

Nonempirical DFT models: better performances with more theoretical constraints

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Modern computational approaches based on Density Functional Theory (DFT) provide valuable answers for most of the chemical problems to which they are applied, and this success well correlates with their widespread use. Despite these achievements, DFT still faces some challenges that cannot be ignored in view of their relevance in Chemistry and Physics. Among others, noncovalent interactions and charge transfer excitations can be mentioned.

In order to deal with these problems and further expand the domain of applicability of DFT, better performing exchange-correlation functionals are systematically proposed. They can be classified into two broad families, following the procedure used for their construction. The first family is composed by semi-empirical approaches, that is by all the functionals whose internal coefficients are determined by an error minimization procedure with respect to external reference datasets. By opposition, the second family contains nonempirical functionals whose coefficients are fully determined on the basis of theoretical arguments.

In this talk we describe our non-empirical approach which, starting from well-defined theoretical considerations, allows for the definition of new functionals whose performances are comparable with those obtained by semi-empirical approaches. Discussion of selected cases, including ground and excited states properties, not only shows the large domain of applicability of non-empirical functionals, but also underlines how increasing the number of theoretical constraints induces an improvement of the numerical performances.

References

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