The role of the basis set: Assessing density functional theory

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When developing and assessing density functional theory methods, a finite basis set is usually employed. In most cases, however, the issue of basis set dependency is neglected. Here, we assess several basis sets and functionals. In addition, the dependency of the semiempirical fits to a given basis set for a generalized gradient approximation and a hybrid functional is investigated. The resulting functionals are then tested for other basis sets, evaluating their errors and transferability. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1589004]

I. INTRODUCTION

In the past years, Density Functional Theory (DFT) has become a very important approach for computational quantum chemistry. The Kohn-Sham implementation of DFT critically depends on the quality of the exchange-correlation functional for its success. Recently, various second-generation functionals (such as PBE,[1] mPW91,[2] VSXC,[3] PBE0,[4] PKZB,[5] HCTH/93 and B97-1,[6] HCTH/120,[7] HCTH/407,[8] OPTX,[9] B972,[10] τ-HCTH and its hybrid,[11] mPW1K,[12] B97,[13] and B98[14]) have been developed. These add to the numerous functionals that are already available and commonly used in standard program packages (such as B88X,[15] B3P91 and B3LYP,[16] VWN,[17] P86,[18] LYP,[19] P91X,[20] and P91c[21]). All of the functionals were developed from a wide variety of considerations, with most of them focused on the exchange-correlation hole and employing different philosophies in their approximations.

Usually, after deciding upon the mathematical form of the functional, its parameters have to be obtained. The latter is a difficult process where different routes can be followed. Some of these functionals only use parameters that were determined by considering known boundary conditions that the functional or density should obey, and for properties of certain idealized systems like the uniform electron gas;[1,2,17–21] hence their parameters are mainly determined by physical properties. The majority of commonly used functionals have been determined by fitting at least one of their parameters to atomic or molecular data. A number of the latter functionals have been generated using numerical DFT (i.e., basis set-free) methods[13–16] in their fits (although they in principle introduce numerical noise), but most of the functionals have been fit to molecular sets with limited basis sets, usually of triple-zeta[3–11] or even double-zeta[12] quality.

Many DFT users are thus overwhelmed by the sheer number of functionals and possibilities that can be used, whereas with *ab initio* methods, the choices are clearly defined and mainly determined by a trade-off between rigor and computational cost. Very often because of sheer user inertia, first-generation functionals are applied rather than the more accurate second-generation functionals. Generally, a basis set of double- or triple-zeta quality is applied. Meanwhile, systematic studies on the dependency of the basis set and functionals remain sparse.[22–28] In addition, it is not a priori clear that basis sets optimized for wave function *ab initio* methods are the most optimal choice of DFT. Recently, new basis sets especially optimized for DFT[29–32] have been proposed. However, we have to keep in mind that in these cases the basis sets have been optimized for specific functionals, like BLYP[29,30] or the Local Spin Density Approximation (LSDA),[31,32] further adding to the confusion. In sum, we have a plethora of functionals developed for specific basis sets and additionally, a variety of basis sets developed for specific functionals. In the former case, the question arises which basis sets can and should be used for developing new functionals, and which basis set should then be employed when applying them. This is a major consideration in functional development, since the question remains: with which basis set the error of the basis set becomes comparable to that of the functional? Even if part of the basis set error is absorbed into the parameters of the functional, the question remains of how transferable such a functional will be to other basis sets, be they further from, or nearer to the infinite basis set limit.

In this contribution, we will evaluate and compare various functionals using basis sets of double-zeta sp to quadruple-zeta $spdfg$ quality. In addition, we will fit a functional, in this case the Hamprecht-Cohen-Tozer-Handy (HCTH) functional,[6] to slightly modified G2-1[33] and G3 sets of molecules.[34] These sets are denoted as the 147[7] and 407 Sets.[35] All these fits will be carried out for several basis sets of double-zeta, triple- and quadruple-zeta quality. The same fitting procedure was employed for the functional[6–8,36] using the TZ2P basis set.

HCTH is a post-local spin density approximation (post-LSDA) functional, meaning that it factorizes the LSDA functional forms (F_{LSDA}), which can be found elsewhere:[37]

TABLE I. The HCTH functional errors when fitted to the respective basis sets with the 147 Set. The final column is the value of Q_1 which excludes the potential in the sum of Q.

Property Functional	rms energy [kcal/mol]	Gradient Σ[a.u.]	Potential Σ[a.u.]	Q [a.u.]	Q_1 [a.u.]
HCTH/147@3-21G	46.89	7.50	45.4	925.1	879.6
HCTH/147@6-31G	18.53	6.07	43.8	295.6	251.8
HCTH/147@6-31G*	10.60	2.99	24.2	77.6	53.4
HCTH/147@6-31G**	10.29	2.71	24.9	75.2	50.3
HCTH/147@6-31G(2d,p)	9.70	2.11	27.4	63.9	36.5
HCTH/147@DZP	9.25	2.99	29.2	88.6	59.4
HCTH/147@DFO1	7.44	2.85	26.5	63.8	37.3
HCTH/147@cc-pVDZ	9.51	4.04	26.9	100.6	73.7
HCTH/147@6-31+G**	6.31	2.66	28.8	61.3	32.5
HCTH/147@6-31+G(2d,p)	4.82	2.47	27.4	51.3	23.9
HCTH/147@aug-cc-pVDZ	6.91	3.40	30.0	72.4	42.4
HCTH/147@6-311G(2d,p)	7.00	2.48	21.4	49.1	27.7
HCTH/147@TZ2P	4.89	2.11	19.4	36.5	17.1
HCTH/147@DFO2	7.37	2.83	32.9	74.5	41.6
HCTH/147@cc-pVTZ	5.92	2.27	24.2	45.4	21.2
HCTH/147@6-311+G(2d,p)	4.82	2.48	21.4	42.8	21.4
HCTH/147@6-311+G(2d,2p)	4.93	2.11	26.3	43.7	17.4
HCTH/147@6-311+G(3d,2p)	4.59	2.05	25.8	40.8	15.0
HCTH/147@6-311+G(3df,2pd)	4.68	1.95	26.5	40.7	14.2
HCTH/147@aug-cc-pVTZ	5.08	2.42	20.2	41.0	20.8
HCTH/147@cc-pVQZ	4.96	2.10	25.4	42.2	16.8

$$E_{xc} = \sum_{\gamma = x, c_{\sigma\sigma}, c_{\alpha\beta}} E_\gamma$$

$$= \sum_\gamma \sum_{q=0}^m c_{q,\gamma} \int F_{LSDA,\gamma}(\rho_\alpha, \rho_\beta)$$

$$\times f_{\gamma,q}(\rho_\alpha, \rho_\beta, x_\alpha^2, x_\beta^2) d\mathbf{r}, \tag{1}$$

where $f_{\gamma,q}$ denotes the perturbation from the uniform electron gas if $c_{0,\gamma} = 1$.

$$f_{\gamma,q} = u_\gamma^q = \left(\frac{\theta_{\gamma\sigma} x_\sigma^2}{1 + \theta_{X\sigma} x_\sigma^2} \right)^q . \tag{2}$$

x_γ is closely related to the reduced density gradient, and θ are fixed coefficients, which have been fit to atomic data:[13]

$$x_\sigma^2 = \frac{(\nabla \rho_\sigma)^2}{\rho_\sigma^{8/3}} . \tag{3}$$

When employing the form in Eq. 1 up to fourth order in m, we obtain 15 linear coefficients (because of exchange, like-spin and opposite-spin correlation), which are easily parameterized by minimizing Ω:

$$\Omega = \sum_m^{n_E} w_m (E_m^{exact} - E_m^{K-S})^2 + \sum_{l,X}^{n_G} w_{l,G} \left(\frac{\partial E_l^{K-S}}{\partial X} \right)^2$$

$$+ \sum_{j,\sigma}^{n_v} w_{j,v} \int (v_{j,\sigma}^{ZMP} + k_{j,\sigma} - v_{j,\sigma}^{K-S})^2 \rho_{j,\sigma}^{2/3} d\mathbf{r}. \tag{4}$$

The three summations correspond to errors of the energies, gradients and exchange-correlation potentials of each molecule, respectively. In all cases, K-S denotes the calculated property; hence we have the energy difference between the exact and calculated energy in the first sum. In the second sum the exact gradients (at equilibrium geometry) should be

zero. In the final term, we fit to the exchange-correlation potentials determined by the Zhao-Morrison-Parr method[38] from high-level *ab initio* densities, which are shifted by a constant k because of the effects of the quantum-mechanical integer discontinuity. All these contributions need to be weighted by appropriate weights w, which have been determined and reported in previous papers.[8] The weights w consist of several factorized weights making contributions for each molecule in order to ensure a balanced functional.

In the next section, we will refit the HCTH generalized gradient approximation (GGA) functional to numerous basis sets. In addition, we will assess the performance of these functionals with basis sets other than those used for the parameterization. In the third section we will apply the same procedure to hybrid functionals, focusing on the amount of exact exchange needed for those functionals depending on the basis set. In the last section, we will assess several functionals with two triple-zeta basis sets (namely, TZ2P[39] and cc-pVTZ[40,41]).

II. GGA FUNCTIONALS AND BASIS SETS

For all calculations, we used the Cadpac suite of programs,[42] using a standard ''high'' grid for the density functional calculations. In the basis set evaluation, we used the 3-21G,[43,44] 6-31G,[45,46] 6-311G[47,48] (the latter two with various combinations of diffuse and polarization functions), DZP, TZ2P,[39] DFO,[32] cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ and cc-pVQZ basis sets.[40,41] Some of the basis sets specifically constructed for density functionals discussed in the Introduction are not available (yet) for second-row atoms[29-31] and thus could not be used.

In Table I, we compare the performance of the functionals with the basis set with which they were fit. HCTH/147@3-21G, for example, denotes an HCTH functional fit-

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ted to the 147 set with a 3-21G basis set. The first column contains the rms energy error of the functional for the atomization and dissociation energies, electron affinities, proton affinities, and ionization potentials in the 147 Set. The second column displays the sum of all the gradients calculated at the equilibrium geometry in atomic units. The gradients have been shown to correlate with the accuracy of the bond distances and angles obtained.[8,11] The third column is the square of all the errors in the exchange-correlation potential contributions. All three errors are actually fitted according to Eq. 4. In the fourth column, we evaluate Q, which is the sum of all three weighted errors with uniform weights rather than Ω:

$$Q = 750 \times \sum_{m}^{n_E} (E_m^{exact} - E_m^{K-S})^2 + 500 \times \sum_{l,X}^{n_G} \left(\frac{\partial E_l^{K-S}}{\partial X} \right)^2$$
$$+ \sum_{j,\sigma}^{n_v} \int (v_{j,\sigma}^{ZMP} + k_{j,\sigma} - v_{j,\sigma}^{K-S})^2 \rho_{j,\sigma}^{2/3} \, d\mathbf{r}. \quad (5)$$

Since all three contributions are important and the GGA functionals have been fit to a value similar to Q, it is probably the most important diagnostic. Nevertheless, as only the first two sums are directly apparent from the energy calculations, we also evaluate Q_1, which excludes the potential:

$$Q_1 = 750 \times \sum_{m}^{n_E} (E_m^{exact} - E_m^{K-S})^2 + 500 \times \sum_{l,X}^{n_G} \left(\frac{\partial E_l^{K-S}}{\partial X} \right)^2. \quad (6)$$

We have to bear in mind that both the "exact" exchange-correlation potentials and densities were calculated using the TZ2P basis set. This, however, does not necessarily imply that the HCTH/147@TZ2P functional has a distinct advantage when we fit to these quantities since basis set convergence with angular momentum is much slower in *ab initio* methods than for density functionals. Nevertheless, the density calculations using the Brueckner Doubles method include core correlation. This might suggest that the TZ2P basis set has a slight advantage over the other basis sets when fitting it to ZMP potentials that have been obtained from BD densities.[49] Unlike the cc-pVTZ and 6-311G basis sets, the TZ2P basis set is (albeit unpolarized) of triple-zeta quality in the inner-shell orbitals.

Ignoring for the moment the Pople basis sets that just differ in the polarization component on the hydrogen, the following ordering of HCTH/147@ in Q is observed:

$$\text{TZ2P} < 6\text{-}311 + G(3df,2pd) \approx 6\text{-}311 + G(3d,2p)$$
$$\approx \text{aug-cc-pVTZ} \approx \text{cc-pVQZ} \approx 6\text{-}311 + G(2d,2p)$$
$$< \text{cc-pVTZ} < 6\text{-}311G(2d,p) \ll \text{DFO2}.$$

All basis sets are ordered by their errors (unlike Table I), with $<$ and $\ll$ corresponding to a difference of more than 5% or 20% between the functionals, respectively. From Table I, the HCTH/147@TZ2P functional clearly yields the best overall results. The Pople large basis sets also exhibit surprisingly low errors, although some polarization and diffuse functions are needed to achieve this performance. Interestingly, Dunning's correlation consistent basis sets, which

were optimized at the CISD level, show high errors despite having more basis functions. Even at the quadruple-zeta level, the "basis set functional" yields higher errors than both HCTH/147@TZ2P and HCTH/147@6-311 $+G(3d,2p)$. HCTH/147@DFO2, whose basis set was developed specifically for density functionals, shows an extraordinarily poor performance, probably due to built-in constraint of DFO2 that the different angular momentum functions share the same exponents.

When excluding the potentials at the triple-zeta level, Q changes to Q_1, and the ordering of HCTH/147@basis set becomes:

$$6\text{-}311 + G(3df,2pd) \approx 6\text{-}311 + G(3d,2p) < \text{cc-pVQZ}$$
$$\approx \text{TZ2P} \approx 6\text{-}311 + G(2d,2p) < \text{aug-cc-pVTZ} \approx \text{cc-pVTZ}$$
$$< 6\text{-}311G(2d,p) \ll \text{DFO2}.$$

Here, the HCTH/147@TZ2P functional exhibits a somewhat higher error compared to the HCTH/147@6-311 $+G(3d,2p)$ functionals for Q_1, yet still has an error comparable to the only quadruple-zeta basis set tested, HCTH/147@cc-pVQZ. The latter basis sets yield only slightly lower errors than when fitting to a TZ2P basis. For the double-zeta quality basis sets, the energies and gradients have much larger error contributions to Q than the potentials, hence the exclusion of the latter has no impact on the ordering in the HCTH/147@ functionals:

$$6\text{-}31 + G(2d,p) < 6\text{-}31 + G** < \text{DFO1}$$
$$\approx 6\text{-}31G(2d,p) < \text{aug-cc-pVDZ} < 6\text{-}31G**$$
$$< 6\text{-}31G* < \text{DZP} \ll \text{cc-pVDZ} <<< 6\text{-}31G <<< 3\text{-}21G.$$

As for the double-zeta basis sets, the unpolarized basis sets are clearly not very useful for the purpose. HCTH/147@DFO1 and the functionals fitted to the Pople basis sets yield the lowest errors. The former should not be surprising as it was developed specifically for DFT whereas the Pople basis sets were developed for Hartree-Fock. Nevertheless, with the exception of the HCTH/147@6-31+G(2d,p) functional, the double-zeta "basis set functionals" yield much higher errors than those obtained by the triple-zeta quality basis sets. *Hence, if computationally feasible, basis sets of triple-zeta quality are preferable over basis sets of double-zeta quality when doing calculations employing DFT.* Overall, and consistent with earlier observations made by Jensen,[30] Dunning's basis sets do not seem to be an optimal choice for density functional calculations. On the other hand, diffuse functions are more important with the Pople basis sets, in that they provide a significant error reduction. A detailed analysis of the results shows that predominantly the total atom energies, atomization energies and electron affinities of anions are affected, with the error for the latter in-

TABLE II. The coefficients of selected HCTH/147 basis set fitted functionals.

Coefficients	@3-21G	@6-31+G**	@DZP	@aug-cc-pVDZ	@6-311+G($3d,2p$)	@TZ2P	@aug-cc-pVTZ	@cc-pVQZ
$c_1 = c_{X\sigma,0}$	0.962 69	1.096 17	1.107 28	1.099 03	1.094 34	1.090 25	1.086 94	1.087 82
$c_2 = c_{C\sigma\sigma,0}$	5.460 39	0.863 60	1.164 35	1.005 58	0.356 53	0.562 58	0.433 59	0.476 82
$c_3 = c_{C\alpha\beta,0}$	1.357 55	0.618 11	0.538 57	0.365 06	0.481 29	0.542 35	0.552 40	0.465 67
$c_4 = c_{X\sigma,1}$	1.016 33	−0.616 54	−1.070 61	−0.684 59	−0.680 22	−0.799 19	−0.521 52	−0.678 53
$c_5 = c_{C\sigma\sigma,1}$	1.649 66	−0.658 61	−2.451 61	−0.719 13	0.604 60	0.017 14	−0.071 42	0.296 97
$c_6 = c_{C\alpha\beta,1}$	4.777 88	5.029 01	7.217 06	8.781 71	6.797 69	7.014 64	6.319 72	7.215 49
$c_7 = c_{X\sigma,2}$	−1.902 08	3.874 19	5.965 61	4.426 88	5.009 18	5.572 12	3.771 29	4.784 45
$c_8 = c_{C\sigma\sigma,2}$	−10.334	−0.3721	5.4245	−1.2823	−3.8674	−1.3063	−1.1795	−2.1521
$c_9 = c_{C\alpha\beta,2}$	−49.342	−16.913	−28.774	−30.845	−24.128	−28.382	−16.407	−22.881
$c_{10} = c_{X\sigma,3}$	11.314	−1.4469	−7.5266	−2.7257	−3.8054	−5.8676	−0.3338	−3.5355
$c_{11} = c_{C\sigma\sigma,3}$	3.6314	−1.0619	−9.2072	2.8592	5.1594	1.0575	0.3399	2.8817
$c_{12} = c_{C\alpha\beta,3}$	77.455	11.587	37.650	34.961	22.585	35.033	3.4357	19.866
$c_{13} = c_{X\sigma,4}$	−3.7768	1.3633	5.7849	6.1824	5.4561	3.0454	−2.1418	0.5397
$c_{14} = c_{C\sigma\sigma,4}$	−5.4840	2.2222	7.0638	−1.4161	−1.5290	0.8854	1.1322	−0.6523
$c_{15} = c_{C\alpha\beta,4}$	−46.989	−7.5787	−24.401	−20.981	−11.340	−20.428	0.5629	−9.7235

creasing by more than a factor of 2 when omitting diffuse functions. In comparison, with the HCTH/147@cc-pVTZ functional the error of the atomization energies and ionization potentials of the anions decreases by less than 20% when diffuse functions are included in the basis set. This is a general indication that despite their limited usefulness for DFT, Dunning's basis sets are more "balanced" than the 6-31 family of basis sets with respect to diffuse functions. The HCTH/147@TZ2P functional yields a similar error as the HCTH/147@cc-pVTZ basis set for the anions, suggesting that diffuse functions might reduce its error further. Changing the basis functions on the hydrogen atom, as has been suggested in a prior assessment of different density functionals,[50,51] degraded the performance of the HCTH/147@TZ2P "basis set functional" in all tests.

Having obtained a number of functionals, comparing their coefficients in Table II yields further insight. Here, only the HCTH/147@3-21G functional obtained from fitting to the split-valence 3-21G basis set differs blatantly from the other functionals. Both the HCTH/147@DZP and HCTH/147@aug-cc-pVDZ functionals have large zeroth-order like-spin correlation coefficients ($c_{C\sigma\sigma,0}$) probably thus compensating for the basis set error. Note that this coefficient also increases when going to larger molecules.[8] The HCTH/147@6-31+G** coefficients are closer to the ones obtained by the triple-zeta basis sets than the other double-zeta quality "basis set functionals," confirming its lower basis set error. No clear conclusions on this effect can be made with the triple- and quadruple-zeta functionals, since both the HCTH/147@TZ2P (including the potential) and HCTH/147@6-311+G($3d,2p$) functionals yield the lowest errors and not the HCTH/147@cc-pVQZ functional. The latter basis set has supposedly the lowest basis set error compared to the basis set limit.[30] The exchange coefficients ($c_{X\sigma,n}$ with m going from 0 to 4) of all the functionals at this level of basis set quality seem to be similar for the different functionals reported in Table II. In contrast, the correlation parameters exhibit a wider variation upon switching between the fitting sets with 93, 147 or 407 systems.[8] The effect of the diffuse functions on the basis set going from the HCTH/147@cc-pVTZ to the HCTH/147@aug-cc-pVTZ functional

is not as significant as the change between the different "basis set functionals" of triple-zeta quality. Nevertheless, the coefficients still differ by a significant amount, suggesting that convergence towards the basis set limit has not been achieved. However, if similar basis set errors are absorbed into the parameterization of functionals fitted to different triple and quadruple-zeta basis sets, the functionals are expected to be fairly transferable. In addition, the functional error is only very slightly influenced by changing some of the functionals coefficients. We have to note that using functionals with quadruple-zeta quality or higher is not useful, since the basis set error is probably about an order of magnitude lower than the functional error itself.

In Tables III–VI we investigate the transferability of the "basis set functionals" in more detail. Here, all the new functionals developed are evaluated with the 6-31+G**, aug-cc-pVDZ, 6-311+G($3d,2p$) and TZ2P basis sets. The results for the 6-31+G** basis for selected functionals that are listed in Table I are shown in Table III. As expected, the HCTH/147@3-21G and HCTH/147@6-31G functionals are clearly insufficient to describe the properties investigated. Reasonably low errors are obtained with all functionals be-

TABLE III. The errors of the HCTH/147@ "basis set functionals" evaluated over 147 systems with the 6-31+G** basis set.

Property Functional	rms energy [kcal/mol]	Gradient Σ[a.u.]	Q_1 [a.u.]
HCTH/147@3-21G	70.4	6.07	1460.2
HCTH/147@6-31G	30.0	5.11	377.57
HCTH/147@6-31G**	9.1	2.55	41.3
HCTH/147@cc-pVDZ	10.7	2.29	46.1
HCTH/147@DZP	7.7	2.57	33.6
HCTH/147@aug-cc-pVDZ	8.4	2.58	38.9
HCTH/147@6-311G($2d,p$)	6.4	3.39	41.1
HCTH/147@cc-pVTZ	6.9	3.58	45.3
HCTH/147@TZ2P	6.9	3.63	46.8
HCTH/147@6-311+G($2d,2p$)	6.5	3.51	43.7
HCTH/147@6-311+G($3d,2p$)	6.7	3.67	46.5
HCTH/147@6-311+G($3df,3pd$)	6.8	3.89	50.3
HCTH/147@aug-cc-pVTZ	7.0	3.94	58.0
HCTH/147@cc-pVQZ	7.5	3.90	52.6

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TABLE IV. The errors of the HCTH/147@ ''basis set functionals'' evaluated over 147 systems with the aug-cc-pVDZ basis set.

Property Functional	rms energy [kcal/mol]	Gradient Σ[a.u.]	Q_1 [a.u.]
HCTH/147@3-21G	70.8	4.88	1380.8
HCTH/147@6-31G	32.6	5.65	536.2
HCTH/147@6-31G**	9.3	3.40	52.3
HCTH/147@cc-pVDZ	9.7	3.15	49.8
HCTH/147@DZP	8.3	3.40	48.4
HCTH/147@6-31+G**	7.2	3.49	45.5
HCTH/147@6-311G($2d,p$)	6.3	4.16	52.1
HCTH/147@cc-pVTZ	6.9	4.31	56.9
HCTH/147@TZ2P	8.3	4.37	64.0
HCTH/147@6-311+G($2d,2p$)	6.5	4.21	54.9
HCTH/147@6-311+G($3d,2p$)	8.3	4.37	64.5
HCTH/147@6-311+G($3df,3pd$)	7.3	4.54	63.6
HCTH/147@aug-cc-pVTZ	7.3	4.61	65.1
HCTH/147@cc-pVQZ	7.8	4.58	65.6

TABLE VI. The errors of the HCTH/147@ ''basis set functionals'' evaluated over 147 systems with the 6-311+G($3d,2p$) basis set.

Property Functional	rms energy [kcal/mol]	Gradient Σ[a.u.]	Q_1 [a.u.]
HCTH/147@3-21G	73.9	4.88	1415.9
HCTH/147@6-31G	29.6	5.29	340.9
HCTH/147@6-31G**	11.8	1.72	45.0
HCTH/147@cc-pVDZ	12.8	1.77	52.0
HCTH/147@DZP	7.4	1.72	23.4
HCTH/147@6-31+G**	7.8	1.67	23.9
HCTH/147@aug-cc-pVDZ	9.8	1.63	33.0
HCTH/147@6-311G($2d,p$)	6.9	1.96	21.6
HCTH/147@cc-pVTZ	5.8	2.02	18.7
HCTH/147@6-311+G($2d,2p$)	6.3	1.98	20.2
HCTH/147@6-311+G($3d,2p$)	5.6	2.09	18.6
HCTH/147@6-311+G($3df,3pd$)	5.9	2.23	20.5
HCTH/147@aug-cc-pVTZ	5.9	2.26	21.1
HCTH/147@cc-pVQZ	5.6	2.28	19.5

ing fit to the 6-31G* basis set or larger. Interestingly, in the case of the 6-31+G** basis set, only the HCTH/147@DZP and HCTH/147@aug-cc-pVDZ functionals show Q_1 errors below 40 a.u., affected mainly by the gradient error contribution. In comparison (Table I), the functional optimized for this basis set has a Q_1 value of 32.5 a.u. For all the triple-zeta quality functionals, the rms energy error is lower, but the gradients (geometries) counterbalance this effect. All of these ''basis set functionals,'' with the exception of HCTH/147@6-311+G($3df,3pd$) and HCTH/147@aug-cc-pVTZ, give very similar Q_1 errors, with rms energy errors of 6.7 $\pm$0.3 kcal/mol and a gradient error around 3.6 a.u. Overall, the triple-zeta and quadruple-zeta quality functionals vary by at most 20% in both errors.

The evaluation of the functionals with the aug-cc-pVDZ basis set yields similar results (Table IV). Of course, the overall error Q_1 is higher, as is evident from the larger error obtained by the HCTH/147@aug-cc-pVDZ functional compared to the HCTH/147@6-31+G** functional displayed in Table I. The gradient errors are especially affected. Only the double-zeta quality ''basis set functionals'' yield errors that can be compared to the Q_1 value of 42.4 a.u. obtained

TABLE V. The errors of the HCTH/147@ ''basis set functionals'' evaluated over 147 systems with the 6-311+G($3d,2p$) basis set.

Property Functional	rms energy [kcal/mol]	Gradient Σ[a.u.]	Q_1 [a.u.]
HCTH/147@3-21G	73.3	4.90	1452.7
HCTH/147@6-31G	28.8	6.02	432.7
HCTH/147@6-31G**	11.0	1.65	40.17
HCTH/147@cc-pVDZ	13.0	1.73	53.7
HCTH/147@DZP	7.7	1.69	24.4
HCTH/147@6-31+G**	7.2	1.65	21.3
HCTH/147@aug-cc-pVDZ	9.5	1.60	31.6
HCTH/147@6-311G($2d,p$)	6.9	1.89	20.9
HCTH/147@cc-pVTZ	6.1	1.99	18.7
HCTH/147@TZ2P	4.8	2.03	15.5
HCTH/147@6-311+G($2d,2p$)	5.6	1.96	16.9
HCTH/147@6-311+G($3df,3pd$)	5.0	2.19	17.0
HCTH/147@aug-cc-pVTZ	5.1	2.25	18.0
HCTH/147@cc-pVQZ	5.4	2.20	18.1

with the HCTH/147@aug-cc-pVDZ functional (Table I). Here, the HCTH/147@6-311+G($3d,2p$), HCTH/147 @6-311+G($3df,2pd$), HCTH/147@TZ2P, HCTH/147@aug-cc-pVTZ and HCTH/147@cc-pVQZ functionals again yield higher errors, mainly because of the gradient (and partly due to the energy) contributions to the error Q_1. Thus, the functionals fit to the double-zeta quality basis sets give the lowest errors when applied to *other* basis sets of double-zeta quality.

If we evaluate the functionals with triple-zeta quality basis sets, we observe, as expected, that their errors are a lot closer to the lowest error possible obtained by the basis sets to which the functionals were fit. When using the 6-311+G($3d,2p$) basis set, the double-zeta ''basis set functionals'' yield the lowest gradient errors, although again this is only achieved when including diffuse functions. As for the other entire basis set evaluations in Tables III to VI, the double-zeta basis sets give a much lower error for the gradients, but not for the energy. This is an interesting phenomenon; the same observation was made in a different context[52] when GGA functionals were developed solely for the description of accurate structures and frequencies.[53] Hence, it is probably a lot harder to develop a single functional for both accurate geometries and energies rather than one for each individual property. However, the former approach of separating the calculations can lead to other problems, namely that energetic properties will be calculated at nonequilibrium structures. The HCTH/147@cc-pVQZ, HCTH/147@cc-pVTZ and HCTH/147@aug-cc-pVTZ functionals again yield higher errors than the other functionals developed with a triple-zeta quality basis set. Noteworthy is the low error of the HCTH/147@TZ2P functional when applied to the 6-311+G($3d,2p$) basis set, resulting in a Q_1 value of 15.5 compared to the minimum value of 15.0 a.u. obtained by the HCTH/147@6-311+G($3d,2p$) functional. This is even lower than the error of the HCTH/147@6-311+G($3df,2pd$) functional obtained with the 6-311+G($3d,2p$) basis set. This emphasizes the transferability of the functionals that have been fitted to the higher basis sets, since the variation is less than 10% on Q_1 and on the rms energy error and the gradient errors (with the exception

of the HCTH/147@cc-pVTZ and HCTH/147@6-311 +G$(2d,p)$ functionals for the rms energy error). A number of the functionals parameterized for the triple-zeta basis sets yield a lower error when evaluating Q_1 with the 6-311 +G$(3d,2p)$ basis set rather than for the basis set to which they were fit (compare to Table I). This indicates that a large amount of the remaining basis set errors absorbed into these functionals is of a similar magnitude.

In Table VI, the performance of the different "basis set functionals" with the TZ2P basis set is shown. All errors are slightly larger (by about 10%), but the trends are again the same. The HCTH/147@DZP basis set functional now gives a lower error than the HCTH/147@6-31+G** functional, but only by a small margin. Again, the functionals fitted to Dunning's basis sets of double-zeta quality yield larger errors than the other functionals fitted to basis sets of double-zeta quality. Among the triple-zeta level "basis set functionals," the errors vary by only 10%, supporting the observations made for the 6-311+G$(3d,2p)$ basis set. When evaluating the HCTH/147@3-21G and HCTH/147@6-31G functionals in Tables IV to VI, the former functional has a lower gradient error. Still, polarization functions are essential when calculating geometries, reducing the gradient errors by a factor of 2 and more.

In summary, the triple-zeta "basis set functionals" are transferable between each other, indicating that when fitting using basis sets of this quality, the basis set error absorbed in the parameterization does not play a role. The variation in error of 10% or less when evaluating one functional fit with a certain basis set with a different one is probably not important. This has further implications in the use of density functionals. *Since the errors do not change significantly when going to higher basis sets, the triple-zeta basis set level is likely to be sufficient for use in density functional calculations.* With still larger basis sets, the basis set truncation error will "drown in the noise" that is the inherent error of the functional itself. In general, Dunning's correlation-consistent basis sets developed for correlated *ab initio* methods yield higher errors than the various Pople basis sets or TZ2P. When we investigated this behavior in more detail, we found that the inclusion of core-valence basis functions[54,55] only lowers the rms energy error by 0.1 kcal/mol. Inclusion of an additional tight d-function,[56] which has been shown to be important for second-row elements,[57] reduces this error by a further 0.3 kcal/mol. Moreover, these contributions lower the sum of the gradient error by another 0.1 a.u. If we assume that the same contributions were added to the HCTH/147@aug-cc-pVTZ functionals results, we would probably arrive at a Q value close to the lowest value obtained. Thus, although several enhancements for correlation-consistent basis sets could be introduced, extensive complements of higher-angular momentum functions, in particular, do not appear to be necessary. Out of all basis sets tested, the HCTH functional fit to the 6-311+G$(3df,2pd)$ basis set gives the lowest energies and gradients errors, and the HCTH functional fit to the TZ2P basis set yields the lowest errors for the quantity Q, which includes energies, gradients and potential points. We believe that this is due to correlation effects de-

TABLE VII. The errors of selected hybrid functionals evaluated for the 147 Set.

Property Functional	rms energy [kcal/mol]	Gradient Σ[a.u.]	Q_1 [a.u.]	% HF exchange
B97-1/147@6-31+G**	7.64	2.42	34.1	0
B97-1/147@aug-cc-pVDZ	8.29	3.17	44.1	0
B97-1/147@6-311+G$(3d,2p)$	5.83	2.04	18.4	0
B97-1/147@TZ2P	6.04	2.03	19.2	0
B97-1/147@aug-cc-pVTZ	6.82	2.18	24.8	0
B97-1/147@6-31+G**	4.29	1.79	15.0	30
B97-1/147@aug-cc-pVDZ	4.29	2.68	24.5	27
B97-1/147@6-311+G$(3d,2p)$	2.94	1.86	10.3	15
B97-1/147@TZ2P	3.47	1.83	12.0	18
B97-1/147@aug-cc-pVTZ	3.04	2.07	13.2	18

scribed by the exchange-correlation potential in the core that cannot be adequately described by the 6-311+G basis sets.

III. HYBRID FUNCTIONALS AND BASIS SETS

The method applied in the last section to the GGA functionals is now used for hybrid functionals to assess the different basis sets. There is, however, one complication: the varying amount of exact Hartree-Fock exchange. Here, we fitted hybrid functionals to the 6-31+G**, aug-cc-pVDZ, 6-311+G$(3d,2p)$, TZ2P and aug-cc-pVTZ basis sets, using the abovementioned procedure. While the inclusion of the exchange-correlation potential points into the fits for hybrid functionals is possible,[10] it is not clear if the overall performance of these functionals is generally better,[58] as we will also see in the final section. Therefore, we restrict ourselves to fitting to gradients and energies only (similar to the determination of Q_1 in the last section, see Eq. 6). All functionals were again fit to the 147 systems, but with $m=2$ in the power series in Eq. 2. This cut-off in the power series expansion yields the B97-1 form rather than the HCTH form. Here, 9 linear coefficients are fit instead of the 15 in the GGA. The amount of exact exchange was varied over a range from 0% to 50% in order to determine the minimum.

Before discussing the outcome of the results of the hybrid functionals, it is worth comparing the values at 0% Hartree-Fock exchange to the functionals obtained in the previous section. The difference between them is the fit to exchange-correlation potentials, which will raise the Q_1 error for the GGA functionals in contrast to the "hybrid" functional at 0%. Of course, another discrepancy is the different number of coefficients. The newly obtained GGA functionals are displayed in Table VII, and can be compared (with the differences mentioned) to those in Table I. For the TZ2P, 6-31+G** and aug-cc-pVDZ basis sets, the higher-order coefficients seem to change very little (see Table I). While the energy error increases going from $m=2$ to $m=4$, the gradient error decreases, with Q_1 close to the errors when fitting only to gradients and energies with $m=2$. This has been previously reported[13,50] and has led to the conclusion that it is unnecessary to include orders higher than 2 in the power series. Here, mainly the error in the potential is affected as an additional calculation with the TZ2P basis set and the variable Q shows. In this case, Q for the HCTH/147
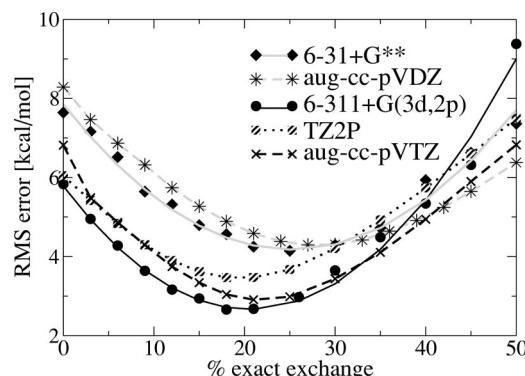
FIG. 1. rms error (in kcal/mol) of the 147 Set with different hybrid "basis set functionals."

FIG. 2. Q_1 error (in atomic units, see Eq. 6) of the 147 Set with different hybrid "basis set functionals."

with $m=4$ form yields 37 a.u., compared to 51 a.u. for the B97-1/147 form with $m=2$, hence the overall Q value is raised by 40%. Comparing Tables I and VII, we realize that *not only is the functional somwehat dependent on the basis set for which it was parameterized, but also the basis set dependence itself is dependent on the class of functional used.*

Let us now return to the hybrid functionals. Since the error of the resulting functional also correlates slightly with the starting guess used, the points will not necessarily fit a curve. Unlike the GGA functionals where we can determine the starting guess by fitting to exchange-correlation points, with hybrid functionals the initial coefficients are, at best, educated guesses. Thus, we sometimes had to fit a curve through the points, and in Fig. 1, the rms energy error is plotted as a function of amount of exact exchange for various functionals. This plot shows a disturbing property of hybrid functionals: *the amount of exact exchange in the functional depends on the basis set for which it is fit.* All hybrid density functionals known have their exchange coefficient fit to a specific basis set (or are using numerical DFT), hence the variation of the exact exchange, in the range of 15% to 25%, might well be due to basis set effects. In the case of the tested functionals, the optimized exact exchange-fractions for all three triple-zeta basis sets (obtaining B97-1/147@6-311+G($3d$,$2p$), B97-1/147@TZ2P and B97-1/147@aug-cc-pVTZ) hover around 18%. However, fitting to a double-zeta basis set (B97-1/147@6-31+G** and B97-1/147@aug-cc-pVDZ) yields minima located around 28%. In Fig. 2, the value of Q_1 is displayed, exhibiting generally the same behavior as the energy in Fig. 1. Since this is the value used in the fit (with more sophisticated weights), it is more informative, albeit more abstract. Here, the differences between the basis sets, which were already exhibited with the GGA functionals, can be seen again. While the B97-1/147@6-31+G** and the B97-1/147@aug-cc-pVDZ functionals show similar minima in the energies, with the B97-1/147@6-31+G** curve shifted a bit towards lower values. Still, the gradient error when fitting to the 6-31+G** basis is much lower than with the aug-cc-pVDZ basis set. Similar behavior is observed for the basis sets of triple-zeta quality. Only when the gradients are included does the B97-1/147@TZ2P functional yield a lower error for its mini-

mum than B97-1/147@aug-cc-pVTZ, with the values obtained by the B97-1/147@6-311+G($3d$,$2p$) functional marginally lower still. Detailed results of the minima are given in Table VII displaying the lowest energy points calculated. The minima obtained when fitting a separate curve through the points are at 29% and 28% for the B97-1/147@6-311+G** and B97-1/147@aug-cc-pVDZ "basis set functionals," and the minima for the B97-1/147@6-311+G($3d$,$2p$), B97-1/147@TZ2P and B97-1/147@aug-cc-pVTZ "basis set functionals" are at 16%, 17% and 17%, respectively.
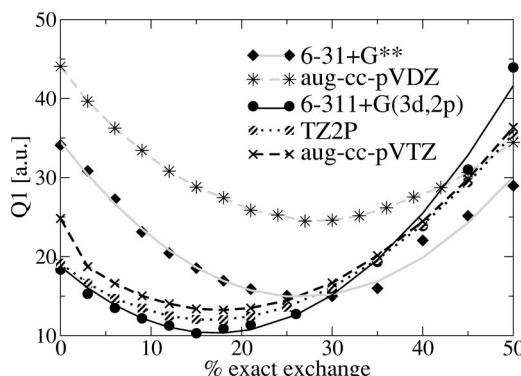
IV. ASSESSMENT OF DENSITY FUNCTIONALS

In this section we assess several density functionals with two basis sets: cc-pVTZ and TZ2P. The former basis set has been used in the construction of VSXC,[3] and the latter in the parameterization of the HCTH-type functionals.[6–8,10,11] For this evaluation, we use the large 407 Set,[35] again comparing rms energy, gradient and Q_1 errors. A similar comparison for most of the functionals evaluated has been done before, using the TZ2P basis set and the much smaller sets of 93 and 147 molecules. Thus, we can assess if the results will remain transferable between the G2-1 and G3 sets.[50] Table VIII shows all results obtained.

- The simplest density functional method, LSDA in its VWN parameterization, is already a vast improvement over the Hartree-Fock method. The LSDA geometries are surprisingly accurate, even more so when comparing the gradient error to a vast number of GGA and meta-GGA functionals.

- For molecular systems, PKZB yields no clear improvement over PBE, although it was developed as an improvement over PBE including a semi-empirical fit and an extra variable, the kinetic energy density τ. Both functionals give rms energy errors close to 20 kcal/mol. In addition, we would expect geometry errors similar to the ones obtained by the LSDA method. We would discourage the use of these functionals for the calculation of both molecular thermochemical data and geometries.

- mPW1K is a hybrid functional with a large percentage of exact exchange, developed for accurate reproduction of reaction barriers, reducing the error of B3LYP for this property by about 50%.[65] However, its performance

TABLE VIII. Errors evaluated with the 407 Set of contemporary functionals, using the TZ2P and cc-pVTZ basis sets.

Basis Set Functional	TZ2P			cc-pVTZ		
	rms energy	Gradient	Q_1	rms energy	Gradient	Q_1
HF	155	34.81	17917			
LSDA	105	15.93	7846			
PKZB	18.0	20.45	428.6			
PBE	20.7	15.68	426.0	20.5	16.42	449.5
mPW1K	16.8	19.18	399.6	17.7	18.27	483.2
PW91PW91	19.2	14.64	373.1	19.1	15.08	378.3
BP86	16.9	16.16	338.2	11.8	16.51	331.4
mPW91PW91	13.8	15.66	274.0	13.9	15.41	263.4
BLYP	9.8	18.50	249.7	11.0	18.91	283.9
BPW91	10.3	15.51	203.1	10.9	16.80	258.4
PBE0	11.9	11.19	199.8	12.2	12.05	219.8
OLYP	9.6	13.52	172.5	10.0	14.32	205.5
B98	8.7	13.40	166.2	8.9	13.39	175.7
B3LYP	9.6	11.36	165.3	10.2	11.62	177.3
B97-2	7.4	11.50	161.6	8.4	11.77	175.7
VSXC	9.4	11.39	158.6	9.4	11.43	167.5
HCTH/147	9.1	11.37	137.3	9.5	12.36	173.3
HCTH/407	8.0	11.28	135.3	9.3	12.46	187.6
HCTH/93	8.4	11.66	134.2	9.8	12.50	178.6
B97-1	7.3	10.81	130.9	8.1	11.19	143.7
τ-HCTH	7.3	10.65	114.2	8.4	11.72	150.4
τ-HCTH hybrid	6.3	10.36	107.5	7.3	11.11	133.2

for minimum geometries and energetics of stable molecules is the worst of all hybrid functionals tested and even standard GGA's yield lower errors.

- PW91PW91, the original GGA proposed by Perdew, yields slightly lower errors than PBE, that largely come from the evaluation of the gradients.

- When replacing the PW91 exchange functional with mPW91, the rms energy error is reduced, yet the gradient error increases.

- The BP86 GGA functional, albeit an improvement over these methods, still gives a Q_1 error almost three times larger than the best functionals available. The rms energy error is lowered by 5 kcal/mol when using the cc-pVTZ basis set instead of TZ2P; the gradient error however increases.

- BLYP is one of the more accurate functionals, but generally overestimates bond distances, and its gradient error is extremely large. This leads to rms errors in bond lengths that are almost twice as high as for hybrid functionals.[8] Nevertheless, it is still one of the commonly used functionals, very often employed when calculating hydrogen bonds[59] or in Car-Parrinello Molecular Dynamics simulations of liquid water.[60] Its rms and gradient errors both increase when using the cc-pVTZ basis set. In contrast to the smaller sets, the BLYP functional now clearly outperforms BP86 for the 407 set, whereas this was not the case for the 93 set.[50]

- The BPW91 functional uses Becke's exchange functional in combination with PW91 correlation, and yields lower errors than the PW91 and mPW91 exchange functionals for the properties tested. Here, the functional gives a performance similar to BLYP, perhaps slightly better. Again, its gradient error is higher for the cc-pVTZ basis set.

- PBE0 does not yield better energy predictions than the GGA functionals mPW91PW91, BPW91 and BLYP. Interestingly, its gradient error is lower than the one obtained for the most commonly used functional B3LYP, thus we would expect a pretty accurate description of geometries and higher-order properties.

- OLYP[61] is a clear improvement over BLYP for atomization energies and reactions, and even more so for molecular structures.[62,63] Its overall errors are almost comparable to those of the hybrid functionals, much better than BLYP and BPW91. Here, an improved exchange functional OPTX is used instead of Becke's exchange functional. However, its performance for hydrogen bonds is not as good as BLYP.[64]

- B98 does exactly the opposite of PBE0: We would expect its geometries to be further away from the equilibrium than B3LYP, but its energy error is slightly decreased. In the overall Q_1 evaluation, the error is very similar to the one obtained by the older B3LYP.

- The B3LYP functional is probably the most widely used hybrid functional, and every new functional is compared to its accuracy. The rms error for the 407 Set is close to 10 kcal/mol, which is considerably larger than a "chemical accuracy" of 2 kcal/mol. The gradient error is again slightly increased for the cc-pVTZ basis set compared to TZ2P.

- B97-2 is a reparameterization of B97-1 including the ZMP potential points into the fit of the exchange-correlation functional. Hence, we can expect its energy error to be worse than B97-1, since the fit to an extra quantity usually worsens the performance to the energies. However, its advantages over B97-1 still have to be established since even its gradient error is larger.

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- The performance of VSXC for the 407 set is very similar to B3LYP. This contrasts with the bad performance of VSXC for the smaller 93 Set where it returned an error barely lower than the BLYP functional.[50] Fitted to the cc-pVTZ basis set, it is the only functional yielding similar errors for both basis sets.

- All HCTH functionals give errors which differ in Q_1 by less than 3% for the TZ2P basis set and less than 8% for the cc-pVTZ basis set. These functionals, while they are pure GGA functionals, yield errors that can be compared to hybrid functionals like B3LYP for both the TZ2P and cc-pVTZ basis sets. Here, the additional value added to the functional by reparameterizing it to 147 or 407 systems is not obvious, although the HCTH/407 functional outperforms the other parameterizations in the rms energy error. The Q_1 value of HCTH/407 is the worst for the HCTH functionals with the cc-pVTZ basis set. The justification for the reparameterization, making HCTH/407 a better functional than HCTH/93 or HCTH/147, will become only visible when considering hydrogen bonds or inorganic molecules[52,59] where error cancellation plays an important role. Generally, this error cancellation cannot be expected in DFT methods. In some post-Hartree-Fock methods like MP2 it is inherent, and hence the reparameterization of the functionals remains important to recapture such effects.

- B97-1 is probably the best choice when it comes to using density functional hybrid calculations, since it is already well tested and its calculated structures are similar to those obtained by B3LYP (or even slightly better), and it outperforms B3LYP by about a third in Q_1 when predicting energetic properties.

- τ-HCTH is for both basis sets an improvement over the HCTH functional showing that the inclusion of the kinetic energy density can lower the error further. Unfortunately, it lacks the performance of the HCTH/407 functional for weak interactions.[11,36]

- The τ-HCTH hybrid, when additionally including exact exchange, clearly yields the lowest Q_1 value of all methods tested. Its error for the TZ2P basis set is 50% lower than the one obtained by B3LYP in addition to yielding a lower gradient error and structures[11] than B3LYP.

Summarizing the results in Table VIII, by ranking all GGA functionals based on their Q_1 value, we get the following order (taking into account that some functionals have been fit to one of the basis sets):

HCTH/147≈HCTH/93≈HCTH/407<OLYP<BPW91

<BLYP<mPW91PW91<BP86<PW91PW91<PBE.

For the meta-GGA's and hybrid functionals, the ordering is

τ-HCTH hybrid<B97-1<τ-HCTH<VSXC≈B97-2

≈B3LYP≈B98<PBE0≪mPW1K<PKZB.
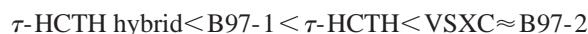
Although rms errors can give a lot of insight, the maximum errors are also considered important. In light of this, we have examined in Table IX the number of molecules in the 407 set for each functional that have large rms energy errors (over 15 kcal/mol). As we have discussed in the basis set evaluation, the cc-pVTZ basis set generally exhibits more outliers (mol-

TABLE IX. Number of molecules in the 407 set with an energy error larger than 15 kcal/mol for the functionals tested, using the TZ2P and cc-pVTZ basis sets.

Functional	TZ2P	cc-pVTZ
PBE	159	140
BP86	130	116
PBE0	50	48
BPW91	44	48
BLYP	36	46
OLYP	34	46
B3LYP	31	37
HCTH/147	30	38
VSXC	30	33
HCTH/93	24	38
HCTH/407	23	38
τ-HCTH	22	30
B98	21	24
B97-1	18	23
τ-HCTH hybrid	14	21

ecules with atypically large errors) than the TZ2P basis set. The results are very similar to the ones obtained in Table VIII, and compared to B3LYP, the best available functional (the τ-HCTH hybrid) cuts the number of outliers in half, yielding a considerable improvement. With regard to the accuracy of density functional theory with all the evaluations which are done with the 407 Set, the rms error of the functionals ranges between 6 (τ-HCTH hybrid) and 21 kcal/mol (PBE), with the most commonly used hybrid functional B3LYP yielding an error around 10 kcal/mol. The mean error of these functionals is between 3.8 kcal and 15.6 kcal mol, with B3LYP yielding 6.2 kcal/mol. This can be compared to empirical correction methods like G3,[34] which yield errors around 1 kcal/mol for the G3 set that, however, does not include some of the molecules with the largest errors in our 407 set. Extrapolation methods like W2[66] give mean errors around 0.5 kcal/mol for a considerably smaller set similar to our 147 Set. Full MP2 yielded an rms error of about 20 kcal/mol for the 407 Set using the TZ2P basis set. This generally places the accuracy of DFT between raw perturbation theory results and coupled-cluster theory when calculating ground state energies.

V. CONCLUSIONS

From the above, we can make a number of observations concerning the use of DFT functionals and the basis sets used with them. All results regarding the basis sets are obtained by fitting functionals to basis sets, and then evaluating their errors, thus the results are independent of the functional parameterization. For most of the properties investigated, including energies and gradients, the Pople basis sets can be recommended. Dunning's basis sets, fit to CISD, give considerably higher errors despite having a larger number of basis functions. Although it yields a higher error than the 6-311+G($3df$,$2pd$) basis set for energies and gradients, the TZ2P basis set still gives the lowest overall error for the GGA functionals when including the ZMP exchange-correlation potentials into the fit. The basis set error, which might still be significant at the triple-zeta level, shows that

the functionals obtained by fitting to one basis set are transferable to other basis sets. Hence, it is probably not important to reach the basis set limit when developing new density functionals, since the overall DFT error is considerably larger. Basis sets developed for DFT methods might alleviate this problem, but the problem remains as to which functional to use for their development. The same analysis for hybrid density functionals shows that the amount of exact exchange obtained is dependent on the basis set itself. Whereas basis sets of double-zeta quality yielded minima around 28%, the triple-zeta basis sets evaluated had their minima around 18%. Concerning the difference between the hybrid "basis set functionals," the same conclusions as for the GGA functionals can be drawn. The same trends are also visible when evaluating several other published functionals to a large test set. We can deduce that several hybrid functionals, such as B97-1 and the τ-HCTH hybrid functional render errors which are significantly lower than the ones obtained by B3LYP. As a pure GGA functional, the HCTH functional types give errors comparable to B3LYP for the investigated properties.

Nevertheless, the accuracy of modern density functional theory cannot be compared to that of *ab initio* extrapolation methods. The best functional tested yields an rms energy error as large as 6.3 kcal/mol for a large set of molecules, which is still far away from the desired "chemical accuracy" of 1-2 kcal/mol.

ACKNOWLEDGMENTS

[1] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[2] C. Adamo and V. Barone, J. Chem. Phys. **108**, 664 (1998).
[3] T. Van Voorhis and G. E. Scuseria, J. Chem. Phys. **109**, 400 (1998).
[4] C. Adamo and V. Barone, Chem. Phys. Lett. **298**, 113 (1998).
[5] J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999).
[6] F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, J. Chem. Phys. **109**, 6264 (1998).
[7] A. D. Boese, N. Doltsinis, N. C. Handy, and M. Sprik, J. Chem. Phys. **112**, 1670 (2000).
[8] A. D. Boese and N. C. Handy, J. Chem. Phys. **114**, 5497 (2001).
[9] N. C. Handy and A. J. Cohen, Mol. Phys. **99**, 403 (2001).
[10] P. J. Wilson, T. J. Bradley, and D. J. Tozer, J. Chem. Phys. **115**, 9233 (2001).
[11] A. D. Boese and N. C. Handy, J. Chem. Phys. **116**, 9559 (2002).
[12] B. J. Lynch, P. L. Fast, M. Harris, and D. G. Truhlar, J. Phys. Chem. A **104**, 21 (2000).
[13] A. D. Becke, J. Chem. Phys. **107**, 8554 (1997).
[14] A. D. Becke, J. Chem. Phys. **109**, 2092 (1998).
[15] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[16] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[17] S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[18] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[19] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[20] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[21] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[22] F. De Proft, F. Tielens, and P. Geerlings, J. Mol. Struct.: THEOCHEM **506**, 1 (2000).
[23] F. De Proft, J. M. L. Martin, and P. Geerlings, Chem. Phys. Lett. **256**, 400 (1996).
[24] A. C. Scheiner, J. Baker, and J. W. Andzelm, J. Comput. Chem. **18**, 775 (1997).
[25] J. M. Martell, J. D. Goddard, and L. A. Eriksson, J. Phys. Chem. A **101**, 1927 (1997).
[26] P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, Chem. Phys. Lett. **197**, 499 (1992).
[27] J. M. L. Martin, J. El-Yazal, and J. P. François, Mol. Phys. **86**, 1437 (1995).
[28] J. M. L. Martin, in *Density Functional Theory: A Bridge Between Chemistry and Physics*, edited by P. Geerlings, F. De Proft, and W. Langenaeker (VUB Press, Brussels, 2000), pp. 111.
[29] F. Jensen, J. Chem. Phys. **115**, 9113 (2001).
[30] F. Jensen, J. Chem. Phys. **116**, 7372 (2002).
[31] N. Godbout, D. R. Salahub, J. Anzelm, and E. Wimmer, Can. J. Chem. **70**, 560 (1992).
[32] D. Porezag and M. R. Pederson, Phys. Rev. A **60**, 2840 (1999).
[33] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).
[34] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **112**, 7374 (2000).
[35] http://www-theor.ch.cam.ac.uk/people/nch/fit/; see also supplementary material to Ref. 8, EPAPS Document No. E-JCPSA6-114-30111; please note that the geometry of benzene in the latter document contained an error.
[36] A. D. Boese, A. Chandra, J. M. L. Martin, and D. Marx, J. Chem. Phys. (to be published).
[37] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[38] Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994).
[39] T. H. Dunning, J. Chem. Phys. **55**, 716 (1971).
[40] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[41] D. E. Woon and T. H. Dunning, J. Chem. Phys. **99**, 3730 (1993).
[42] The Cambridge Analytic Derivatives Package (Cadpac), Issue 6.5, Cambridge, 1998, developed by R. D. Amos with contributions from I. L. Alberts, J. S. Andrews, S. M. Colwell *et al.*
[43] J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. **102**, 939 (1980).
[44] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, J. Am. Chem. Soc. **104**, 5039 (1982).
[45] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).
[46] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).
[47] M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).
[48] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, Theor. Chem. Acc. **72**, 650 (1980).
[49] R. A. Chiles and C. E. Dykstra, J. Chem. Phys. **74**, 4544 (1981).
[50] A. J. Cohen and N. C. Handy, Chem. Phys. Lett. **316**, 160 (2000).
[51] R. Ahlrichs, F. Furche, and S. Grimme, Chem. Phys. Lett. **325**, 317 (2000).
[52] G. Menconi and D. J. Tozer, Chem. Phys. Lett. **360**, 38 (2002).
[53] G. Menconi, P. J. Wilson, and D. J. Tozer, J. Chem. Phys. **114**, 3958 (2001).
[54] K. A. Peterson and T. H. Dunning, Jr., J. Chem. Phys. **117**, 10548 (2002).
[55] M. A. Iron, M. Oren, and J. M. L. Martin, Mol. Phys. (to be published).
[56] T. H. Dunning, Jr., K. A. Peterson, and A. Wilson, J. Chem. Phys. **114**, 9244 (2001).
[57] J. M. L. Martin, J. Chem. Phys. **108**, 2791 (1998).
[58] A. D. Boese and J. M. L. Martin (unpublished results).
[59] C. Tuma, A. D. Boese, and N. C. Handy, Phys. Chem. Chem. Phys. **1**, 3939 (1999); note that the HCTH/120 functional is denoted HCTH-38 in this paper.
[60] M. Sprik, J. Hutter, and M. Parrinello, J. Chem. Phys. **105**, 1142 (1996).
[61] N. C. Handy and A. J. Cohen, Mol. Phys. **99**, 403 (2001).
[62] W. M. Hoe, A. J. Cohen, and N. C. Handy, Chem. Phys. Lett. **341**, 319 (2001).
[63] J. Baker and P. Pulay, J. Chem. Phys. **117**, 1441 (2002).
[64] A. D. Boese and N. C. Handy (unpublished results).
[65] M. Harris and D. G. Truhlar, J. Phys. Chem. A **105**, 2936 (2001).
[66] J. M. L. Martin and G. De Oliveira, J. Chem. Phys. **111**, 1843 (1999).