

Multiconfiguration Pair-Density Functional Theory for Excited States and Reactivity

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We develop electronic structure methods for modelling chemical systems in their ground and excited states. We will give an overview of these methods and then present an example of a photocatalytic study. Some $\text{LNi}^{\text{II}}(\text{Ar})\text{X}$ (L = bipyridine type ligand, $\text{X} = \text{Br}, \text{Cl}$) complexes are fundamental intermediates in photoredox-Ni catalysis for the activation of $\text{C}_{\text{sp}^3}\text{-H}$ bonds in $\text{C}_{\text{sp}^3}\text{-C}_{\text{sp}^2}/\text{C}_{\text{sp}^3}$ cross-coupling reactions. Their interaction with a light-excited Ir-photocatalyst is assumed to promote the Ni-complex to an excited state from which the Ni-X bond homolysis event occurs. Debate is open on which is the preferred mechanism, either single electron transfer (SET) or energy transfer (EnT). In an effort to solve this puzzle, we report an electronic structure analysis of these complexes and their $1e^-$ oxidized form using multi-configuration pair density functional theory (MC-PDFT), a method that aims at combining the advantages of wave function and density functional theories to allow robust modeling of strongly correlated systems.

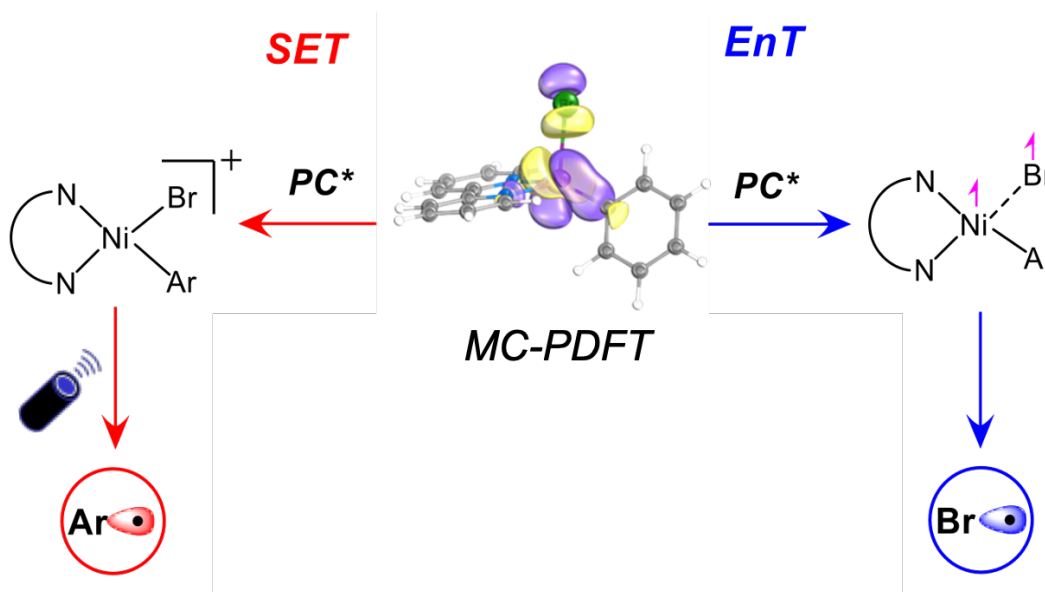


Figure 1. Our MC-PDFT study predicts an energy transfer mechanism for Ni-Br bond homolysis and suggests a single electron transfer mechanism for Ni-aryl bond homolysis.