

Polarisation and response in Frozen Density Embedding

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The unfavourable scaling of accurate quantum-mechanical electronic structure methods makes them feasible only for small systems. This is a major hurdle for modelling real chemical systems such as molecules in an environment, be it a solvent, an enzyme, or a crystalline structure. Multi-level methods try to overcome this issue by using different levels of theory in different spatial regions, with consequent challenges in how to interface them.

Frozen Density Embedding Theory (FDET) [1] is a multi-level method which describes the effect of a frozen electron density of the environment, $\rho_B(\vec{r})$, on the wavefunction of the system of interest (Ψ_A), maintaining a quantum-mechanical description for the whole supermolecular system.

FDET exhibits large flexibility [2]: any choice of methods for the subsystems A and B is possible, including for instance the generation of $\rho_B(\vec{r})$ as a superposition of densities or time-averaging [3]. Additionally, the multi-level approach of this formalism can be further extended by combining it with other environment models (e.g. PCM, MM).

Three factors determine the accuracy of FDET-based embedded wavefunctions:

- the basis set expansion, which may excessively localise the wavefunction
- the approximate nature of the DFT functionals used for exchange-correlation and kinetic component of the interaction [4]
- violations of the condition $\rho_B^{frozen}(\vec{r}) \leq \rho_{TOT}^I(\vec{r})$

In particular, the latest relates to chemical phenomena such as polarisation and environment response.

In order to investigate the influence of such phenomena on the quality of FDET results, we selected embedding protocols which differ in the way $\rho_B(\vec{r})$ is generated, resulting in different manners of accounting for polarisation effects [5]. Via the application of such protocols to chemical systems with varying extent of polarisation and environment response, we aim to understand the sources of error in different types of interactions, and guide the selection of an appropriate protocol for the system at hand.

References

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