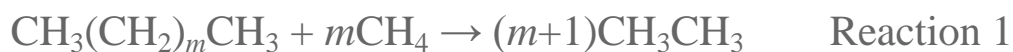


# ORIGIN OF DFT FAILURES – PART III

The much publicized failure of common DFT methods to accurately describe alkane isomer energy and bond separation reactions (which I have blogged about many times) has recently been attributed to long-range exchange<sup>1</sup> or simply just DFT exchange<sup>2</sup>. Grimme now responds by emphatically claiming that it is a failure in accounting for medium-range electron correlation.<sup>3</sup>

First, Grimme notes that the bond separation energy for linear alkanes (as defined in Reaction 1) is underestimated by HF, and slightly overestimated by MP2, but SCS-MP2 provides energy in nice agreement with CCSD(T)/CBS energies. Since MP2 adds in coulomb correlation to the HF energy (which treats exchange exactly within a one determinant wavefunction), the traditional wavefunction approach strongly suggests a correlation error.



Next, bond separation energies computed with PBE and BLYP (which lack exact exchange), PBE0 (which has 25% non-local exchange) and BHLYP (which has 50% non-local exchange) are all similar and systematically too small. So, exchange *cannot* be the culprit. It must be correlation.

He also makes two other interesting points. First, inclusion of a long-range correction – his recently proposed D3 method<sup>4</sup> – significantly improves results, but the bond separation energies are still underestimated. It is only with the double-hybrid functional B2PLYP and B2GPPLYP that very good bond separation energies are obtained. And these methods do address the medium-range correlation issue. Lastly, Grimme notes that use of zero-point vibrational energy corrected values or enthalpies based on a single conformation are problematic, especially as the alkanes become large. Anharmonic corrections become critical as does inclusion of multiple conformations with increasing size of the molecules.

Source: <http://comporgchem.com/blog/?p=1203>