TRANSFERABILITY OF THE TKATCHENKO-SCHEFFLER AND THE MANY-BODY DISPERSION METHOD BETWEEN QUANTUM CHEMICAL CODES

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AIM AND SCOPE

Many density functional theory (DFT) methods miss the dispersion interaction between molecules and materials. These interactions are, however, known to be important in (for example) describing

- physics and chemistry of medium-to-large molecules,
- biomolecules and biochemistry in general,
- surface and nano science; material science

The many-body dispersion (MBD) [1] is a popular DFT dispersion method; implementation and validation of this method would improve our understanding of the aforementioned fields.

OBJECTIVES

The objective was twofold

- implement the MBD method in different codes,
- benchmark with different DFT ideas.

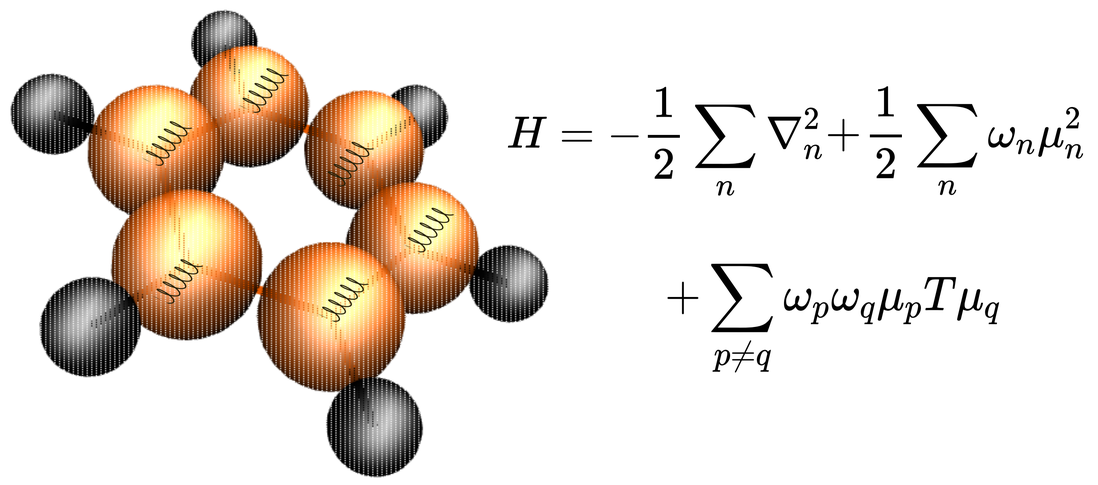
The implementations should be based on the publicly available library LibMBD. For FHI-AIMS this was already the case, for Quantum Espresso I've implemented the library myself, for Q-Chem this is in progress - but a direct implementation is available (D. Barton).

METHODOLOGY

The technical details of the implementation were tested with the core developers against FHI-AIMS (as reference).

For the benchmarking purposes, the S66 dataset [2] containing 66 medium-sized van der Waals bound molecules was used. Tests were done to ensure the reproducibility of the binding energy and the dispersion forces, as well as the geometry optimization.

FIGURE 1



Many-body Hamiltonian: electron cloud as a collection of oscillators.

FIGURE 2

The three ab initio codes examined in this work.

REPRODUCIBILITY CRITERIA

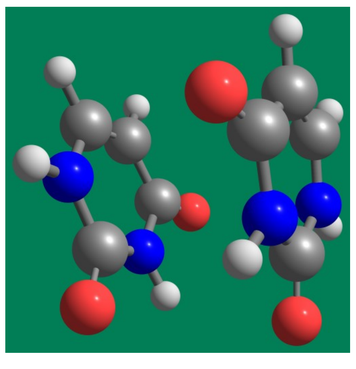
For the DFT simulations to be reproducible, two main criteria need to be true

- chemical accuracy of the energies (1 kcal/mol),
- transferability of forces.

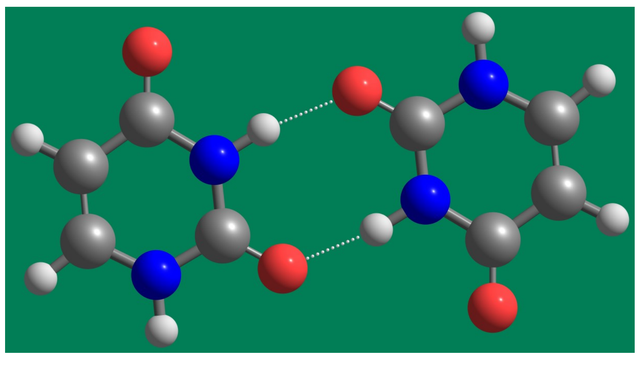
If the force components for the same structure are reproducible, then differences between optimized geometries stem from the underlying algorithms.

EFFECT OF DISPERSION INTERACTION ON THE GEOMETRIES

MBD

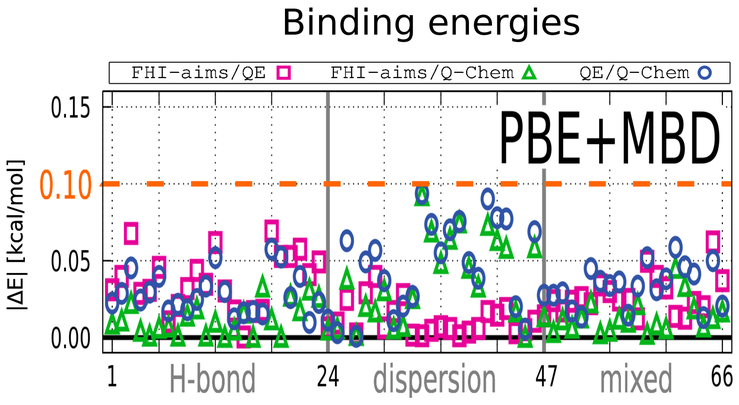


No dispersion

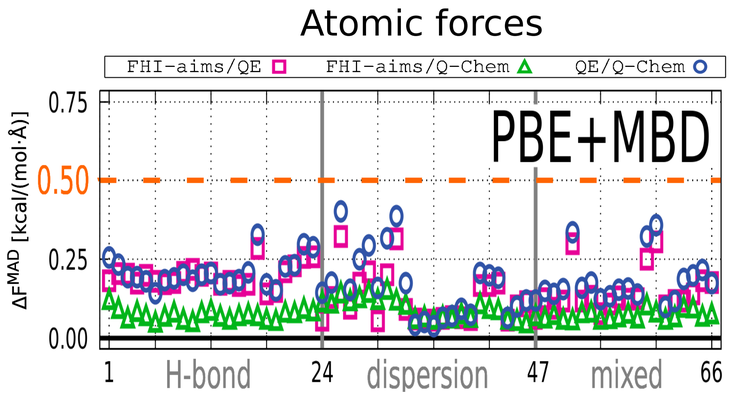


REPRODUCIBILITY OF THE IMPLEMENTATION

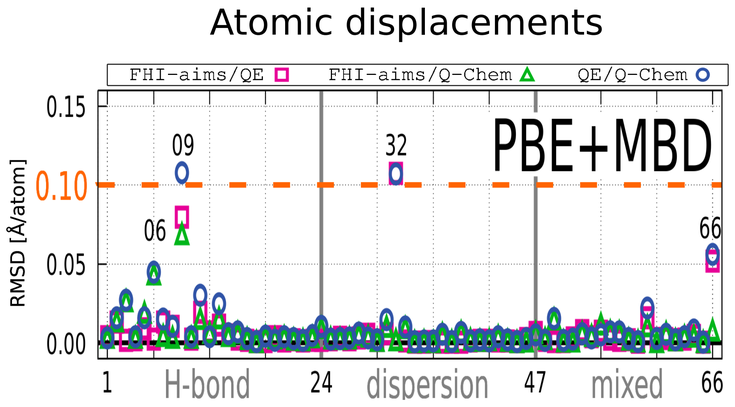
Binding energies



Atomic forces



Atomic displacements



CONCLUSION

The many-body dispersion (MBD) method gives reliable and transferable energies and atomic force components between different basis set ideas: plane waves, Gaussian basis and numerical basis. Suggested convergence criteria are also given [3].

ACKNOWLEDGEMENT

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[1] A. Ambrosetti, A. M. Reilly, R. A. DiStasio Jr., A. Tkatchenko: *Long-range correlation energy calculated from coupled atomic response functions.* J. Chem. Phys. **2014**, 140, 18A508
[2] J. Rezac, K. E. Riley, P. Hobza, *S66: A Well-balanced Database of Benchmark Interaction Energies Relevant to Biomolecular Structures.* J. Chem. Theory Comput. **2011**, 7, 8, 2427–2438
[3] D. Barton, S. Goger, K. U. Lao, R. A. DiStasio Jr., A. Tkatchenko *Implementation, Validation and Reproducibility of the Tkatchenko-Scheffler and Many-Body Dispersion Methods in Three Electronic-Structure Codes.* in preparation.