

**When LDA provides the highest reaction barriers: Insight into quantum chemistry from  
density functional theory**

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The calculation of accurate chemical reaction barriers is of vital importance to many theoretical and experimental chemistry problems. It is well known that LDA and GGA DFT approximations frequently underestimate chemical reaction barriers, and their use in molecular calculations has been largely superseded by hybrid-GGA functionals. We present results that show that inversions to this accepted paradigm exist in multiple classes of chemical reactions, including cluster adducts, organometallic catalysts, and electrocyclic reactions. We present results from a wide range of DFT functionals on molecular reactions with high LDA barriers and show that errors in the reactions results vary widely with existing DFT functionals, with or without the incorporation of Hartree-Fock exchange, as well as the presence or lack of symmetry restrictions on the Kohn-Sham orbitals.