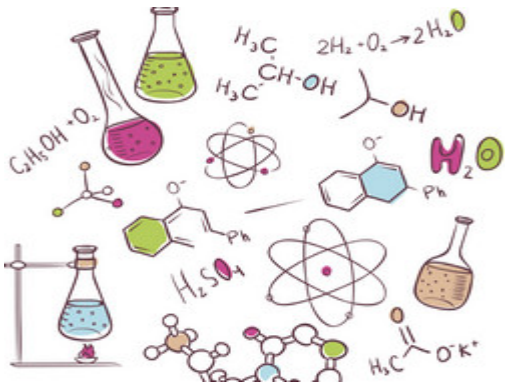
Development of Modern Density Functional Methods: Combining the Correlation Factor Model and the Local
Hybrid Approach

Results in Brief

New computational methods to study electron behaviour

The Kohn-Sham equations provide the framework for finding the exact energy (principally the ground state) of many-body systems that require an explicit expression of the exchange-correlation (XC) functional. EU-funded scientists succeeded in developing functionals that more faithfully represent electron collective behaviour compared to currently used approximations.

ENERGY



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Global hybrids, which are typical examples of XC functionals employing exact exchange, are amongst the most widely used density functionals in quantum chemistry. Despite their success, they are unable to reproduce the exact exchange energy in regions with zero or negligible correlation. These include the core, the density tail and the one-electron regions.

Design of XC functionals that are not constructed with empirical fitting of their

parameters has to date been a major problem. Within the project CFMLHA (Development of modern density functional methods: Combining the correlation factor model and the local hybrid approach), scientists compensated for the lack of such functionals by successfully designing new non-empirical XC functionals that are better alternatives to global hybrids.

The focus was on the correlation factor model that has hitherto received little attention. To develop the functionals from it, the team presented new formulas for the XC hole that are written as a product of two factors: the exchange hole and the correlation factor. The XC hole is a region of space around an electron in which the probability of finding another electron is close to zero.

To reduce complexity, the correlation factor model was based on a model exchange hole reproducing the exact exchange energy per electron. The model exchange hole was then multiplied by a correlation factor consisting of five parameters. The team developed four correlation factor models.

The XC model and the correlation factor were implemented in Mathematica and a modified version of Gaussian, a commercially available suite of quantum chemistry programmes. The performance of all correlation factor models was evaluated against commonly used functionals. Results demonstrated that the correlation factor approach is flexible enough to construct exact exchange-based functionals without the parallel development of local hybrids.

CFMLHA showed new paths to first-principle construction of XC functionals based on full exact exchange. The first principle-based design is crucial in density functional theory – a method that revolutionised computational chemistry. Project results have important implications for diverse fields, including biochemistry or medicinal chemistry, physics, pharmacology, materials science and catalysis.

Keywords

Exchange-correlation | XC functionals | quantum chemistry | exchange energy | correlation factor model

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CFMLHA

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