Towards an accurate WFT-in-DFT subsystem approach to computational chemistry

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In the conventional approach to electronic structure theory a system is viewed as an unstructured collection of nuclei and electrons, requiring only the specification of nuclear positions and charges and the total number of electrons to start a calculation. This truly *ab initio* approach is very appealing and can for small molecules lead to results that rival high-resolution spectroscopic techniques, thereby providing a numerical laboratory to study electronic properties and reactivity. One realization of this approach is relativistic coupled-cluster method[1] in which electron correlation and relativity are treated on equal footing. I will show some examples of applications[2] done with the implementation available in the Dirac programme suite[3] to illustrate its capabilities.
While the application of large-scale supermolecular calculations is still gaining popularity, due to the ever-increasing computational power, such an uncompromising approach also has its disadvantages, however. For complex systems one would ultimately like to understand trends observed upon substitution of functional groups in terms of familiar concepts like chemical bond strength, steric hindrance, atomic or molecular charges, etc. Rather than just obtaining these concepts in an a posteriori analysis, one would ideally like to utilize chemical knowledge concerning the distinction between metal and ligands, solvent molecules, functional groups already in the setup of the calculations. In the flexible subsystem scheme[4] implemented in the Amsterdam Density Functional[5] (ADF) code this is made possible. The theoretical framework for this technique is the frozen-density embedding method, that was first formulated by Wesolowski and Warshel[6], and defines the total electron density of a supermolecular system as a sum of densities obtained in individual calculations of chemically well-defined subsystems. We have extended this theory to include also magnetic interactions[7] and introduced a capping approach[8] to treat connections between strongly coupled systems. We are now working on the improvement of currently available kinetic energy functionals by studying the properties of accurate reference potentials[9]. I will give an overview of our experiences[10] with this subsystem formulation of density functional theory and discuss perspectives for its further development as a WFT-in-DFT subsystem method[11].

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