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Long-range exchange interactions in DFT and their significance in chemical reactions

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The significance of long-range exchange interactions is presented from the viewpoint of DFT in quantum chemistry [1] in the first part, and then, it is shown focusing on chemical reactions in the second part.
So far, we have developed the long-range corrected (LC) DFT [2] and have applied it to a wide variety of chemical and physical properties [3]. As a result, we have confirmed that the long-range exchange interactions are required to calculate various types of the properties: e.g. charge transfer excitations [4], van der Waals bonds [5], nonlinear optical properties [1] and so forth. Orbital energies may be the most significant property that LC-DFT makes it possible to calculate quantitatively [6]. Since orbital energies are the solution of the Kohn-Sham equation, this indicates that the long-range correction essentially improves DFT (or exactly the generalized DFT). In the first part, I will briefly review our past studies on LC-DFT.
Recently, we are investigating chemical reactions using the quantitative orbital energies. As the exact orbital energies are proven to inhere, LC-DFT orbital energies hardly vary dependent on occupation numbers. Chemical reactions usually proceed through charge transfers in the initial processes. We found that LC-DFT orbital energies are kept almost constant in the initial processes of many reactions, and then, they rapidly increase toward the products [7]. We have recently developed an orbital energy-based reaction theory as the modification of conceptual DFT [8]. I will present this topic in the second part.

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