MOLECULAR PHYSICS
2022, VOL. 120, NO. 3, e1983056 (18 pages)
https://doi.org/10.1080/00268976.2021.1983056

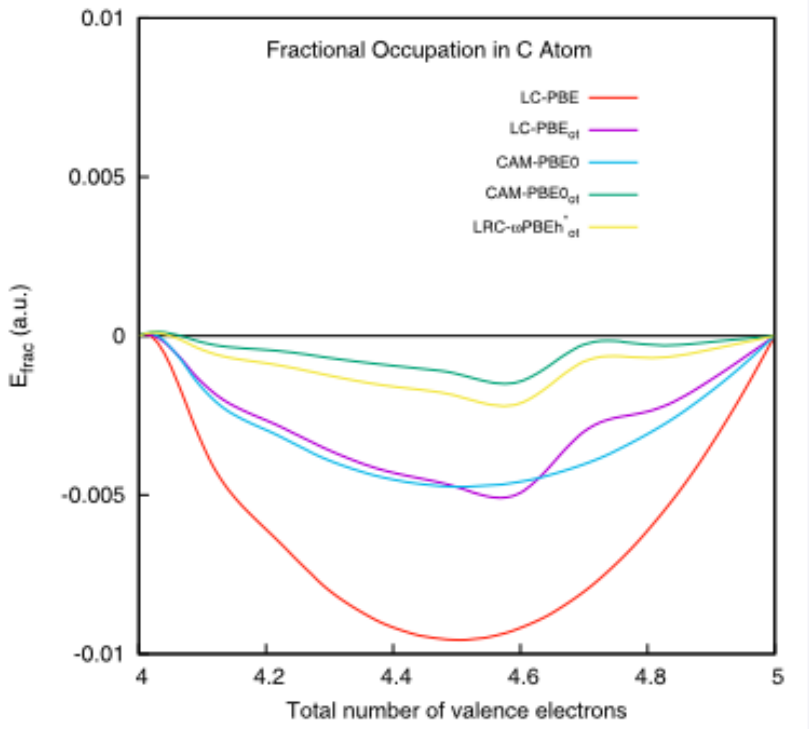
Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

A self-consistent systematic optimisation of range-separated hybrid functionals from first principles

Abhisek Ghosal* and Amlan K. Roy

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Nadia, Mohanpur, India



ABSTRACT

In this communication, we represent a self-consistent systematic optimisation procedure for the development of optimally tuned (OT) range-separated hybrid (RSH) functionals from *first principles*. This is an offshoot of our recent work, which employed a purely numerical approach for efficient computation of exact exchange contribution in the conventional global hybrid functionals through a range-separated (RS) technique. We make use of the size-dependency based ansatz, i.e. RS parameter, γ, is a functional of density, $\rho(\mathbf{r})$, of which not much is known. To be consistent with this ansatz, a novel procedure is presented that relates the characteristic length of a given system (where $\rho(\mathbf{r})$ exponentially decays to zero) with γ self-consistently via a simple mathematical constraint. In practice, γ_{OT} is obtained through an optimisation of total energy as follows: $\gamma_{\mathrm{OT}} \equiv \underset{\gamma}{\mathrm{opt}}\, E_{\mathrm{tot},\gamma}$. It is found that the parameter γ_{OT}, estimated as above can show better performance in predicting properties (especially from frontier orbital energies) than conventional respective RSH functionals, of a given system. We have examined the nature of highest fractionally occupied orbital from exact piecewise linearity behaviour, which reveals that this approach is sufficient to maintain this condition. A careful statistical analysis then illustrates the viability and suitability of the current approach. All the calculations are done in a Cartesian-grid based pseudopotential (G)KS-DFT framework.