Ab initio study of chemical shifts of X-ray emission spectra in ytterbium halides by the coupled cluster method

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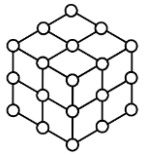

Study of the electronic structure of crystalline compounds

Difficulties:

- High density of low-lying states; (multiconfiguration nature)
- Significant contribution of relativistic effects

=> The need to simultaneously account for relativistic and correlation effects at the highest level of accuracy.

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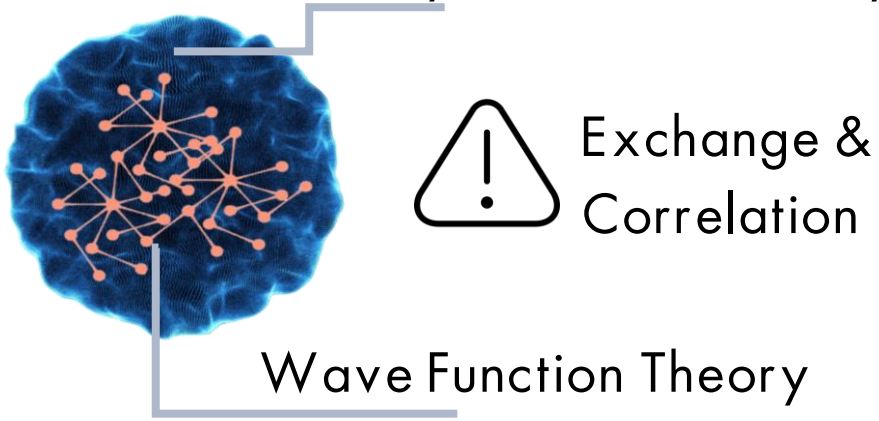

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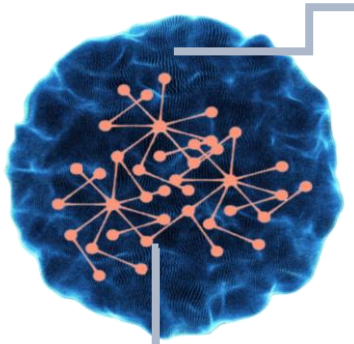
Density Functional Theory



Exchange & Correlation

Semilocal pseudopotentials

Wave Function Theory

This approach makes it possible:

- description of crystals with impurity centers
- to predict the optical properties of crystals

Methods for studying complex structures

Step 1: Quantum chemical calculation of the electronic structure

Relativistic coupled cluster method[1]

[1] Oleynichenko A.V. et al. // Phys. Rev., 2024, V. 109, p. 125106. doi: 10.1103/PhysRevB.109.125106

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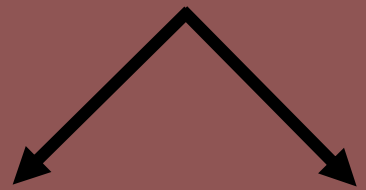
Step 1: Quantum chemical calculation of the electronic structure

Relativistic coupled cluster method[1]

Generalized relativistic core pseudopotential method[2]



Reducing the number of explicit electrons in the calculation

Increasing accuracy

[1] Oleynichenko A.V. et al. // Phys. Rev., 2024, V. 109, p. 125106. doi: 10.1103/PhysRevB.109.125106
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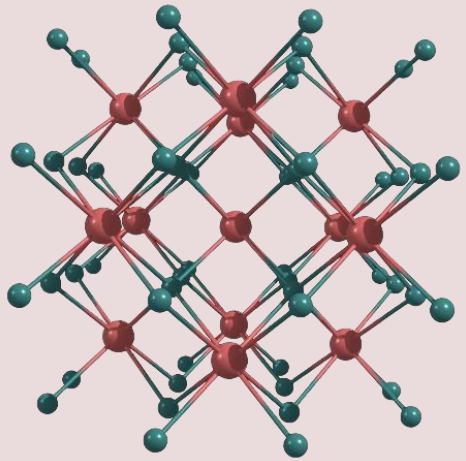
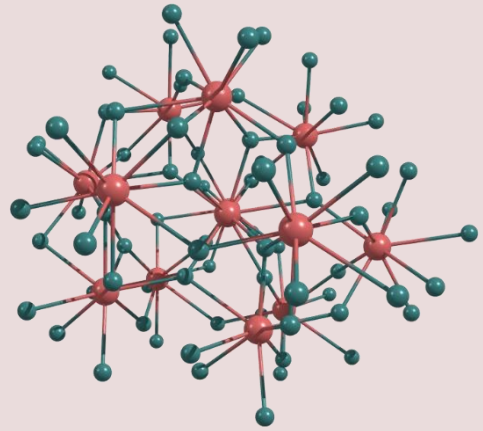
CTEP (**C**ompound **T**unable **E**mbedding **P**otential) method[3,4,5,6]



Pic 1: YbF_2@CTEP

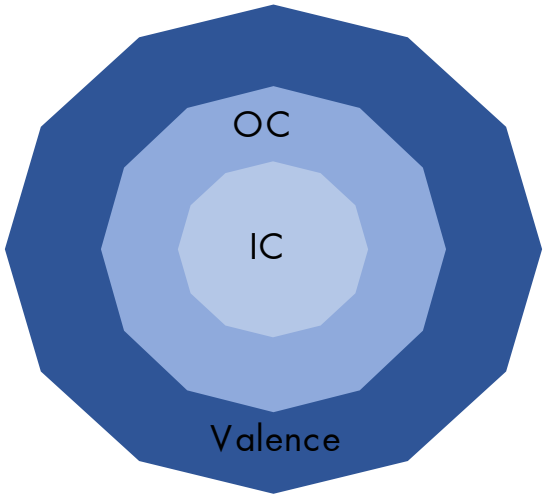


Pic 2: YbF_3@CTEP

[1] Oleynichenko A.V. et al. // Phys. Rev., 2024, V. 109, p. 125106. doi: 10.1103/PhysRevB.109.125106
[2] Titov A V, Mosyagin N S. // GRECP: Theoretical grounds, 1999, V. 71, PP. 359–401.
[3] Lomachuk Y. V. et al. // Phys. Chem. Chem. Phys, 2020, V. 22, PP. 17922-17931. doi: 10.1039/D0CP02277B.
[4] Maltsev D. A. et al. // Phys. Rev. B. 2021. May. V. 103. p. 205105. doi: 10.1103/PhysRevB.103.205105.
[5] Shakhova V. M. et al. // Phys. Chem. Chem. Phys. 2022. V. 24. PP. 19333–19345. doi: 10.1039/D2CP01738E.
[6] Oleynichenko A.V. et al. // Phys. Rev., 2024, V. 109, p. 125106. doi: 10.1103/PhysRevB.109.125106.

Methods for studying complex structures

Step 2: Restoration method[7]



Obtaining a four-component wave function after calculation with the pseudopotential

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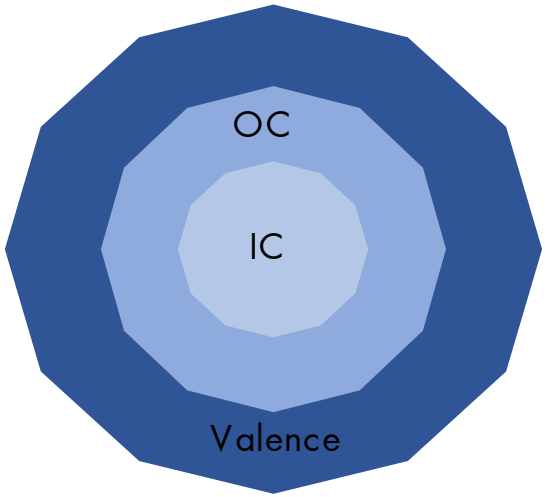

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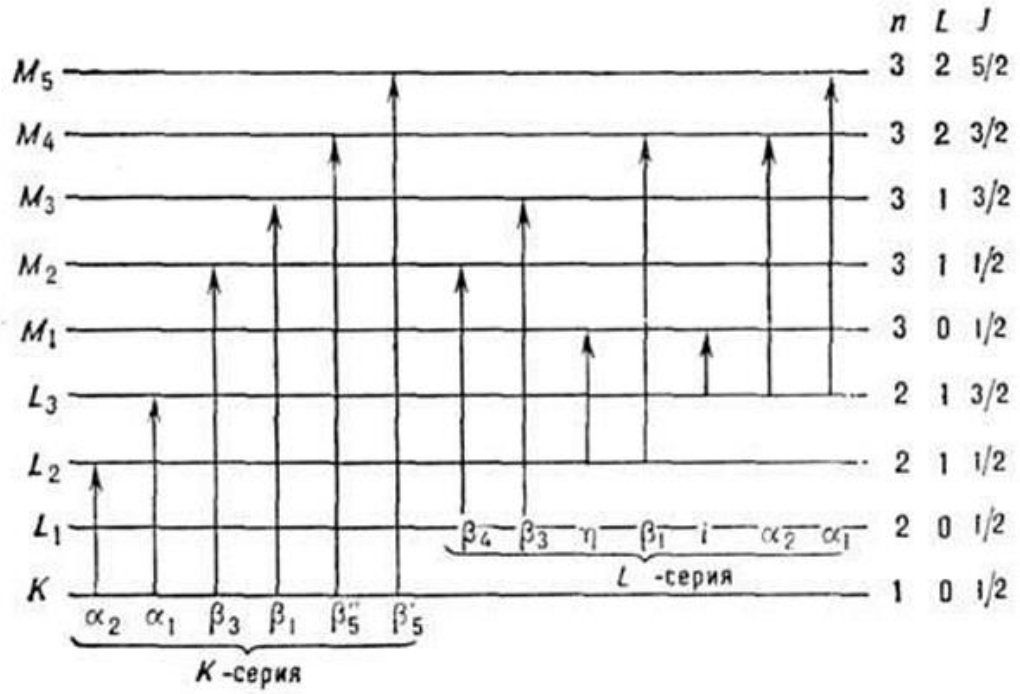
Chemical shifts of X-ray emission spectrum:



Pic 3: Diagram of the K-, L- and M-levels of atomic energy

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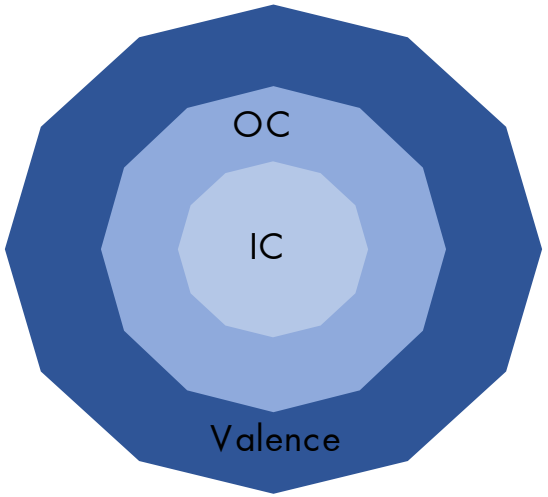

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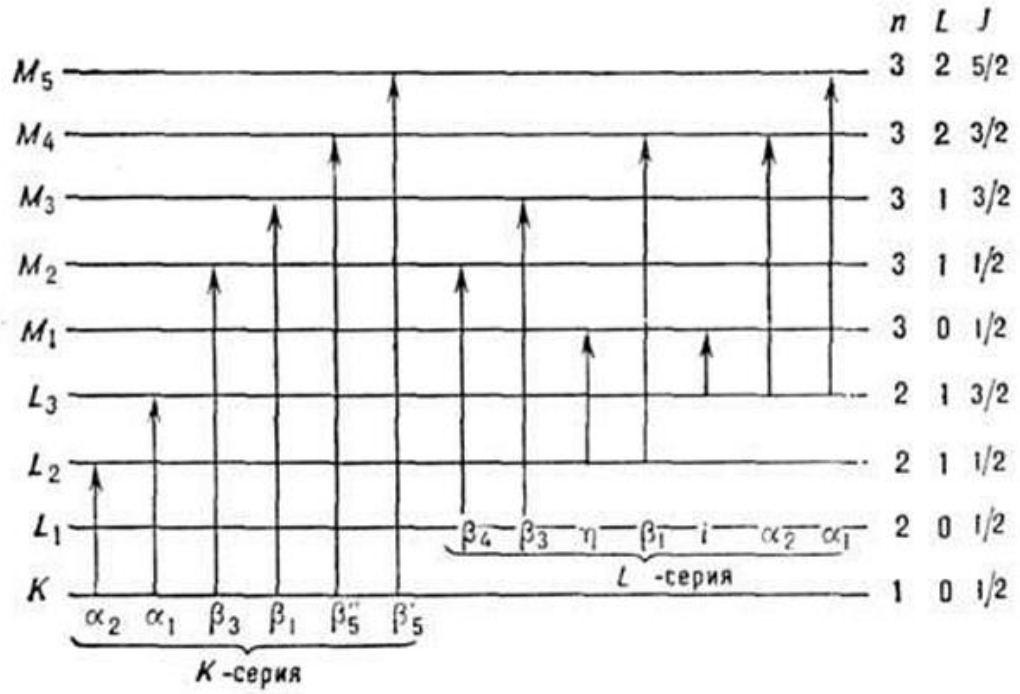


Pic 3: Diagram of the K-, L- and M-levels of atomic energy

Step 3: Method for calculating chemical shifts of X-ray emission spectrum lines[8]

Calculation of the difference quantity upon excitation of inner core states

[7]Titov A.V. et al. // Springer, Dordrecht. 2006. PP. 253-283.

[8] Lomachuk Y.V., Titov A.V. // PRA. 2013. V. 88, 6. p. 062511

Computational details

Research objects:

Crystal fragments with CTEP for $YbHal_n$(Hal=F, Cl; n=2, 3)

Method of calculations:

Dirac-Hartree-Fock

Relativistic Coupled Clusters (RCC-SD)

Program:

Dirac

EXP-T

Basis set:

F – 4s3p1d
Cl – 5s4p1d

Yb:
4s4p2d2f for compound with Yb^{2+}
6s6p4d4f for compounds with Yb^{3+}

Pseudopotentials:

11ve-PP (for compounds with Yb^{3+}):

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{13} 5s^2 5p^6 6s^2 6p^1$

59 | 11

10ve-PP (for compounds with Yb^{2+}):

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^2$

60 | 10

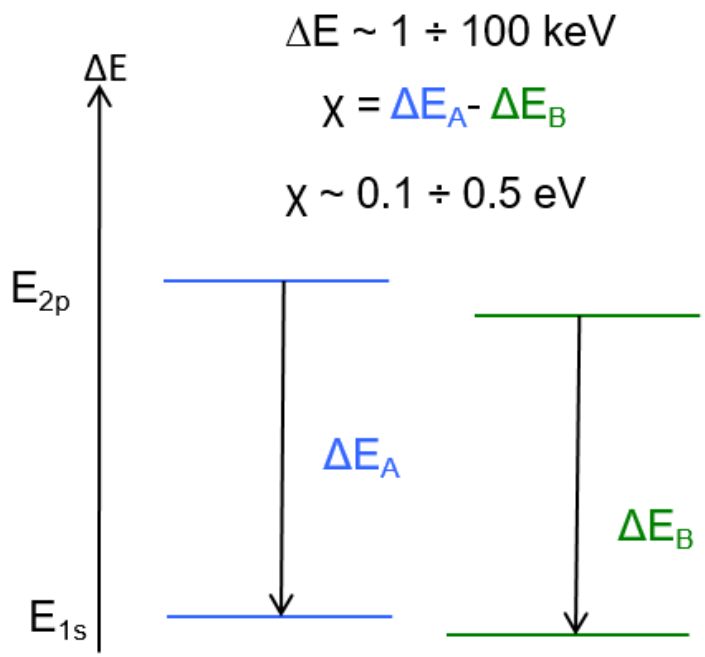
Medium-core pseudopotential

Results

Pilot calculations of chemical shifts of X-ray emission spectrum lines in crystal fragment with CTEP

CTEP	$K_{\alpha 1}$	$K_{\alpha 2}$
YbF_3/YbF_2	513	452
Experiment	579±26[9]	570±114[9]
	557±27[10]	
$YbCl_3/YbCl_2$	517	455
Experiment	574±35[11]	

Table 1: Chemical shifts of the XES lines of the Yb atom in the $YbHal_3$ crystal relative to the $YbHal_2$ crystal, meV



$$K_{\alpha 1} = 2p_{3/2} - 1s_{1/2}$$
$$K_{\alpha 2} = 2p_{1/2} - 1s_{1/2}$$

[8] Matsushita T., Hofmann H. F. Origin of meter fluctuations in weak measurement interactions // Phys. Rev. A. 2024. V. 109. p. 022224.
[9] E.V. Petrovich et al. Valence states of rare earth elements according to data on chemical displacements of X-ray lines // Radiochemistry. 1976. № 288
[10] A. Sovestnov, Academy of Sciences of the USSR, Leningrad Institute of Nuclear Physics named after B.P. Konstantinov, 1982

Contributions to the corrections to the mc-PP-CCSD calculations

Accounting for outer core electrons in Yb

Estimation of triple excitations using perturbation theory

Increasing the basis set on halogen

	System 1		System 2
Pseudopotential on Yb			
	10ve-PP (for compounds with Yb^{2+}) Frozen + $5s^25p^66s^2$ 11ve-PP (for compounds with Yb^{3+}) Frozen + $5s^25p^66s^26p^1$	**mc-PP** / **sc-PP**	42ve-PP Frozen + $4s^24p^64d^{10}4f^{14}5s^25p^66s^2$
Basis set on halogens			
	6-31G*+2s,2p F 5s4p1d Cl 6s5p1d		aug-cc-pVTZ F 5s4p3d2f Cl 6s5p3d2f
Calculation method			
	CCSD		**CCSD(T)**

Results

$$K_{average} = \frac{1}{3}(2K_{\alpha 1} - K_{\alpha 2})$$

Table 2: Chemical shifts value for ytterbium fluorides, meV

YbF_3/YbF_2	Molecules			Crystal fragment with CTEP		Experiment
	mc-PP	sc-PP	Δ	mc-PP	mc-PP+Δ	
$K_{\alpha 1}$	539	630	92	513	605	579±26[8]
$K_{\alpha 2}$	473	559	85	452	538	570±114[8]
$K_{average}$	517	607	90	493	583	557±27[9]

Table 3: Chemical shifts value for ytterbium chlorides, meV

$YbCl_3/YbCl_2$	Molecules			Crystal fragment with CTEP		Experiment
	mc-PP	sc-PP	Δ	mc-PP	mc-PP+Δ	
$K_{\alpha 1}$	521	605	84	517	601	
$K_{\alpha 2}$	457	536	79	455	534	
$K_{average}$	500	582	82	496	579	574±35[10]

Conclusions

For the first time, the chemical shifts of the X-ray emission spectrum on heavy atoms in crystals were calculated using the relativistic coupled cluster method

From the results obtained it is clear that in order to calculate the properties near a heavy atom it is necessary to carry out high-precision calculations of the electronic structure

Thanks for your attention