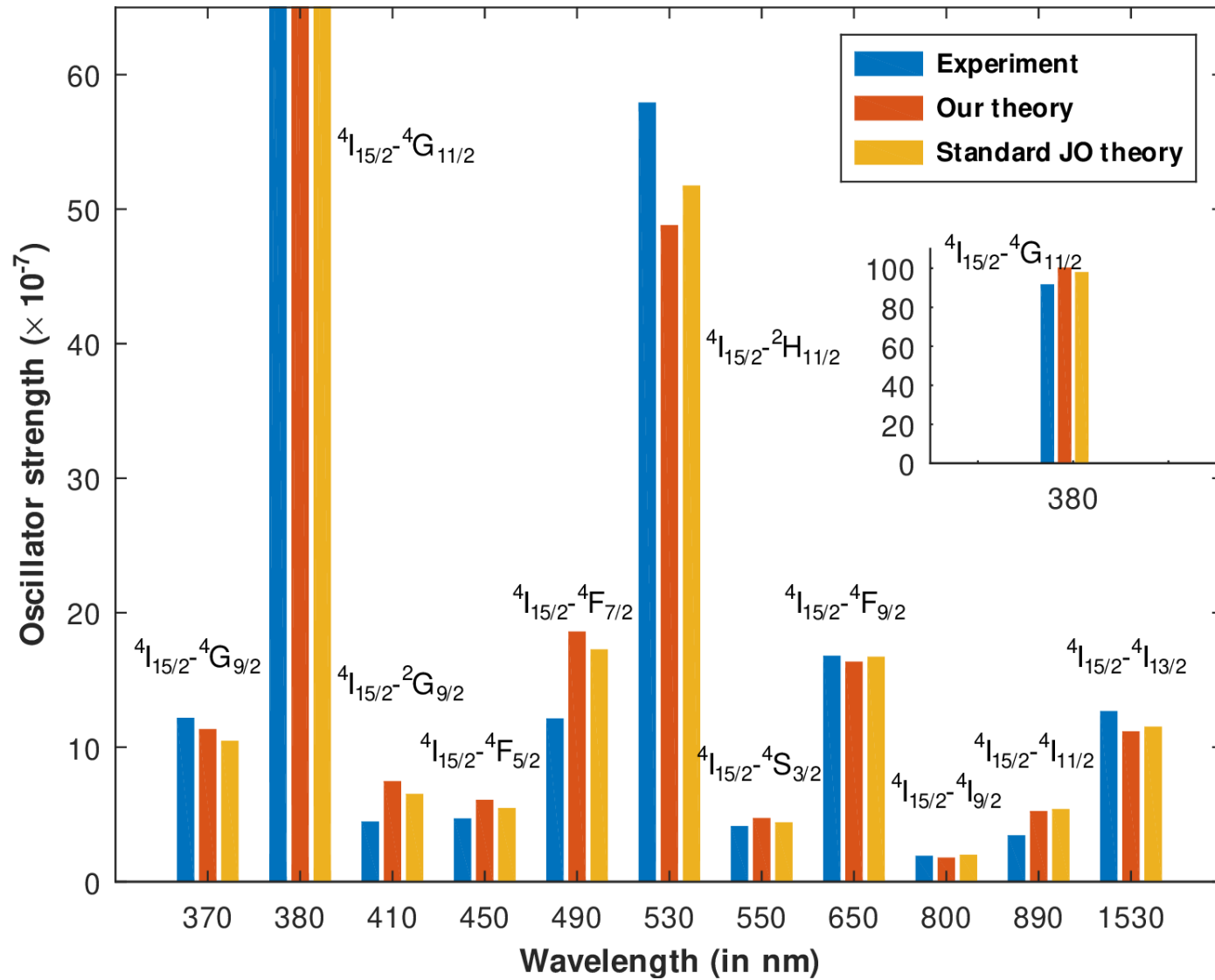


Results on Er³⁺

Piao *et al.*:
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- ✓ An extension of the Judd-Ofelt theory is developed.



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Conclusion

- ✓ An extension of the Judd-Ofelt theory is developed.
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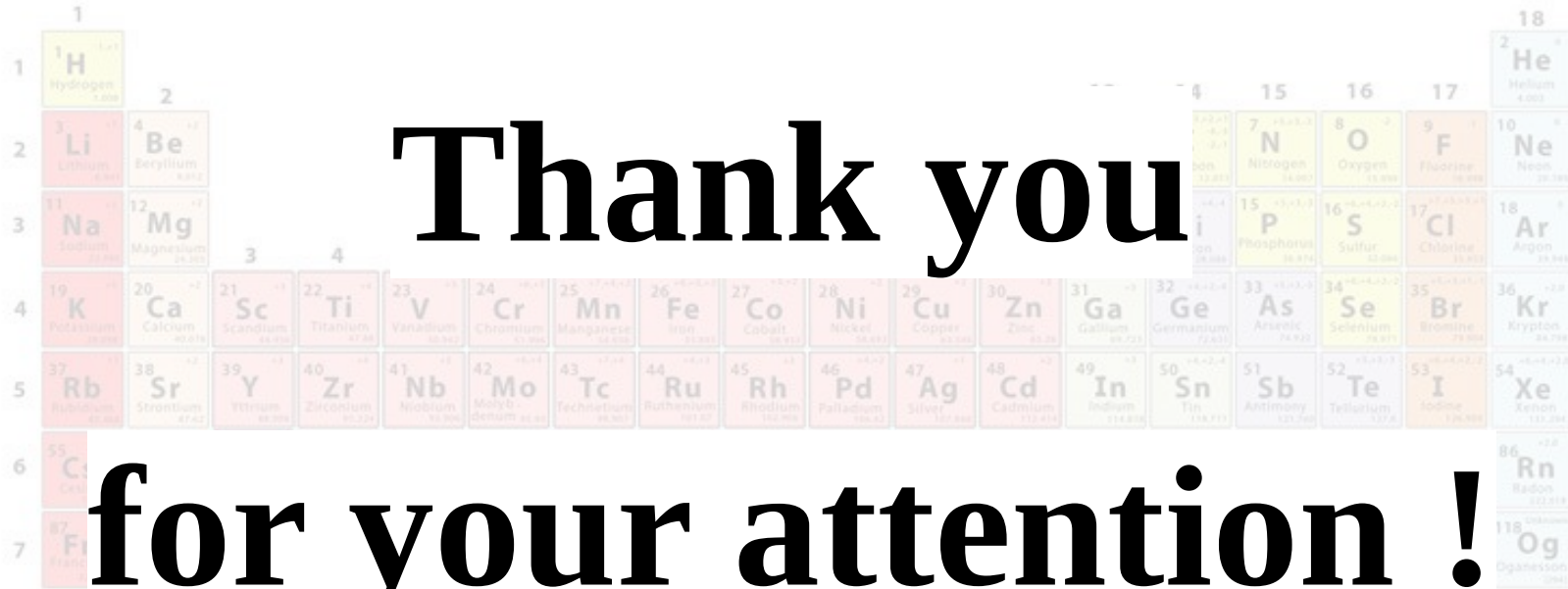
Future improvements

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

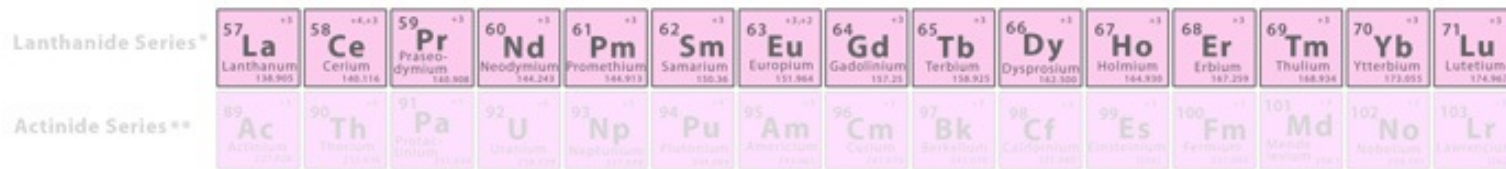


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Thank you



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

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

Description of calculations

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

$k = 1, 3, 5$

ED transition amplitude:

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

$$D_{12} = \sum_t \left[\frac{\langle \Psi_1^0 | V_{CF} | \Psi_t^0 \rangle \langle \Psi_t^0 | P_p^{(1)} | \Psi_2^0 \rangle}{E_1 - E_t} + \frac{\langle \Psi_1^0 | P_p^{(1)} | \Psi_t^0 \rangle \langle \Psi_t^0 | V_{CF} | \Psi_2^0 \rangle}{E_2 - E_t} \right. \\ \left. + \sum_u \left\{ \frac{\langle \Psi_1^0 | V_{CF} | \Psi_t^0 \rangle \langle \Psi_t^0 | H_{SO} | \Psi_u^0 \rangle \langle \Psi_u^0 | P_p^{(1)} | \Psi_2^0 \rangle}{(E_1 - E_t)^2} \right. \right. \\ \left. \left. + \frac{\langle \Psi_1^0 | P_p^{(1)} | \Psi_t^0 \rangle \langle \Psi_t^0 | H_{SO} | \Psi_u^0 \rangle \langle \Psi_u^0 | V_{CF} | \Psi_2^0 \rangle}{(E_2 - E_u)^2} \right\} \right]$$

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

Unperturbed levels:
free-ion levels:

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

Results on JO parameters

Eu³⁺

	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
Kedziorski	0.7887	6.991	-	0.1317	8.326	-	0.1008	4.940	-

Nd³⁺

	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
Chanthima	5.035	1.547	1.09	1.859	2.850	1.97	1.702	2.388	3.37

Er³⁺

	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
Piao	19.17	2.792	2.46	11.97	0.8883	1.24	2.387	0.9541	0.51