

The role of exchange in systematic DFT errors for some organic reactions†

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Serious (up to 87 kJ mol⁻¹) systematic DFT errors in a series of isodesmic reactions are found to be due to the DFT exchange component, and can be largely corrected by substitution of the DFT exchange energy with the Fock exchange energy.

I. Introduction

It has recently been noted by us¹⁻⁴ and by others⁵⁻¹⁵ that density functional theory (DFT) methods fail dramatically for organic reactions in which the extent of substitution changes dramatically. This failure has been demonstrated for isodesmic reactions involving alkanes,⁹⁻¹² organic molecules containing heteroatoms,¹³ and radicals.¹⁻⁴ These results are surprising, considering that isodesmic reactions have a large degree of intrinsic error cancellation; even the relatively modest second order Møller–Plesset perturbation theory (MP2) method gives good results for reactions of this type.¹

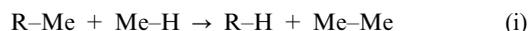
The cause of these errors remains unclear. The self-interaction error is often invoked to explain DFT errors, however this is usually prevalent in systems with abnormally stretched bonds.^{16,17} The errors considered in the investigations above are observed for hydrocarbons near their equilibrium geometries, and self-interaction error is therefore unlikely to be the cause of the problem.

Wodrich *et al.*¹¹ claimed that poorly described van der Waals interactions are responsible. This was subsequently shown by Grimme⁹ to be unlikely, given that DFT methods model the rotational barrier about the central C–C bond of *n*-butane adequately. We have also found that DFT performs well for rotational potentials in general.

Grimme⁹ attributed the DFT errors for alkane isomerisation reactions to a poor description of “medium-range correlation effects”, based on a localised orbital MP2 analysis. He assumed, however, that DFT was modelling all other components of the DFT energy well, which is not necessarily the case.

We wish to investigate further. We began by defining a new test set, which is designed to compare the

performance of DFT for neutral, radical, anionic and cationic reactions:



where the change in the extent of substitution increases across a series as R is varied through Et, *i*-Pr, *t*-Bu. The radical reactions¹ and analogues of the neutral reactions¹¹ have been examined previously, but the ionic reactions have not, and the test set compares all four types of reaction in a consistent manner.

Using this test set, in combination with a set of simple DFT functionals, we investigate the scope of the systematic errors. Subsequent analysis shows that the DFT exchange component is at fault.

II. Results and discussion

Computational results for our new test set are shown in Fig. 1, using CCSD(T)/cc-pVTZ as the reference.²⁴ The systematic DFT failures are obviously not restricted to reactions involving radicals and neutral species, but are also present in reactions involving anions and cations. This result is particularly interesting because the errors are present to a greater or lesser extent, even though the chemistry in each of these reaction series is very different. The errors are particularly dramatic for the cationic reactions; BLYP has an error of -68.9 kJ mol⁻¹ for the *t*-butyl cation reaction, for example. The problem is not confined to DFT methods that are based on the uniform electron gas (UEG); the BR89B94hyb method,^{18,19} whose construction makes no appeal to the UEG, also performs poorly. In contrast to the DFT methods, G3(MP2)-RAD (and even MP2) perform well. It is also clear that functionals with a large admixture of Fock exchange, such as BMK (42%) and KMLYP (55.7%), perform better than “pure” functionals that depend on the density only; for the anionic reactions, it appears that admixing Fock exchange can rectify the problem, or even over-correct it. B3LYP, which is not as bad as the pure functionals, but worse than BMK and KMLYP, has 20% Fock exchange. We hypothesise, therefore, that the DFT exchange component is the cause of these systematic DFT errors, and note that the error seems to be less prominent in the anionic series.

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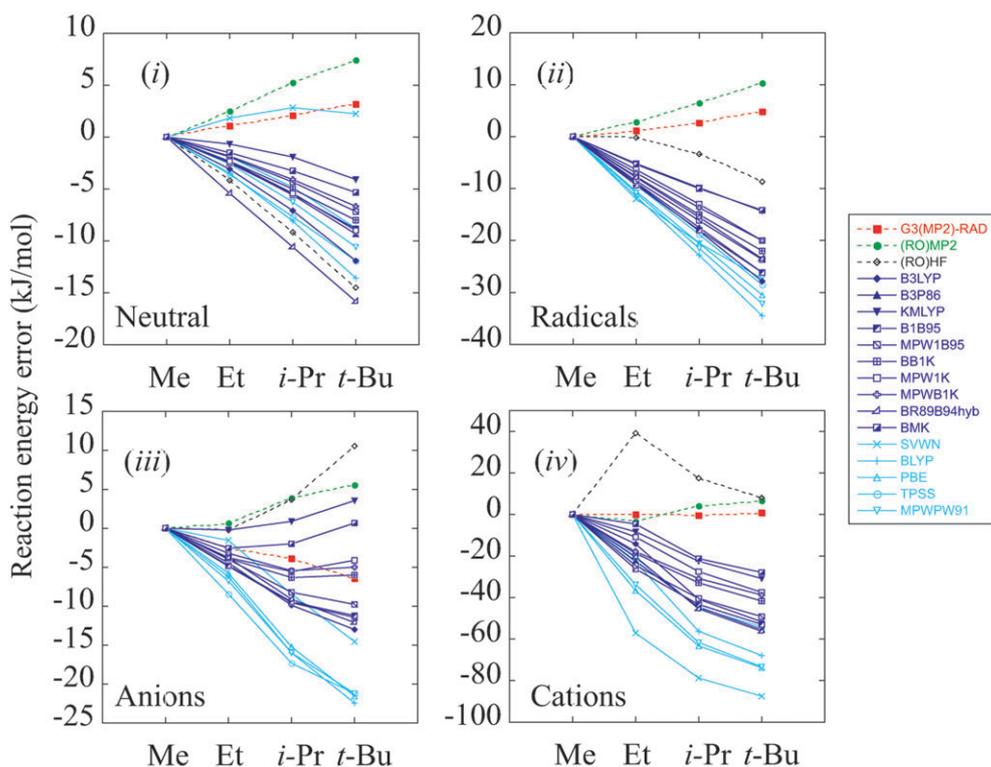


Fig. 1 Electronic reaction energy errors for reactions (i)–(iv) at various levels of theory. The 6-311+G(3df,2p) basis set was used for non-composite methods. Further computational details, as well as the data in tabular form, are given in the ESI.†

We turn now to the problem of showing more conclusively that the DFT exchange energy is causing the errors observed in Fig. 1. The first step is to put all of the DFT methods on an equal footing by re-calculating all of the DFT reaction energies using Hartree–Fock (HF) densities. This means that the kinetic, potential and Coulomb energies now have the exact HF values, and are identical for all of the DFT methods. As shown in Fig. 2, the errors are qualitatively similar; in particular, the pure functionals BLYP, PBE, TPSS and MPWPW91 still progressively overestimate the exothermicities of all four reaction series. There are some surprising improvements; the errors are generally smaller for the radical, anionic and cationic reaction series, and the performance of SVWN is dramatically improved in all cases; however the systematic errors remain. We have now eliminated the DFT kinetic, potential and Coulomb energies as possible causes of the problem, leaving only the DFT exchange and correlation components.

Given that an increased amount of Fock exchange seems to result in better performance, the DFT exchange functionals are likely to be the cause of the problem. The simplest way of testing whether or not this is the case is to take the DFT energies that have been calculated using HF orbitals, and remove the DFT correlation energy. We investigated this for the typical functional PBE. The behaviour of the exchange and correlation components of both BLYP and PW91 are similar. Fig. 3 shows clearly that when the PBE correlation energy is removed from the PBE energy calculated using HF orbitals, the errors persist. PBE exchange must therefore be the cause of the problem, as it is the only piece of the DFT energy that remains.

Alternatively, when the PBE correlation energy is removed from the PBE energy calculated on HF orbitals, the energy can be interpreted as the HF energy with the Fock exchange energy substituted with the PBE exchange energy of the HF orbitals. HF does not exhibit the systematic errors that this method does, as seen in Fig. 1, so the cause of the systematic errors must be the DFT exchange component.

Looking at the results from yet another viewpoint, HF + PBE correlation (calculated using HF orbitals) gives dramatically improved errors compared to PBE (calculated using HF orbitals, also shown in Fig. 3) and HF itself. The only difference between the first two methods is that the former has the Fock exchange energy in place of the PBE exchange energy. This shows that the PBE correlation energy is doing a relatively good job of approximating the true correlation energy, while PBE exchange is doing a very poor job of approximating the true Fock exchange energy.²⁵ In summary, DFT methods yield serious systematic errors that are due to DFT exchange functionals. This error manifests itself in reactions where the extent of substitution changes dramatically. It occurs for reactions involving radical, anionic and cationic species, as well as reactions involving neutral species only.

The reactions we have been investigating are obviously difficult for DFT, and should clearly be used to test new functionals. The question is, which parts of the true energies of these reactions does an approximate method need to recover in order to model the reactions correctly? The Fock exchange energy is an obvious requirement from our results. It is also clear from Fig. 1 that HF itself does not perform

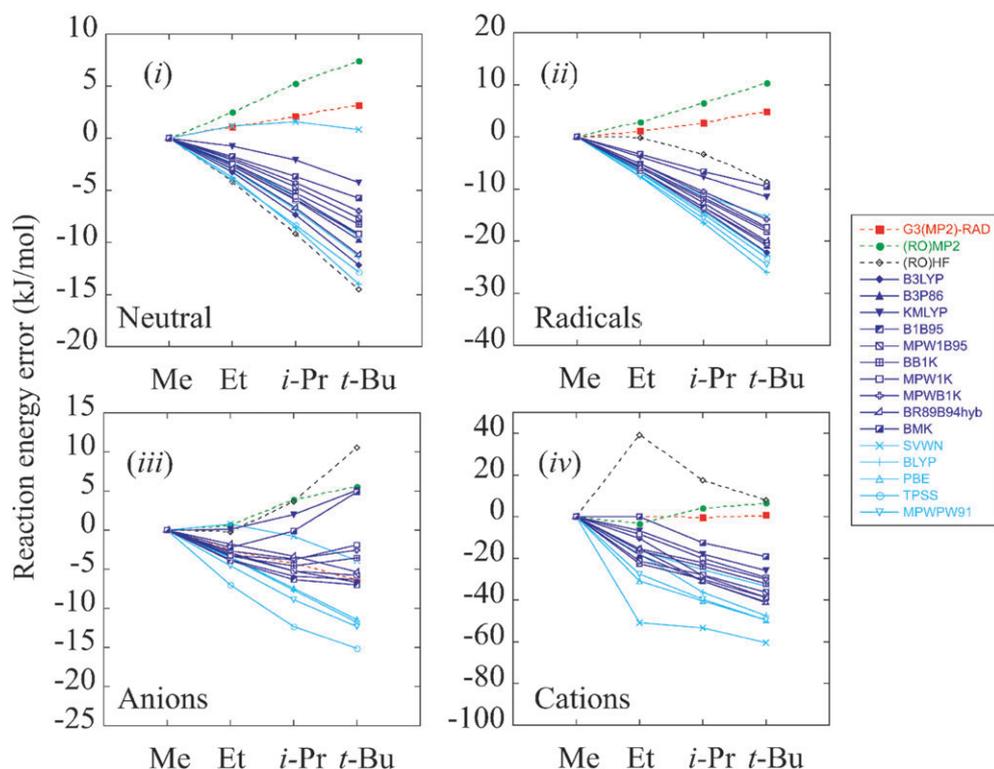


Fig. 2 Electronic reaction energy errors for reactions (i)–(iv) at various levels of theory, using (RO)HF/6-311 + G(3*df*,2*p*) densities for the DFT calculations.

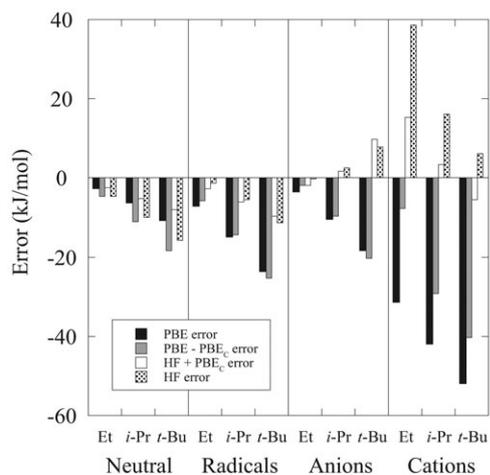


Fig. 3 Errors for PBE, PBE with PBE correlation omitted, HF + PBE correlation, and HF. (RO)HF/aug-cc-pVTZ orbitals were used for all calculations.

particularly well, and that there is a significant correlation energy component to at least some of the reaction energies. An obvious decomposition of the correlation energies is into static and dynamic correlation components, and it would be interesting to see which of these dominates the reaction correlation energies. Unfortunately, the static correlation energy, which we take to be the full-valence CASSCF correlation energy, is intractable to calculate for all but the smallest of molecules, and we need some accurate approximation to it. For species near their equilibrium geometries, the frozen-core

CCSD/STO-3G and CCSD(T)/STO-3G correlation energies are excellent approximations to the full-valence CASSCF/STO-3G correlation energies, as shown in Table 1, and henceforward, we use the cheaper CCSD/STO-3G correlation energy as a measure of the static correlation energy. At first glance, the use of CCSD theory with such a small basis set may seem strange, but static correlation energy does not require high angular momentum basis functions, and the active space for the frozen-core CCSD/STO-3G calculation comprises the valence orbitals and the virtual valence orbitals; exactly what is necessary to describe static correlation. We also note that this combination of a minimal basis set and a high-level treatment of electron correlation has been used to successfully approximate static correlation energy in the context of intracule functional theory.²⁰ It is worth noting that these calculations are feasible for quite large molecules; C₂₀H₄₂ can be treated at this level in a few hours on a standard desktop personal computer.

The errors of HF/aug-cc-pVTZ + (CCSD/STO-3G correlation energy) are shown in Fig. 4, together with HF as a reference. The observation that such a small basis set recovers so much of the reaction correlation energies reveals that the static correlation energy is the dominant part for the radical, anionic and cationic reactions, while the dynamic correlation energy dominates for the neutral reactions. Given that the behaviour of HF is also quite different for the four reaction series, this twelve-reaction test set is a stringent one. Even though the reactions are all isodesmic, and a significant amount of error cancellation is expected, any approximate DFT method must be able to capture the different chemistry

Table 1 Full-valence CASSCF, CCSD(T), CCSD, CCD and MP2 correlation energies for a variety of small molecules, radicals and ions, using the STO-3G basis set (kJ mol^{-1})^a

	CASSCF	CCSD(T)	CCSD	CCD	MP2
H ₂	-54.2	-54.2	-54.2	-54.2	-34.7
LiH	-54.1	-54.1	-54.1	-52.9	-33.7
BeH ₂	-91.2	-90.6	-90.1	-89.7	-60.2
BH ₃	-139.9	-139.4	-138.8	-138.7	-95.3
CH ₄	-208.4	-208.2	-207.8	-207.8	-148.1
NH ₃	-174.4	-174.0	-173.7	-173.3	-126.0
H ₂ O	-134.1	-133.8	-133.7	-133.0	-95.8
HF	-71.2	-71.2	-71.2	-70.5	-47.4
Me ⁺	-153.4	-152.8	-152.1	-151.9	-107.4
NH ₄ ⁺	-213.8	-213.5	-213.0	-212.1	-162.2
H ₃ O ⁺	-153.5	-153.3	-152.4	-151.1	-118.2
Me ⁻	-150.4	-150.0	-149.6	-149.3	-104.8
OH ⁻	-63.8	-63.7	-63.7	-63.6	-43.4
NH ₂ ⁻	-118.9	-118.7	-118.5	-118.2	-82.7
Me [•]	-164.5	-164.2	-163.9	-155.8	-108.3
NH ₂ [•]	-129.3	-129.1	-129.0	-124.4	-86.2
OH [•]	-69.5	-69.4	-69.4	-67.1	-44.5
Mean absolute deviation		0.3	0.6	1.8	38.0
Maximum deviation		0.6	1.3	8.7	60.3
Standard deviation		0.2	0.4	2.0	12.6
Mean deviation		0.3	0.6	1.8	38.0

^a B3LYP/6-31G(*d*) geometries were used, except for the anionic species, where B3LYP/6-31+G(*d,p*) geometries were used. The frozen-core approximation was used for coupled cluster and MP2 calculations.

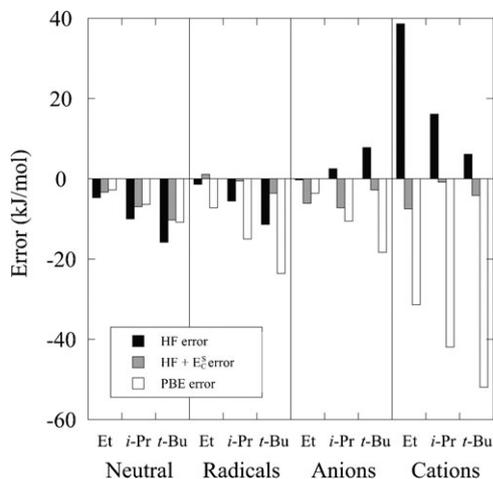


Fig. 4 Errors for HF, HF + static correlation energy E_C^S (as measured by the CCSD/STO-3G correlation energy), and PBE. (RO)HF/aug-cc-pVTZ orbitals were used for the HF and PBE calculations.

occurring in each of the reaction series (including both static and dynamic correlation effects), as well as avoiding the systematic error that we have highlighted. None of the DFT methods tested can do this.

III. Conclusion

By introducing a test set of 12 isodesmic reactions, we have shown that the scope of a serious systematic DFT error is not limited to reactions involving radicals and neutral species, but also appears in reactions involving anions, and especially reactions involving cations. This error occurs when the degree of substitution changes significantly over the reaction. The use of HF densities instead of self-consistent DFT densities

improves the results to some extent, but large systematic errors still remain.

When HF densities are used, and PBE exchange is added to the HF kinetic, potential and Coulomb energies, the errors are comparable to those of PBE calculated on HF orbitals. The PBE exchange must therefore be the cause of the problem, since it is the only piece of the DFT energy that was included. This is supported by the relatively strong performance of the HF + PBE correlation (HF orbitals). The only difference between this and PBE calculated on HF orbitals is the substitution of PBE exchange with Fock exchange, further implicating the DFT exchange as the cause of the systematic errors.

Given that DFT performs so poorly for these 12 “easy” reactions, and that the errors are systematic despite the wide range of chemistry the reactions represent, including both static and dynamic correlation effects, we advocate their use for the testing and design of future DFT methods. However, until DFT methods have been shown to work for this test set (in addition to, for example, a test set of atomization energies) we strongly suggest that *ab initio* methods be used instead. G3(MP2)-RAD calculations, for example, have been shown to be extremely reliable,⁴ and are feasible for systems with up to about 20 non-hydrogen atoms. Larger systems can be treated using an ONIOM-type approach; modelling a “core” reaction using G3(MP2)-RAD, and the substituent effects using MP2.⁴

Given our conclusions on the nature of the systematic error, it seems that the form of DFT exchange functionals needs significant improvement. Empirical schemes, such as those of Truhlar^{21,22} provide one possible way forward. In fact, Truhlar’s M05-2X functional performs very well on our test set, the largest error being $-11.1 \text{ kJ mol}^{-1}$ for the reaction involving the *t*-Bu cation. Unfortunately, the high degree of parametrization of functionals of this type makes it difficult to pinpoint the underlying reasons behind their success.

Görling's recent multi configuration optimized effective potential method²³ is another possible way to address this problem.

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References

- 1 E. I. Izgorodina, M. C. Coote and L. Radom, *J. Phys. Chem. A*, 2005, **109**, 7558.
- 2 E. I. Izgorodina and M. L. Coote, *J. Phys. Chem. A*, 2006, **110**, 2486.
- 3 E. I. Izgorodina and M. L. Coote, *Chem. Phys.*, 2006, **324**, 96.
- 4 E. I. Izgorodina, D. R. B. Brittain, J. L. Hodgson, E. H. Krenske, C. Y. Lin, M. Namazian and M. L. Coote, *J. Phys. Chem. A*, 2007, **111**, 10754.
- 5 C. C. Choi, M. Kertesz and A. Karpfen, *Chem. Phys. Lett.*, 1997, **276**, 266.
- 6 L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *J. Chem. Phys.*, 2000, **112**, 7374.
- 7 H. L. Woodcock, H. F. Schaefer III and P. R. Schreiner, *J. Phys. Chem. A*, 2002, **106**, 11923.
- 8 C. E. Check and T. M. Gilbert, *J. Org. Chem.*, 2005, **70**, 9828.
- 9 S. Grimme, *Angew. Chem., Int. Ed.*, 2006, **45**, 4460.
- 10 P. R. Schreiner, A. A. Fokin, R. A. Pascal, Jr and A. de Meijere, *Org. Lett.*, 2006, **8**, 3635.
- 11 M. D. Wodrich, C. Corminboef and P. von Ragué Schleyer, *Org. Lett.*, 2006, **8**, 3631.
- 12 M. D. Wodrich, C. Corminboef, P. R. Schreiner, A. A. Fokin and P. von Ragué Schleyer, *Org. Lett.*, 2007, **9**, 1851.
- 13 S. Grimme, M. Steinmetz and M. Korth, *J. Chem. Theory Comput.*, 2007, **3**, 42.
- 14 P. R. Schreiner, *Angew. Chem., Int. Ed.*, 2007, **46**, 4217.
- 15 V. Polo, L. R. Domingo and J. Andrs, *J. Org. Chem.*, 2006, **71**, 754.
- 16 B. G. Johnson, C. A. Gonzales, P. M. W. Gill and J. A. Pople, *Chem. Phys. Lett.*, 1994, **221**, 100.
- 17 F. Gräfenstein, E. Kraka and D. Cremer, *Phys. Chem. Chem. Phys.*, 2004, **6**, 1096.
- 18 A. D. Becke, *Int. J. Quant. Chem. Symp.*, 1994, **28**, 625.
- 19 E. Proynov, Z. Gan and J. Kong, *Chem. Phys. Lett.*, 2008, **455**, 103.
- 20 D. L. Crittenden and P. M. W. Gill, in preparation.
- 21 Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Phys.*, 2005, **123**, 161103.
- 22 Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157.
- 23 M. Weimer, F. D. Salla and A. Görling, *J. Chem. Phys.*, 2008, **128**, 144109.
- 24 CCSD(T)/aug-cc-pVTZ reference reaction energies were used for the anionic and cationic reaction series. CCSD(T) reaction energies are given in the ESI.†
- 25 The largest error is for the ethyl cation reaction. The geometry of Et⁺ itself is anomalous; it has a three-centre two-electron bond, and can be described as the ethene η₂ complex of a proton. The reaction is therefore notisodesmic, and additional errors are likely. In this case, there is a significant error in the PBE correlation energy, as well as the exchange energy. This molecule also has considerable multi reference character, which explains the anomalous HF points in Fig. 1–4.