Molecular dynamics in finding non-adiabatic coupling for β-$NaYF_4$: Ce^{3+} nanocrystals using spin-polarized DFT+U

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Ce^{3+} ions act as blue phosphors doped in β-$NaYF_4$ nanocrystals have been a steadily increasing interest for their fundamental and technological importance. Based on previous researches on β-$NaYF_4$ modeling[1] and systematic investigating on the lanthanide ion doped in β - $NaYF_4$ nanocrystals (Ln = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+}) using spin-polarized DFT[2], a spin-polarized DFT+U approach is applied in β-$NaYF_4$: Ce^{3+} nanocrystals, in which the U value is determined by empirical results including the p-d band-gap of $NaYF_4$,[3] energy difference from $4f^n$ to $4f^{n-1}d^1$ determined through spectroscopic methods,[4] the energy differences between the first and second Russell-Saunders terms from Carnall's results,[5] and Dorenbos's relationship.[6] On-the-fly nonadiabatic couplings between electronic states at ambient temperature are simulated by combining time-dependent density matrix methodology and ab initio electronic structure methods. The absorption and the emission spectra as well as the nonradiative lifetime are simulated and compared to experiment results. Our calculations could be valuable for the better understanding of the doping material, and then for novel materials designing.

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