Tightening “Loose” Electrons Within the DFT Framework: An Effective One-Particle Approach Based on the GKS-spRPA Method

Vamsee K. Voora and Ritaj Tyagi

Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005

E-mail: vamsee.voora@tifr.res.in; Ph: 022-2278-2978

Commonly used density functional approximations, such as the PBE and B3LYP functionals, often underestimate electron affinities due to an incorrect long-range potential resulting from self-interaction errors and a lack of dispersion-type correlation effects. In certain cases, stable anions are predicted to be unstable. Here I will show that the effective potential from generalized Kohn-Sham semicanonical projected random phase approximation (GKS-spRPA) has the correct long-range behavior necessary for the description of anionic states. As a result, valence and nonvalence anionic states of molecules are equally well-described. Using an improved algorithm for GKS-spRPA, with $O(N^4)$ computational scaling, I will discuss interesting variations in the nature of anionic states of perhalobenzene molecules (C_6X_6; X=F,Cl, Br or I) [1]. Finally I will discuss the development of practical approximations to enable the simulation of electron affinities of large molecular-clusters.

[1] V. K., Voora, *J. Phys. Chem. Lett.* **12** (2021) 433-439.