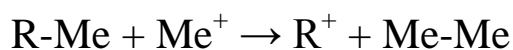
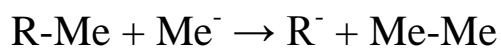
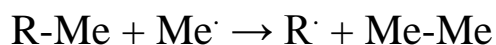
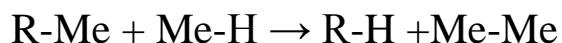


ORIGIN OF DFT FAILURE

The failure of DFT in dealing with some seemingly straightforward reactions (as discussed in these previous blog posts: A, B, C, D, E, F) has become a bit clearer. Brittain and co-workers have identified the culprit.¹ They examined twelve different reactions, involving neutral, radical, cations and anions:



where R is ethyl, *i*-propyl and *t*-butyl. They used a variety of different functionals, and benchmarked the energies against those found at CCSD(T)/cc-pVTZ.

By systematically using different densities and different exchange and correlation components, DFT exchange is responsible for the poor performance – and it can be very poor: the error for the cation reaction with R=*t*-butyl is 12 kcal mol⁻¹ with B3LYP and 18 kcal mol⁻¹ with PBE. It should be noted that the maximum error with G3(MP2) and MP2 is 1.5 and 2.5 kcal mol⁻¹, respectively. These authors make three important conclusions: (a) that traditional *ab initio* methods are preferred, (b) that development of new functionals should target the exchange component, and (c) Truhlar's highly parameterized functional MO5-2X works quite well (maximum error is 2.6 kcal mol⁻¹ – again for the cation *t*-butyl case) but the reason for its success is unknown.

Source: <http://comporgchem.com/blog/?p=115>