Title:

Critical analyses and fundamental theoretical developments in computational chemistry

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Abstract:

We advance audacious revisiting of backgrounds of computational chemistry, by key revisions of basis set conceptual and technical aspects and innovative contributions to the Density Functional Theory (DFT).

The Gaussian Type Orbitals (GTOs) were drawn at dawn of computational chemistry as replacement of Slater type functions. Initial compromises done in this view became, in meanwhile, hidden and overlooked, since the intense routine with GTOs seemed to act are quality warrantor. However, the drawbacks and limitations of GTOs are serious, denounced in actual project, altogether with a plan of rationales to cure the situation. A major issue is the tacit limitation of radial factors to r^l powers related with the l secondary quantum number of a given shell, impeding the account of radial profile at superior orbital levels. A good part of the rich bases are unnecessarily oversized patches to these limitations, while introducing the higher radial monomial factors is a better alternative. We also devised a strategy to tailor basis sets by equating the spectral terms with the help of Slater-Condon integrals, done by radial-angular factorization (a regularity obscured in GTO practice).

In DFT, we point the inconsistencies emerging from Local Density Approximation (LDA), assuming spherical symmetry of exchange hole, valid for homogenous electron gas, but offending the symmetry in atoms, when placed in general acentric position. The gradient corrected methods are only partly alleviating the effect. We propose a new principle, imposing, for atoms, exchange-correlation hole devised as spherical crust with sharp cusp profile. Conceiving the atomic body energy as continuous function of shell populations, we draw unprecedented strategies to asses DFT-alike energy derivatives based on experimental spectroscopy or multi-configuration calculations. The principle leads to a new generation of Density Functional Tight Binding (DFTB) approximate methods, best suited for nanoscale system.