Performance of Density Functionals with Small Split Valence Basis Sets[†]

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Though there have been many studies of density functional theory and various density functionals for large basis sets, there have been extremely limited studies of DFT with smaller basis sets. This paper discusses the ability of a series of density functionals to reproduce experimental heats of formation at the 3-21G*, 3-21+G*, and MIDI! basis sets. Also included are G3, G3MP2, MNDO, and PM3 calculations for comparison purposes. Good results for 3-21G* were obtained using mPW exchange with gradient-corrected correlation functionals LYP, PBEc, and PW91c, and 3-21+G* performed well with PBEx and PW91x exchange functionals when coupled with these same gradient-corrected correlation functionals. Unexpectedly good results were also obtained with G96P86/3-21G*, given each individual functionals performance in other functional pairings. MIDI! was outperformed, in general, by both 3-21G* and 3-21+G*.

Introduction

Accurate quantum chemical calculations performed on large systems, such as biomolecules, promise to significantly increase our understanding of the structure and function of these systems.[1,2] Although QM calculations can be easily performed on these systems using semiempirical methods with divide and conquer techniques,[3,4] density matrix minimization,[5] or localized molecular orbital techniques,[6] ab initio calculations on large systems are still not common due to their expense in both computer time and memory requirements,[1] though they are becoming more practical.[2,7−11] It would, therefore, be extremely useful to continue the search for an ab initio based method cheap enough to allow calculations on large systems while still providing reasonably accurate results.

One way to limit calculation expense is to decrease the size of the basis set. The rate determining step for ab initio based calculations is the formation of the repulsion integrals, which formally scales as N^4 where N is the number of basis functions, although this in practice can be decreased to N^2 or even linear scaling through the use of various techniques.[12] Nonetheless, a smaller basis set increases the practicality of calculations on large systems. That being said, it was decided to restrict ourselves to the split-valence variety, as they significantly outperform single valence basis sets.[13] The most common and well validated small split valence basis sets include 3-21G*,[13−15] 3-21+G*,[16] and MIDI!,[17] and thus these where the basis sets chosen for consideration in this study.

Once a basis set has been chosen, the next step is the selection of an electronic structure method. This study focuses on DFT[18,19] because this method has generated a great deal of excitement for molecular calculations over the past decade.[20−22] Simply examining the table of contents of a current theoretical/chemical journal demonstrates the popularity of DFT, and the ability of DFT to reproduce experimental data has been shown in several studies.[22−26] DFT is not, however, a single method but rather a family of related methods because the exact density functional is unknown.[27] Hence, it is necessary to choose an exchange and correlation functional from a broad palette of proposed functionals developed over the last twenty years. Table 1 briefly describes some of the functionals that were considered in this study. Though there are many more functionals,[28−30] it was decided to restrict this study to the functionals included in Gaussian 98,[31] as this constitutes a large set of current functionals of a manageable size.

Modern density functionals most commonly calculate exchange and correlation energy based on the electronic density and the gradient of the electronic density, although early functionals did not include a gradient term.[32]

$$E_{\mathrm{XC}} = \int f(\rho_\alpha,\rho_\beta,\gamma_{\alpha\alpha},\gamma_{\beta\beta},\gamma_{\alpha\beta})\,\mathrm{d}\tau \tag{1}$$

$$\gamma_{\sigma\sigma} = \nabla\rho_\sigma\cdot\nabla\rho_\sigma \tag{2}$$

where E_{xc} is the exchange/correlation energy, f is the user defined function, ρ is the electron density, σ labels the spin, and γ is the gradient invariant.

Also, many popular functionals include exact exchange, where a portion of the functional exchange is replaced with the single-determinantal exchange (of the same form as HF exchange),[33] which results in an extremely powerful family of methods.[22] For an example of how the mixing occurs, the B3LYP and B1LYP functionals are given by

$$E_{\mathrm{XC}}^{\mathrm{B3LYP}} = E_{\mathrm{XC}}^{\mathrm{LSDA}} + a_0(E_{\mathrm{X}}^{\mathrm{HF}} - E_{\mathrm{X}}^{\mathrm{LSDA}}) + a_{\mathrm{X}}E_{\mathrm{X}}^{\mathrm{B88}} + E_{\mathrm{C}}^{\mathrm{LYP-local}} + a_{\mathrm{C}}E_{\mathrm{C}}^{\mathrm{LYP-nonlocal}} \tag{3}$$

with $a_0 = 0.20$, $a_{\mathrm{X}} = 0.72$, and $a_{\mathrm{C}} = 0.81$.

$$E_{\mathrm{XC}}^{\mathrm{B1LYP}} = a_0E_{\mathrm{X}}^{\mathrm{HF}} + (1 - a_0)(E_{\mathrm{X}}^{\mathrm{LSDA}} + E_{\mathrm{X}}^{\mathrm{B88}}) + E_{\mathrm{C}}^{\mathrm{LYP}} \tag{4}$$

where $a_0 = 0.25$. For both eqs 3 and 4, E is the energy and the subscript denotes whether the term is exchange or correlation. The a parameters in B1LYP and B3LYP are for the optimum inclusion of the various forms of exchange and correlation energy.

The most important point about the functionals considered in this study, and indeed all current functionals, is that the exact density functional is unknown, and thus these functionals are

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TABLE 1: Description and References for Functionals Examined[a]

functional	type	ref	notes
Slater	X	51	The earliest exchange functional considered in this study. Slater exchange is only a functional of the density.
B88	X	32	An early gradient-corrected density functional, Becke's 1988 functional has been found to be extremely useful at larger basis sets either with a gradient-corrected correlation functional such as LYP, or as part of the three parameter exact exchange functionals.
G96	X	52	Gill's 1996 exchange functional was designed with simplicity in mind, with the hope of eventual exact integration of the exchange functional.
PW91	X/C	53, 54	Perdew and Wang's 1991 exchange and correlation functionals. The exchange functional adds an additional term to B88. The correlation functional is the descendant of their 1986 correlation functional.
mPW	X	34	A reparametrization of PW91.
PBE	X/C	55	This functional is interesting in that it was not parametrized against any molecular data.
B3PW91	X/C E	33	This is Becke's 3 parameter model that includes exact exchange. Other methods using the same three parameters with different correlation functionals are B3LYP and B3P86.
B1LYP	X/C E	56	Adamo and Barone's version of Becke's 1 parameter model. This model uses a single parameter to mix DFT exchange with HF (exact) exchange. Note that in this case, the parameter was set to 0.25. Functionals with the same form are mPW1PW91, G1LYP, and PBE1PBE.
VWN	C	57	This is one of the early density-only correlation functionals. Note that several equations for the correlation were given in this article. The default in Gaussian[31] is functional version 3.
PL	C	58	Perdew's early density-only correlation functional.
P86	C	59	Perdew's 1986 correlation functional, using his PL functional as the density-only portion.
LYP	C	35	The Lee−Yang−Parr gradient-corrected correlation functional has met with success both as part of B3LYP and as a pure DFT functional.

[a] Under the column labeled "type", X refers to exchange, C refers to correlation, and E refers to exact exchange. Please note that several "X/C" terms appear in the column, as some exchange and correlation functionals have the same name because they were designed together.

approximate. Their mathematical form (and the optimization of their parameters, when used) fundamentally defines the accuracy of the functional. For example, the mPW functional is a reparametrization of the PW91x functional, which can be considered Becke's 1988 exchange functional (B88) with several added terms, and all three of these contain some enhancement factor added to the Slater density dependent functional.[34] To more clearly explain the functionals considered in this paper, their mathematical forms are included. First to be considered are the exchange functionals studied in this paper. Note that all exchange functionals share the following form, where LSDA indicates "local spin density approximation":

$$E_{\mathrm{X}}^{\mathrm{Nonlocal}} = E_{\mathrm{X}}^{\mathrm{LSDA}} - \sum_{\sigma=\alpha,\beta} \int F[x_\sigma] {\rho_\sigma}^{4/3}\, \mathrm{d}\tau \tag{5}$$

$$x_\sigma = \frac{|\nabla \rho_\sigma|}{{\rho_\sigma}^{4/3}} = \frac{{\gamma_{\sigma\sigma}}^{1/2}}{{\rho_\sigma}^{4/3}} \tag{6}$$

$$E_{\mathrm{X}}^{\mathrm{Slater}} = E_{\mathrm{X}}^{\mathrm{LSDA}} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \sum_{\sigma=\alpha,\beta} \int {\rho_\sigma}^{4/3}\, \mathrm{d}\tau = A_{\mathrm{X}} \sum_{\sigma=\alpha,\beta} \int {\rho_\sigma}^{4/3}\, \mathrm{d}\tau \tag{7}$$

As you can see, x introduces the dependence on the gradient of the density. The enhancement factor, $F[x]$, for each exchange functional in this study is

$$F_{\mathrm{B88}}[x_\sigma] = \frac{b{x_\sigma}^2}{1 + 6bx_\sigma \sinh^{-1} x_\sigma} = \frac{b{x_\sigma}^2}{1 + 6bx_\sigma \log(x_\sigma + \sqrt{{x_\sigma}^2 + 1})} \tag{8}$$

with $b = 0.0042$.

$$F_{\mathrm{PW91x}}[x_\sigma] \text{ or } F_{\mathrm{mPW}}[x_\sigma] = \frac{b{x_\sigma}^2 - (b - \beta){x_\sigma}^2 \mathrm{e}^{-c{x_\sigma}^2} - 10^{-6}{x_\sigma}^{\mathrm{d}}}{1 + 6bx_\sigma \sinh^{-1} x - \dfrac{10^{-6}{x_\sigma}^{\mathrm{d}}}{A_x}} \tag{9}$$

with $\beta = 5(36\pi)^{-5/3}$ and $c = 1.6455$ for both, $b = 0.0042$ and $d = 4$ for PW91, and $b = 0.0046$ and $d = 3.73$ for mPW91.

$$F_{\mathrm{G96}}[x_\sigma] = b{x_\sigma}^{3/2} \tag{10}$$

with $b = 1/137$.

$$F_{\mathrm{PBE}x}[x_\sigma] = A_x\left[\frac{\kappa}{1 + \left(\frac{\pi}{3}\right)^{2/3} \frac{\beta x_\sigma}{12\kappa}} - \kappa\right] \tag{11}$$

with $\beta = 0.066725$ and $\kappa = 0.804$.

All parameters are listed with the functional. Please see Table 1 for complete references. Please note that eq 9 includes two exchange functionals, as they are simply two different parameter sets with the same mathematical form. It is also important to note none of the functionals include a dependence on the α−β gradient invariant, as exchange is only possible between electrons of the same spin.

The picture for correlation functionals becomes slightly more complicated for two reasons. First, the density-only dependent correlation term is a parametrized functional as well as the gradient-corrected portion of the functional, which is not the situation for exchange. Second, there is a correlation functional commonly used that does not allow the smooth separation of density dependent and gradient dependent portions of correlation, as is the case with all other functionals in this study. This is the Lee−Yang−Parr functional.[35] In the form given by Johnson et al., it is[20]

$$\begin{aligned} E_{\mathrm{c}}^{\mathrm{LYP}} = \int & -\frac{4a\rho_\alpha\rho_\beta}{(1 + {d_\rho}^{-1/3})\rho} - \\ & 2^{11/3}\frac{3}{10}(3\pi^2)^{2/3} ab\omega\rho_\alpha\rho_\beta({\rho_\alpha}^{8/3} + {\rho_\beta}^{8/3}) - \\ & ab\omega\gamma_{\alpha\beta}\left[\frac{1}{9}\rho_\alpha\rho_\beta(47 - 7\delta) - \frac{4}{3}\rho^2\right] - \\ & \sum_\sigma ab\omega\gamma_{\sigma\sigma}\left[\frac{1}{9}\rho_\sigma\rho_{\sigma'}\left(1 - 3\delta - (\delta - 11)\frac{\rho_\sigma}{\rho}\right) - {\rho_{\sigma'}}^2\right] \mathrm{d}\tau \end{aligned} \tag{12}$$

with $a = 0.04918$ and $b = 0.132$.

$$\omega = \frac{e^{-c\rho^{-1/3}}}{1 + d\rho^{-1/3}}\rho^{-11/3} \tag{13}$$

$$\delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{1 + d\rho^{-1/3}} \tag{14}$$

with $c = 0.2533$ and $d = 0.349$.

For the remaining correlation functionals explored in this study there is a natural separation of the density dependent and gradient dependent portions, as was the case for the exchange functionals described above. These are of the form

$$E_{\mathrm{c}} = E_{\mathrm{c}}^{\mathrm{local}} + E_{\mathrm{c}}^{\mathrm{nonlocal}} = \int \rho\epsilon_{\mathrm{c}}\,\mathrm{d}\tau + E_{\mathrm{c}}^{\mathrm{nonlocal}} \tag{15}$$

The ϵ in the foregoing equation is the correlation energy per particle of a uniform electron gas. Three versions of this parametric function appear in the original paper. (See Table 1.) The first of these is VWN, which in Gaussian[31] is the third formula proposed in the original article:

$$\epsilon_{\mathrm{c}}^{\mathrm{VWN}} = \epsilon_{\mathrm{c}}^{\mathrm{P}} + \epsilon_{\mathrm{c}}^{\mathrm{A}}\frac{9}{8}((1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2) \times \left[1 + \left[\frac{4}{9(2^{1/3}-1)}\frac{\epsilon_{\mathrm{c}}^{\mathrm{F}} - \epsilon_{\mathrm{c}}^{\mathrm{P}}}{\epsilon_{\mathrm{c}}^{\mathrm{A}}} - 1\right]\zeta^4\right] \tag{16}$$

Please note that F and P in the superscripts above refer to ferromagnetic and paramagnetic (i.e., spin-polarized and non-spin-polarized).

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta} \tag{17}$$

ζ is a measure of spin polarization, and appears in all the correlation functionals in this paper. Please note that for the non-spin-polarized case, the α and β densities are equal, and thus $\zeta = 0$.

$$\epsilon_{\mathrm{c}}^{\mathrm{i}} = A_{\mathrm{i}}\left[\ln\frac{r_{\mathrm{s}}}{X_{\mathrm{i}}} + \frac{2b_{\mathrm{i}}}{Q_{\mathrm{i}}}\tan^{-1}\frac{Q_{\mathrm{i}}}{2r_{\mathrm{s}}^{1/2} + b_{\mathrm{i}}} - \frac{b_{\mathrm{i}}x_0}{X_{\mathrm{i}}}\left[\ln\frac{(r_{\mathrm{s}}^{1/2} - x_0)^2}{X_{\mathrm{i}}} + \frac{2(2x_0 + b_{\mathrm{i}})}{Q_{\mathrm{i}}}\tan^{-1}\frac{Q_{\mathrm{i}}}{2r_{\mathrm{s}}^{1/2} + b_{\mathrm{i}}}\right]\right] \tag{18}$$

where

$$\begin{array}{lll} A_{\mathrm{P}} = 0.0621814 & A_{\mathrm{F}} = 0.0310907 & A_{\mathrm{A}} = -1/(3\pi^2) \\ b_{\mathrm{P}} = 13.0720 & b_{\mathrm{F}} = 20.1231 & b_{\mathrm{A}} = 1.06835 \\ x_{0,\mathrm{P}} = -0.409286 & x_{0,\mathrm{F}} = -0.743294 & x_{0,\mathrm{A}} = -0.228344 \end{array}$$

$$r_{\mathrm{s}} = \left(\frac{3}{4\pi\rho}\right)^{1/3} \tag{19}$$

r_{s} is the Wigner−Seitz radius, which is the radius of a sphere whose volume would contain one electron at a given density. Please note that density functionals can be expressed in terms of r_{s} or ρ because r_{s} is determined by ρ. The r_{s} notation is more commonly found in physics literature.

$$X_{\mathrm{i}} = r_{\mathrm{s}} + b_{\mathrm{i}}r_{\mathrm{s}}^{1/2} + c_{\mathrm{i}} \tag{20}$$

$$Q_{\mathrm{i}} = \sqrt{4c_{\mathrm{i}} - b_{\mathrm{i}}} \tag{21}$$

where $c_{\mathrm{P}} = 42.7198$, $c_{\mathrm{F}} = 101.578$, and $c_{\mathrm{A}} = 11.4813$.

This completes the definition of VWN. The next two formulas come from the work of Perdew and co-workers. Note that the functional called PL could be called PL80 to differentiate it from PL92 by chronology, but the title PL is retained because this is the name used in common parlance.

$$\epsilon_{\mathrm{c}}^{\mathrm{PL}} = \epsilon_{\mathrm{c}}^{\mathrm{U}} + \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{4/3} - 2}[\epsilon_{\mathrm{c}}^{\mathrm{P}} + \epsilon_{\mathrm{c}}^{\mathrm{U}}] \tag{22}$$

where U and P are unpolarized and polarized, respectively.

$$\begin{aligned} \epsilon_{\mathrm{c}}^{\mathrm{i}} &= \frac{\Gamma_{\mathrm{i}}}{(1 + \beta_1^{\mathrm{i}}\sqrt{r_{\mathrm{s}}} + \beta_2^{\mathrm{i}}r_{\mathrm{s}})} \qquad r_{\mathrm{s}} \geq 1 \\ \epsilon_{\mathrm{c}}^{\mathrm{i}} &= A_{\mathrm{i}}\ln r_{\mathrm{s}} + B_{\mathrm{i}} + C_{\mathrm{i}}r_{\mathrm{s}}\ln r_{\mathrm{s}} + D_{\mathrm{i}}r_{\mathrm{s}} \qquad r_{\mathrm{s}} < 1 \end{aligned} \tag{23}$$

where

$$\begin{array}{lll} \Gamma_{\mathrm{U}} = -0.1423 & \beta_1^{\mathrm{U}} = 1.0529 & \beta_2^{\mathrm{U}} = 0.3334 \\ \Gamma_{\mathrm{P}} = -0.0843 & \beta_1^{\mathrm{P}} = 1.3981 & \beta_2^{P} = 0.2611 \\ A_{\mathrm{U}} = 0.0311 & B_{\mathrm{U}} = -0.048 & C_{\mathrm{U}} = 0.0020 \\ D_{\mathrm{U}} = -0.0116 & A_{\mathrm{P}} = 0.01555 & B_{\mathrm{P}} = -0.0269 \\ C_{\mathrm{P}} = 0.007 & D_{\mathrm{P}} = -0.0048 & \end{array}$$

Note that the parameter Γ used above corresponds to γ in the original paper; the notation was changed to avoid confusion with the gradient invariants.

$$\epsilon_{\mathrm{c}}^{\mathrm{PL92}} = G_1 + \frac{G_2}{f''}\frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{4/3} - 2}(1 - \zeta^4) + \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{4/3} - 2}\zeta^4[G_3 - G_1] \tag{24}$$

$$G_{\mathrm{i}} = -2A_{\mathrm{i}}(1 + \alpha_{\mathrm{i}}r_{\mathrm{s}})\ln\left[1 + \frac{1}{2A_{\mathrm{i}}(\beta_{1\mathrm{i}}r_{\mathrm{s}}^{1/2} + \beta_{2\mathrm{i}}r_{\mathrm{s}} + \beta_{3\mathrm{i}}r_{\mathrm{s}}^{3/2} + \beta_{4\mathrm{i}}r_{\mathrm{s}}^{2})}\right] \tag{25}$$

where

$$\begin{array}{lll} A_1 = 0.031091 & A_2 = 0.016887 & A_3 = 0.015545 \\ \alpha_1 = 0.21370 & \alpha_2 = 0.1125 & \alpha_3 = 0.20548 \\ \beta_{11} = 7.5957 & \beta_{21} = 3.5876 & \beta_{31} = 1.6382 \\ \beta_{41} = 0.49294 & \beta_{12} = 10.357 & \beta_{22} = 3.6231 \\ \beta_{32} = 0.88026 & \beta_{42} = 0.49671 & \beta_{13} = 14.1189 \\ \beta_{23} = 6.1977 & \beta_{33} = 3.3662 & \beta_{43} = 0.62517 \end{array}$$

$$f'' = 1.709921$$

The PL92 parametrization of ϵ is not a stand alone functional in this study, unlike the VWN and PL density-only functionals. The density-only terms are then used in combination with the gradient-corrected portion to produce the correlation functionals found in this work. The three functionals below are the gradient-corrected correlation functionals with simple separation between the density-only portion and the gradient-corrected portion used in this study. They were developed by Perdew and co-workers and show the evolution of a correlation functional over time. The three functionals are P86, PW91c, and PBEc (from 1996):

$$E_c^{P86} = E_c^{PL} + \int d^{-1} e^{-\Phi} C(\rho) \frac{|\nabla\rho|^2}{\rho^{4/3}} \, d\tau \tag{26}$$

$$d = 2^{1/3} \left[\left[\frac{1+\zeta}{2} \right]^{5/3} + \left[\frac{1-\zeta}{2} \right]^{5/3} \right] \tag{27}$$

$$\Phi = 1.745 \bar{f} \left[\frac{C(\infty)}{C(\rho)} \right] \frac{|\nabla\rho|}{\rho^{7/6}} \tag{28}$$

$$C(\rho) = 0.001667 + \frac{(0.002568 + \alpha r_s + \beta r_s^{\,2})}{(1 + \Gamma r_s + \delta r_s^{\,2} + 10^4 \beta r_s^{\,3})} \tag{29}$$

with $\alpha = 0.023266$, $\beta = 7.389 \times 10^{-6}$, $\Gamma = 8.723$, $\delta = 0.472$, and $\bar{f} = 0.11$.

$$E_c^{PW91} \text{ or } E_c^{PBE} = \int \rho(\epsilon_c^{PL92} + H_0 + H_1) \, d\tau \tag{30}$$

$$H_0 = g^3 \frac{\beta^2}{2\alpha} \ln\left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right] \tag{31}$$

$$g = \frac{[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]}{2} \tag{32}$$

$$t = \frac{|\nabla\rho|}{4g\rho^{7/6}} \left(\frac{\pi}{3} \right)^{1/6} \tag{33}$$

$$A = \frac{2\alpha}{\beta} \frac{1}{e^{-2\alpha\epsilon_c/g^3\beta^2} - 1} \tag{34}$$

where $\beta = 0.066725$ for both $\alpha = 0.09$ for PW91 and $\alpha = \beta^2\pi^2/(2(1 - \ln 2))$ for PBE. For PBE, H_1 is zero. For PW91,

$$H_1 = \left(\frac{16}{\pi} \right) (3\pi^2)^{1/3} \left[C(\rho) - C(0) - \frac{3C_x}{7} \right] g^3 t^2 e^{-100 g^4 4 (3n\pi^5)^{-1/3} t^2} \tag{35}$$

where C is as in eq 29 and $C_x = 0.001667$.

Please note that in some of the equations the notation has been changed from the original papers to avoid confusion. (See Table 1 for citations.)

As will be seen from the data in this study, even a subtle shift in parameters for a given functional form (e.g., PW91x to mPW (see eq 9); these represent the same functional form, just slightly different parameter sets) results in a significant change in the computed results. Differences in performance therefore arise from both parametrization and functional form. Though certain functionals have been shown to have better predictive power than other functionals, no functional is clearly the best in all cases. This is why development of functionals continues unabated.[30,36] Determination of which functional to use still involves a good deal of experimentation.

The specification of appropriate functionals at large or medium basis sets can be guided by several published studies, such as the work of Pople and co-workers,[22,23] as well as others.[37,38] It has been pointed out, however, that there is no reason to expect the best functionals for rich basis sets to be the best also for small sets.[29] To our knowledge, there have been no published systematic studies of DFT at basis sets as small as those utilized in this study, although the study of Handy et al.[38] does include the evaluation of a new functional at 3-21G*. Given that the small basis sets are what will probably be initially used[2,8−11] as ab initio-based calculations become more practical for large molecules, it is necessary to determine what method gives the best performance when coupled with small basis sets. In other words, although larger basis sets can give better results with DFT,[37,38] this study is guided by practical considerations for applications to large systems.

In this paper we assembled a test set of compounds and examined various functionals for their ability to predict the heat of formation of these compounds accurately with three small basis sets. A new test set was assembled rather than using a previously defined set such as the G3/99 set,[22] as some of the functionals were parametrized against those earlier sets, thus making the testing of such functionals almost moot. Nonetheless, there is certainly an overlap between standard test sets and the set used in this study. Heat of formation was chosen as the quantity of interest because there are many experimentally determined values for a wide range of compounds, public databases of these values exist, and the method to calculate heat of formation from ab initio-type calculations has been established.[39]

Method

The test set is composed of 372 compounds that contain five or fewer heavy atoms. Molecules meeting this size criteria and consisting of atoms H, C−F, and P−Cl were taken from the NIST thermochemical database.[40] Please see the Supporting Information for a complete listing. The size limitation was imposed to keep the data set tractable in terms of both the number of compounds and the time required for evaluating the entire set. Though the argument has been raised that error in DFT calculations increases for larger molecules,[22,23] the wide range of molecules in this set provides a reasonable measure of functional efficacy. G3[41] and G3MP2[42] calculations demonstrate the validity of this set, as the errors for this set are close to the published accuracy of these two methods. Also included are semiempirical calculations using MNDO[43,44] and PM3[45,46] to allow the reader a sense of how the DFT methods in question perform in comparison to these extremely common semiempirical methods. AM1[47] was not examined because PM3 is essentially a reparametrization of the AM1 formalism.

All calculations were performed with Gaussian 98[31] on an in-house Linux cluster running Red Hat 7.1. Heats of formation were calculated from the G98 results using the method specified by the “Thermochemistry in Gaussian” white paper[39] available at http://www.Gaussian.com/g_whitepap/thermo.htm. This method involves using the sum of the calculated molecular electronic, translational, rotational, and vibrational energy along with calculated atomic electronic energy and experimental atomic thermal corrections to give the heat of reaction of a molecule being formed from its constituent atoms. Coupled with experimental atomic heats of formation, this allows the calculation of molecular heats of formation.

Molecular geometries were optimized and frequencies were calculated with the basis set and density functional that was being evaluated.

Discussion

Table 2 illustrates that there is a slight difference in the size of three basis sets considered in this study, i.e., 3-21G* < MIDI! < 3-21+G*. Please note that both the number of basis functions and the number of primitive Gaussians is listed, because the importance of each variable to overall execution time is determined by the integral routine used.[48] Because one of the goals of this investigation is to find a functional that performs well at the limit of a small split valence basis set, the assumption was that if a functional performs equally well at all three basis

TABLE 2: Basis Functions and Primitive Gaussians per Atom

atom type	basis functions			primitive Gaussians		
	3-21G*	3-21+G*	MIDI!	3-21G*	3-21+G*	MIDI!
H	2	2	2	3	3	3
C	9	13	9	15	19	15
N, O, F	9	13	14	15	19	21
P, S, Cl	19	23	18	33	37	33

TABLE 3: Unsigned Errors for Functionals[a]

functional	3-21G*	3-21+G*	MIDI!
BVWN	18.8	28.4	22.9
BPL	23.5	33.8	27.3
BP86	15.1	9.6	15.5
BPW91	10.8	19.9	18.8
BPBE	10.7	19.7	19.0
BLYP	16.8	27.7	24.6
G96VWN	31.2	38.6	31.8
G96PL	36.0	44.0	36.5
G96P86	7.9	9.7	11.0
G96PW91	22.4	29.9	25.5
G96PBE	22.1	29.7	25.6
G96LYP	28.3	37.8	22.3
PW91VWN	10.1	10.4	11.1
PW91PL	8.3	13.6	13.0
PW91P86	35.6	24.8	35.5
PW91PW91	15.4	8.0	15.7
PW91PBE	15.6	7.9	16.0
PW91LYP	10.4	7.8	14.8
mPWVWN	9.8	18.8	15.9
mPWPL	13.3	23.9	19.8
mPWP86	24.5	15.6	24.9
mPWPW91	8.0	10.4	9.5
mPWPBE	7.9	10.3	14.7
mPWLYP	7.9	18.2	18.6
PBEVWN	9.0	11.4	11.6
PBEPL	8.3	15.7	14.5
PBEP86	32.9	22.7	33.1
PBEPW91	13.3	7.3	14.7
PBEPBE	13.4	7.2	15.0
PBELYP	8.7	9.8	15.2
HF	275.7	279.7	267.9
MP2	114.7	116.2	100.4
LSDA	124.2	112.3	129.5
SLATER	49.6	58.1	56.6
B3LYP	26.5	36.1	27.1
B3PW91	23.0	31.3	22.6
B3P86	15.1	15.5	9.6
B1LYP	42.0	51.6	41.0
G1LYP	51.4	59.7	48.5
PBE1PBE	20.2	28.7	20.8
mPW1LYP	33.0	43.4	33.4
mPW1PW91	26.3	34.7	25.8
MNDO		15.1	
PM3		6.6	
G3		2.4	
G3MP2		2.6	

[a] All errors are in kcal/mol.

sets, the 3-21G* basis set is a better choice due to size considerations. The issue of basis sets will be addressed at the end of the paper after the functionals have been fully analyzed.

The performance of Hartree−Fock and MP2 theories at this basis set level was expected, because very small basis sets are inadequate for these levels of refinement.[49] The degree of underbinding evidenced by the positive sign of the signed errors is significant. One important thing to note is that, with the exception of LSDA, all DFT functionals outperform these methods at the basis sets under consideration, implying that DFT is less sensitive to basis set size. It is also important to note that MIDI! is a better basis set at the HF and MP2 levels, consistent with observations in the original MIDI! paper.[17]

Early methods such as LSDA and the Slater exchange-only functional do not perform as well as more advanced gradient-corrected functionals. These two functionals lack any contribution from the gradient of the density. As can be seen from Tables 3 and 4, they are outperformed by functionals that contain the gradient correction. Please note that the LSDA functional is Slater exchange with VWN correlation functional; i.e., Slater is just LSDA without correlation. Note also that the Slater functional underbinds, whereas the LSDA functional dramatically overbinds. Thus it might be expected that by scaling the correlation functional in LSDA, a much more accurate functional could be constructed. This is made more interesting because the functionals are not gradient corrected and thus would fundamentally be faster than functionals including gradient corrections, because the gradient of the density would never have to be calculated. As a test of this hypothesis we scaled the correlation function with a simple parameter, which was found to have an optimal value of 0.286 (see Figure 1) As expected, the unsigned error was reduced from 124.2 to 15.7 kcal/mol, which makes this functional, in terms of heat of formation computation, very competitive with several of the more advanced functionals. Clearly, further examination of this approach is warranted, and this scaling should not be used without more testing; i.e., it is being included in this discussion parenthetically and not as a new functional alternative. However, this could open inquiry into parametrized density-only functionals.

Functionals that include exact exchange also faired poorly in this analysis. With the exception of B3P86, functionals using exact exchange had errors much larger than MNDO for the same compound set. It is also important to note that the poor performance of these functionals is due to underbinding, as is the case with HF at these basis sets. The problems occur whether the mixing parameters are optimized to reproduce chemical behavior (B3LYP, B3PW91, B3P86) or are determined due to theoretical considerations (B1LYP, G1LYP, PBE1PBE, mPW1LYP, mPW1PW91). Any inclusion of exact exchange apparently reduces thermochemical accuracy at these basis sets. Further proof of this was discovered during an attempted reparametrization of the three-parameter fit of B3LYP/3-21G*.[50] The parameter that scales exact exchange goes to zero as the fit improves, implying that any inclusion of exact exchange at basis sets this small is not helpful. Hence, there are two important points to take from this. First, exact exchange is not useful at these small split valence basis sets even though it is very powerful at large basis sets.[22] Second, this is a property not of the fit used but rather of exact exchange when used with small basis sets.

The one functional combination that did not follow the trend for exact exchange is B3P86. This is likely due to the P86 correlation functional, because P86 does not follow the trends established by the other correlation functionals when paired with any exchange functional. Though all other exact exchange functionals underbind, it can be seen in Table 4 that B3P86 overbinds at the 3-21G* and MIDI! basis sets by −0.7 and −4.3 kcal/mol, respectively, and only underbinds at the 3-21+G* basis set. In fact, B3P86 is the second best functional combination for the MIDI! basis set. It also violates the trends established by other correlation functionals when coupled with PW91, mPW, or PBE exchange. These combinations give much larger errors than the other correlation and exchange combinations, showing a tendency toward overbinding. It is also the only correlation functional that overbinds when combined with the B88 functional. Most interestingly, P86 overcomes G96's

TABLE 4: Signed Errors for Functionals[a]

functional	3-21G*	3-21+G*	MIDI!
BVWN	18.2	28.2	17.5
BPL	23.0	33.6	22.6
BP86	−12.6	−2.0	−14.2
BPW91	9.0	19.4	7.7
BPBE	8.7	19.2	7.5
BLYP	14.9	27.3	15.1
G96VWN	30.9	38.5	28.5
G96PL	35.7	43.9	33.6
G96P86	0.1	8.2	−3.4
G96PW91	21.6	29.6	18.4
G96PBE	21.3	29.4	18.2
G96LYP	27.6	37.5	13.7
PW91VWN	−4.2	7.2	−3.3
PW91PL	0.6	12.7	1.8
PW91P86	−35.2	−23.2	−35.0
PW91PW91	−13.6	−1.6	−13.0
PW91PBE	−13.9	−1.8	−13.4
PW91LYP	−7.8	6.4	−5.8
mPWVWN	6.9	18.4	7.8
mPWPL	12.1	23.5	12.8
mPWP86	−23.6	−12.0	−24.1
mPWPW91	−1.8	9.6	−3.1
mPWPBE	−2.3	9.4	−2.5
mPWLYP	3.9	17.5	5.2
PBEVWN	−1.4	9.7	−0.9
PBEPL	3.3	15.1	4.4
PBEP86	−32.5	−20.7	−32.8
PBEPW91	−10.9	0.8	−10.8
PBEPBE	−11.1	0.6	−11.0
PBELYP	−5.0	8.8	−3.5
HF	275.7	279.7	267.9
MP2	114.7	116.2	100.4
LSDA	−122.7	−112.3	−129.0
SLATER	42.4	56.3	38.8
B3LYP	26.3	36.0	24.6
B3PW91	22.8	31.2	19.9
B3P86	−0.7	7.3	−4.2
B1LYP	42.0	51.6	40.2
G1LYP	51.4	59.7	48.1
PBE1PBE	20.0	28.6	17.7
mPW1LYP	32.9	43.4	31.9
mPW1PW91	26.2	34.7	23.8
MNDO		7.7	
PM3		1.5	
G3		1.2	
G3MP2		1.2	

[a] All errors are in kcal/mol.

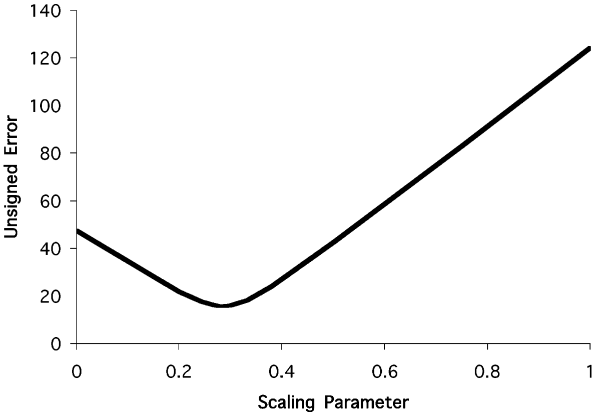

Figure 1. Unsigned error of LSDA when VWNIII is scaled. Please note all errors are in kcal/mol.

tendency to underbind, which results in the second best performance for any exchange/correlation pair for 3-21G* with an average error of 7.9 kcal/mol, and the fifth best method/basis set combination overall. This indicates that the P86 functional itself lowers the energy of a molecule too much to be useful with most exchange functionals with small basis sets, but may have exciting uses with new functionals that show a tendency to predict positive heats of formation with small basis sets.

The performance of the G96 exchange functional when coupled with any correlation functional other than P86 is somewhat disappointing, because this functional is extremely simple when compared to other exchange functionals such as B88 (see eqs 8−11) and as such is something of a departure from common functional design. One interesting point is that it was parametrized to reproduce the exchange energy of argon at HF/6-311++G, rather than using a range of compounds. Another test of G96P86 is warranted to see how it performs over a larger test set and for other chemical properties given it's excellent performance at the 3-21G* level. If G96P86/3-21G*'s efficacy can be confirmed, this may be an ideal functional combination for small basis sets. Nevertheless, the novel G96 exchange functional shows a marked underbinding with these small basis sets for most correlation functionals.

Another exchange functional with a significant tendency to underbind is the B88 functional. This functional has been shown to work well as part of B3LYP at larger basis sets,[22] but with the small basis sets used in this study that success was not repeated. It can be seen that the errors do decrease as correlation functionals include a gradient dependency. However, for small basis sets there are no good combinations that include B88 exchange.

There are three exchange functionals that have not been discussed yet. These are PW91, mPW, and PBE. Rather than considering each exchange functional with each correlation functional, it is instructive to divide the correlation functionals not yet considered into density dependent (VWN and PL) and gradient corrected (PW91, PBE, and LYP). The density-only correlation functionals will be considered first.

When any of the three remaining exchange functionals are coupled with a correlation functional depending on the density only, the best results are seen with the 3-21G* basis set. Though there appears to be no good combination of mPW with a density dependent correlation functional, PW91PL/3-21G* and PBEPL/3-21G* give relatively small unsigned errors versus other functional combinations, and are the 10th and 11th best functional combinations found in this study. This result is quite surprising, as gradient-corrected correlation has been found to work better for larger basis sets in published studies.[22] Another surprise is that these functional combinations have some of the smallest signed errors in the set. This lack of systematic error implies, however, that their performance cannot be improved for small basis sets by scaling either exchange or correlation, as was suggested by the LSDA−Slater data discussed previously. Also, there is no real computational advantage to having a density-only dependent correlation functional with a gradient dependent exchange functional, as the gradient of the electronic density would still have to be calculated, and the only term that can be neglected is the $\alpha-\beta$ gradient invariant, which is trivial to calculate from the density gradient, causing no reduction of computational expense.

The best results of the entire study were found when the gradient-corrected exchange functionals PW91, mPW91, and PBE were combined with the modern correlation functionals PW91, PBE, and LYP. The best results are found at the 3-21+G* level using PBE or PW91, whereas the best results with 3-21G* were found using mPW91. Overall, the top five functional/basis combinations were PBEPBE/3-21+G* < PBEPW91/3-21+G* < PW91LYP/3-21+G* < mPWLYP/3-

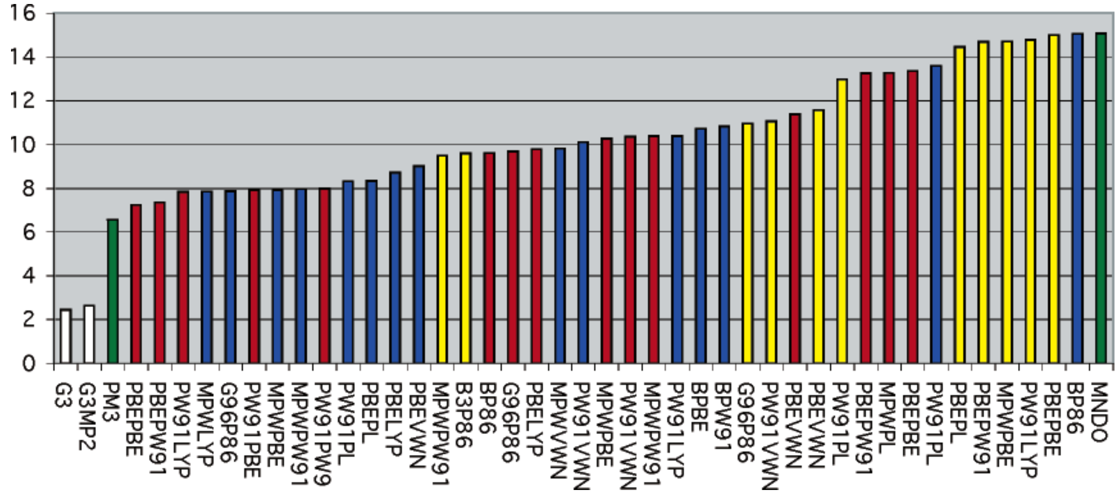

Figure 2. Signed Error. This chart lists all functional/basis set combinations that have smaller errors than MNDO. Functionals are listed across the bottom of the chart. White indicates G3 and G3MP2, green indicates semiempirical methods, and blue, red, and yellow, indicate 3-21G*, 3-21+G*, and MIDI!, respectively. All errors are in kcal/mol.

21G* < G96P86/3-21G*. This is interesting, as it appears that the more recent functionals of Perdew et al. and a reparametrization of the same perform extremely well with small basis sets. This also provides a route for testing the performance of new functionals at the small basis set limit; e.g., if a new correlation functional is to be tested at the 3-21+G* level, it probably will have its best performance with PBE exchange. Note that an inspection of Table 4 indicates that functionals with MIDI! were not among the best found in the study. This is also shown graphically in Figure 2.

This leads back to the basis set considerations mentioned at the beginning of this section. The best small basis set for predicting heat of formation with density functional theory is 3-21+G*. This is not unexpected given recent work showing the importance of diffuse functions for DFT.[37] Moreover, this is the largest basis set of the three examined. Thus PBEPBE/3-21+G* would be the level indicated by this study for small basis sets in general. That being said, 3-21+G* adds four basis functions per nonhydrogen atom in a system. For even a small protein of 500 heavy atoms, this is an additional 2000 basis functions, which is a fairly large computational load. Thus having two density functional combinations that perform well at the 3-21G* level (G96P86 and mPWLYP) is also an important piece of data to come out of this study. The G96P86/3-21G* combination is an odd pairing, and further work to determine that this is in fact an ideal combination of basis set and theory would be interesting. If this would be the case, this method/basis set would be extremely useful for investigations of large systems. Regardless, mPWLYP/3-21G* has been found to be a good functional combination for use with 3-21G*.

Conclusion

Several important issues were clarified during the course of this study of DFT with small split-valence basis sets.

(1) With the correct choice of functionals, thermochemical performance comparable to standard semiempirical methods is possible at extremely small basis sets. This may have important implications for QM/QM studies, as it is easier to combine large basis set ab initio methods with small basis set ab initio based methods than it is to combine ab initio and semiempirical methods.

(2) The addition of exact exchange to a density functional, which has worked extremely well for large basis sets, does not have the same impact on small basis sets. This is not a matter of how the exact exchange is included, but rather the fact that it is being included.

(3) B88 and G96 exchange underbinds unless paired with P86 correlation. A side issue to this is G96P86/3-21G* deserves further study because it appears to be an excellent combination of functionals and a small basis set for calculating thermochemistry.

(4) More recent exchange functionals using the ideas of Perdew et al. (PW91*x*, mPW, PBE*x*) perform very well when coupled with modern correlation functionals.

(5) MIDI! is not as useful as either 3-21G* or 3-21+G* for DFT.

(6) Acceptable accuracy can be obtained at either 3-21G* or 3-21+G*.

(7) The overall best combinations that we observed were PBEPBE/3-21+G* and MPWLYP/3-21G*.

As new functionals become available, the guidelines in this paper can help in the analysis of pairings for small basis sets. As an example, if a correlation functional overbinds, B88 and G96 can be used to try to improve performance. It is hoped that the results described herein will further accelerate the move toward DFT calculations on large biological systems.

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Supporting Information Available: All calculated heats of formation used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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