Semi-empirical fitting of exchange-correlation functionals

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We describe our continuing work to improve the quality of semi-empirical exchange-correlation functionals in DFT by fitting to a diverse range of properties with a large number of training molecules. This highly empirical approach can result in significant improvements in accuracy over competing generalised gradient approximation (GGA) and hybrid functionals.

Previous studies [1,2] have shown that a simple gradient correction to the local density approximation can provide NMR shielding constants for challenging main-group nuclei that are 2-3 times more accurate than those of conventional GGAs and hybrids. These functionals were denoted KT1 and KT2. By adding one additional exchange term, the KT3 GGA functional was developed [3], which retained the quality of shielding constants while substantially improving the performance for other properties. In particular, it gives atomisation energies that are as accurate as the best competing GGA functionals and equilibrium molecular bond lengths that are as accurate as the best hybrid functionals. However, its performance for classical reaction barriers is relatively weak. We describe our attempts to develop new GGA and hybrid functionals that give improved reaction barriers while retaining the high quality performance of KT3 for other properties.

[1] T.W. Keal and D. J. Tozer, *J. Chem. Phys.* **2003**, *119*, 3015.
[2] M.J. Allen, T.W. Keal and D.J. Tozer, *Chem. Phys. Lett.* **2003**, *380*, 70.
[3] T.W. Keal and D.J. Tozer, *J. Chem. Phys.* **2004**, *121*, 5654.