

## Molecular dynamics in finding nonadiabatic coupling for lanthanide ion doped nanocrystals

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Computational studies of lanthanide compounds have been considered difficult due to the presence of lanthanide ions, in which 4f electrons are arranged in an open shell. We explore applicability of the density functional theory (DFT) [1-2] to the lanthanide ion doped nanocrystals, the complicated many-body system, with the compromise between accuracy and low computational cost. Based on the previous work about modeling the hexagonal ( $\beta$ ) -NaYF<sub>4</sub>, [3] a systematic investigation on the lanthanide ion doped in  $\beta$  - NaYF<sub>4</sub> nanocrystals (Na<sub>24</sub>Y<sub>23</sub>Ln<sub>1</sub>F<sub>96</sub>, Ln = La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Pm<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, and Gd<sup>3+</sup>) is reported using the VASP [4] with Perdew–Burke–Ernzerhof (PBE) as GGA tag pseudopotential. [5-6] The f electron energy splitting is compared in non-polarized spin, spin-polarized, and spin-orbital enabled approaches. The phenomenon of lanthanide contraction has been observed after the structure optimization. The computed ground state electronic configuration is carefully analyzed using projection of KS orbitals onto atomic orbitals, while the decomposition of the orbital appreciates the Hunds' rule. The constrained DFT with spin-flip excitation provide reasonable agreement with optical transition energies for a range of lanthanide ions. Ab initio molecular dynamics of studied models at ambient temperature provides on-the-fly nonadiabatic couplings between electronic states. All this contribute to calculation of spectroscopic properties such as nonradiative lifetimes of excited states. As lanthanide ions doped  $\beta$  -NaYF<sub>4</sub> is well known as the efficient fluorescent phosphors, the theoretical research will benefit for the better understanding of these the doping material, and then for novel materials designing.

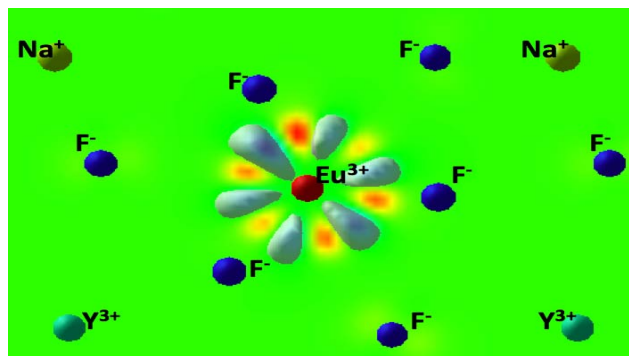


Figure: Partial charge density of  $\text{Na}_{24}\text{Y}_{23}\text{Eu}_1\text{F}_{96}$  (LUMO)

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