

Density based index based tuning of range-separated hybrid functionals

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ABSTRACT

Many literature surveys allowed to show how DFT in conjunction with widely used global hybrid functionals while being successfully in the prediction of several properties may dramatically fail to correctly predict the energetic of excited states with relevant through-space charge-transfer (CT) character. Range separated hybrids and especially optimally tuned RSH have been proven to provide an elegant and efficient solution to this problem.

With the aim of proposing a procedure to identify the range separation parameter in a consistent, system adaptable and computationally inexpensive way, in this contribution we made use of the inverse of the highest predicted CT length computed for excited states of interests as range separation distance. This distance of charge transfer associated to each transition was estimated by the means of the density based index (D_{CT}) by a vertical TDDFT calculation. [1]

In particular we tested the accuracy of the so obtained range separated hybrids for a RSH hybrid casting 25% HF_x at the short range and 100% HF_x in the long range and making use of the PBE exchange and correlation counterpart (that we will name shortly as LC-PBE0*). [2-3]

The functional so obtained has been tested for both intra- and inter-molecular charge-transfer excited states both on model systems and on chemically relevant compounds showing high accuracy in the prediction of both CT and Locally Excited states, encouraging for its wider application to chemically relevant compounds.

References

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