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Adequate representation of charge polarization effects leads to a successful treatment of the $\text{CF}_4 + \text{SiCl}_4 \rightarrow \text{CCl}_4 + \text{SiF}_4$ reaction by density functional theory†

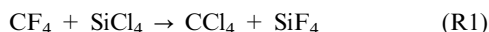
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Adequate polarization functions reduce the error of density functional theory (DFT) for the heat of reaction for $\text{CF}_4 + \text{SiCl}_4$ from $\sim 9\text{--}12 \text{ kcal mol}^{-1}$ to $\sim 2\text{--}4 \text{ kcal mol}^{-1}$, and using an improved density functional further reduces it to $\sim 1 \text{ kcal mol}^{-1}$. This reaction was previously identified as a stumbling block for DFT, but we show that the problem with the previous calculations was not DFT but rather inadequate basis sets to account for intramolecular charge polarization.

Kohn–Sham density functional theory (KS-DFT) is a powerful tool for modeling, understanding, and predicting molecular and chemical behavior,¹ but since the exact density functional is unknown and probably unknowable the success of DFT rests on the quality of available approximate density functionals.^{2,3} Most practical approximate density functionals, for example, the generalized gradient approximations (GGAs), meta GGAs, and hybrid meta GGAs, depend on the spin-up and spin-down electron densities, their gradients, and the occupied Kohn–Sham orbitals that are used to represent the densities.⁴ Some approximate density functionals, called doubly hybrid functionals, also depend on unoccupied orbitals.^{5–8} In a recent feature article, on the application of KS-DFT to main-group chemistry, Zhang *et al.*⁹ proposed that the deficiencies of the popular B3LYP¹⁰ density functional (a hybrid GGA) be ameliorated by empirical corrections generated by a neural network, called X1, or by a recent doubly hybrid functional called XYG3. Zhang *et al.* concluded their presentation with a discussion of the reaction



Their calculations implied errors of 11, 9, 9, and 12 kcal mol⁻¹ for B3LYP, XYG3, an older (than XYG3) doubly hybrid functional called B2PLYP,⁷ and the broadly applicable hybrid

meta-GGA called M06-2X,^{11,12} respectively. The neural network corrections to B3LYP reduced the error to 1.5 kcal mol⁻¹.⁹ They concluded that large errors are inevitable in approximate density functionals and anticipated further work on neural network corrections. Many of the deficiencies of B3LYP are also overcome by hybrid meta GGAs, such as M05-2X,^{12,13} M08-HX,¹⁴ and M08-SO,¹⁴ and one of the goals of the present contribution is to test their performance on the difficult test reaction (R1). We also re-test M06-2X. The present article finds a much smaller error than was obtained for this functional in ref. 9, an even smaller error for M05-2X, and a very small error for M08-SO.

The key issue leading to a wrong conclusion in ref. 9 is shown here to be the nature of polarization effects in molecules containing Si and Cl and their proper treatment by polarization functions and sufficiently flexible contraction of the rest of the basis. In the early days of quantum chemistry, there was an emphasis on significant d orbital participation in bonding of 3p elements like Si, P, and S.¹⁵ As electronic structure calculations matured, though, it was realized that d basis functions play a quantitative role in describing polarization of, for example, sp³ hybrid orbitals, but 3d

Table 1 Basis sets for elements in the 3p block

Basis	<i>N</i>	<i>N</i> _d	$\alpha_i(\text{Si})$	$\alpha_i(\text{Cl})$
aug-cc-pVQZ	420	4	0.76	1.55
			0.30	0.63
			0.12	0.25
			0.04	0.10
6-311+G(3df,2p)	235	3	1.80	3.00
			0.45	0.75
			0.11	0.19
MG3S	270	3	Same as 6-311+G(3df,2p)	
def2-TZVPP	210	3	2.30	4.61
			0.48	1.01
			0.16	0.34
			0.04	0.09
aug-cc-pV(Q+d)Z	445	5	2.64	5.19
			0.61	1.28
			0.27	0.58
			0.11	0.24
			0.04	0.09
def2-QZVPP	350	4	Same as first 4 of aug-cc-pV(Q+d)Z	
MG3SXP	295	4	3.04	4.80
			0.76	1.20
			0.47	0.72
			0.19	0.30

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orbitals *per se* do not play a dominant role in the bonding of most 3p block compounds¹⁶ (see also Landrum *et al.*¹⁷). Nevertheless the polarization role of d functions can be very significant, and high-exponent d functions (also called tight d functions or hard d functions) have been shown to be essential for polarizing the bonds in 3p elements,^{18–25} especially in highly polar bonds and the outer core (such as SiF₄).

Table 1 compares the exponential parameters of the d basis functions in several standard basis sets. In this table, N is the number of contracted basis functions on SiCl₄, N_d is the number of d subshells on each 3p-block atom (*e.g.*, Si or Cl), and α_i , $i = 1, 2, \dots, N_d$ are the exponential parameters (rounded to the nearest hundredth) of these basis functions, $\alpha_1 > \alpha_2 > \alpha_3$, *etc.* The basis sets are listed in order of increasing $\alpha_1(\text{Si})$.

The 6-311+G(3df,2p) basis set^{26–29} was used in ref. 9; $\alpha_1(\text{Si})$ is 1.8. The MG3S basis set³⁰ is the same as 6-311+G(3d2f,2df,2p)^{26–29} for C, F, and Si, but significantly improved by Curtiss *et al.*³¹ for Cl. The aug-cc-pVQZ basis set,^{32–34} although very large, was found not to have tight enough d functions, and was corrected in the aug-cc-pV(Q+d)Z basis set.²³ The def2-QZVPP basis set^{35,36} was designed to provide a balanced description of polarization even in cases where other basis sets show deficiencies while keeping the basis set size as economical as possible, and the polarization functions are taken partly from previous work. The MG3SXP basis set¹⁴ differs from MG3S in that, following a recommendation of Curtiss *et al.*³⁷ for a more consistent treatment of electron affinities and other properties, the two d subshells of 2p-block elements and three d subshells of 3p-block elements are replaced by three and four d subshells, respectively, with re-optimization of the exponential parameters. Note that XP denotes “extra polarization functions.”³⁷ (One could also consider basis sets with core functions recontracted for DFT or with greater flexibility for core polarization, but that is beyond our scope.)

The characteristics listed in Table 1 are just one indication of the differences between these basis sets. The reader should keep in mind that other differences, such as the improved contraction scheme³¹ for the 2p orbital space of Cl in the MG3S and MG3SXP basis sets, do not show up in Table 1.

Calculations were carried out for B3LYP,¹⁰ XYG3,^{9,38} and four Minnesota functionals (M05-2X, M06-2X, M08-HX, and M08-SO)^{11–14} with the *Gaussian09*³⁹ and *MN-GFM*⁴⁰

computer packages. We calculated the enthalpy of reaction, ΔH_{298}^0 , using the harmonic approximation for vibrations with unscaled frequencies except for XYG3 (see footnote a of Table 2). In all cases calculations were carried out with two grid sizes: the default fine grid (a pruned grid having 75 radial shells and 302 angular points) and very fine grid with 99 radial shells and 974 angular points. In all cases the two calculated ΔH_{298}^0 values agreed within 0.3 kcal mol⁻¹, with an average absolute deviation of 0.1 kcal mol⁻¹, demonstrating good convergence with respect to grid size. We report only the results with the very fine grid. Table 2 gives these results, with the basis sets in the same order as Table 1 and the six density functionals in chronological order of their development. The experimental value of ΔH_{298}^0 is -27.5 kcal mol⁻¹. Rather than reporting ΔH_{298}^0 directly, Table 2 gives the error. Thus, if the calculated ΔH_{298}^0 is -20.9 kcal mol⁻¹, Table 2 reports +6.6 kcal mol⁻¹.

Table 2 shows that for four of the functionals the 6-311+G(3df,2p) basis used in ref. 9 gives a much larger error than any of the other basis sets and for a fifth functional it gives a different sign of the error than any of the other basis sets. We conclude that this basis set is inadequate to test density functionals for reaction (R1). One draws reasonably similar conclusions from the other basis sets in most but not all cases. The errors with these other six bases are always much smaller than those reported for 6-311+G(3df,2p) in ref. 9. For discussion purposes we average the errors over the last five basis sets; this ensures that if a particular combination of approximate density functional and basis is fortuitously close to experiment, that accidental agreement does not weigh too heavily in our conclusions.

Using the averaged errors in the last row of Table 2, we see that improving the basis set to allow a better representation of polarization effects decreases the error in the B3LYP and M06-2X functionals from 9 and 12 kcal mol⁻¹ (as quoted in the introduction) to 5.5 and 5.3 kcal mol⁻¹. Furthermore the other Minnesota functionals do better with errors of 3.8, 3.3, and 1.1 kcal mol⁻¹, respectively (in the same chronological order as listed in Table 2). The performance of the M08-SO functional is particularly impressive; if we average over only the last three basis sets, the mean error drops to 0.8 kcal mol⁻¹.

We conclude that the situation is not nearly as bad as would be inferred from ref. 9. With the MG3SXP basis set, three of the hybrid meta GGAs, namely M05-2X, M08-HX, and

Table 2 Errors in the heat of reaction (kcal mol⁻¹) at 298 K for various combinations of basis set and approximate density functionals

Basis	B3LYP	M05-2X	M06-2X	M08-HX	M08-SO	XYG3 ^a
aug-cc-pVQZ	6.6	-4.4	4.4	-3.9	3.0	2.9
6-311+G(3df,2p)	10.5 ^b	2.6	11.9	2.2	4.9	8.9
MG3S	5.7	-2.0	7.5	-1.2	0.8	3.2
def2-TZVPP	7.5	-2.5	6.4	-2.5	-2.5	6.0
aug-cc-pV(Q+d)Z	4.1	-6.7	2.3	-5.9	0.7	1.0
def2-QZVPP	4.5	-5.9	3.2	-5.2	1.1	3.4
MG3SXP	5.5	-2.0	7.0	-1.9	0.6	4.0
MUE(last five) ^c	5.5	3.8	5.3	3.3	1.1	3.5

^a Geometries and vibrational contributions for XYG3 calculations are from B3LYP/6-311+G(d,p) calculations with harmonic zero point energies scaled by 0.9877, as was done in ref. 9. For other density functionals, geometries and vibrational contributions for the present table are obtained in each case with the density functional and basis set under consideration, with unscaled frequencies. ^b The X1 neural network method of ref. 9 has an error of 1.5 kcal mol⁻¹. ^c Mean unsigned error, averaged over the last five basis sets (MG3S through MG3SXP).

M08-SO, have errors of 2 kcal mol⁻¹ or less, similar to the errors with the empirical neural net correction, and all four Minnesota functionals have smaller errors than either of the two doubly hybrid results presented in ref. 9. We recommend the M08-SO method with the MG3S or MG3SXP basis set for problems similar to the present one.

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