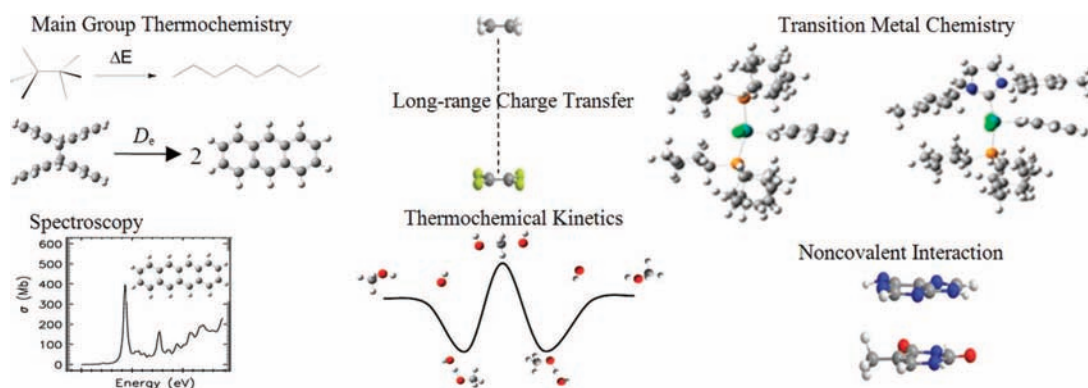# Density Functionals with Broad Applicability in Chemistry

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CONSPECTUS

Although density functional theory is widely used in the computational chemistry community, the most popular density functional, B3LYP, has some serious shortcomings: (i) it is better for main-group chemistry than for transition metals; (ii) it systematically underestimates reaction barrier heights; (iii) it is inaccurate for interactions dominated by medium-range correlation energy, such as van der Waals attraction, aromatic—aromatic stacking, and alkane isomerization energies. We have developed a variety of databases for testing and designing new density functionals. We used these data to design new density functionals, called M06-class (and, earlier, M05-class) functionals, for which we enforced some fundamental exact constraints such as the uniform-electron-gas limit and the absence of self-correlation energy. Our M06-class functionals depend on spin-up and spin-down electron densities (i.e., spin densities), spin density gradients, spin kinetic energy densities, and, for nonlocal (also called hybrid) functionals, Hartree—Fock exchange. We have developed four new functionals that overcome the above-mentioned difficulties: (a) M06, a hybrid meta functional, is a functional with good accuracy "across-the-board" for transition metals, main group thermochemistry, medium-range correlation energy, and barrier heights; (b) M06-2X, another hybrid meta functional, is not good for transition metals but has excellent performance for main group chemistry, predicts accurate valence and Rydberg electronic excitation energies, and is an excellent functional for aromatic—aromatic stacking interactions; (c) M06-L is not as accurate as M06 for barrier heights but is the most accurate functional for transition metals and is the only local functional (no Hartree—Fock exchange) with better across-the-board average performance than B3LYP; this is very important because only local functionals are affordable for many demanding applications on very large systems; (d) M06-HF has good performance for valence, Rydberg, and charge transfer excited states with minimal sacrifice of ground-state accuracy. In this Account, we compared the performance of the M06-class functionals and one M05-class functional (M05-2X) to that of some popular functionals for diverse databases and their performance on several difficult cases. The tests include barrier heights, conformational energy, and the trend in bond dissociation energies of Grubbs' ruthenium catalysts for olefin metathesis. Based on these tests, we recommend (1) the M06-2X, BMK, and M05-2X functionals for main-group thermochemistry and kinetics, (2) M06-2X and M06 for systems where main-group thermochemistry, kinetics, and noncovalent interactions are all important, (3) M06-L and M06 for transition metal thermochemistry, (4) M06 for problems involving multireference rearrangements or reactions where both organic and transition-metal bonds are formed or broken, (5) M06-2X, M05-2X, M06-HF, M06, and M06-L for the study of noncovalent interactions, (6) M06-HF when the use of full Hartree—Fock exchange is important, for example, to avoid the error of self-interaction at long-range, (7) M06-L when a local functional is required, because a local functional has much lower cost for large systems.

I. Introduction

According to the Born−Oppenheimer approximation, the ground-state electronic structure and the nuclear repulsion of a molecule determine its ground-state geometry, potential energy surface, thermochemistry, rate constants, and other physical and chemical properties. Kohn−Sham density functional theory[1] (DFT) has become one of the most popular tools in electronic-structure theory due to its excellent performance-to-cost ratio as compared with correlated wave function theory (WFT). The accuracy of a DFT calculation depends upon the quality of the exchange−correlation (XC) functional.

The past two decades have seen remarkable progress in the development and validation of XC density functionals.[2−4] The first generation of functionals is called the local spin density approximation (LSDA), in which density functionals depend only on the up- and down-spin ($\sigma = \alpha, \beta$) local spin densities ρ_σ. Although LSDA gives surprisingly accurate predictions for solid-state physics, it is not a useful model for chemistry due to its severe overbinding of chemical bonds and underestimation of barrier heights. The second generation of density functionals is called the generalized gradient approximation (GGA), in which functionals depend on the ρ_σ and their gradients $\nabla\rho_\sigma$. GGA functionals have been shown to give more accurate predictions for thermochemistry than LSDA ones, but they still underestimate barrier heights. In third-generation functionals, two additional variables, the spin kinetic energy densities, $\tau_\sigma(r)$, are included in the functional form; such functionals are called meta-GGAs. LSDAs, GGAs, and meta-GGAs are "local" functionals because the electronic energy density at a single spatial point depends only on the behavior of the electronic density and kinetic energy at and near that point;[5−7] local functionals can be mixed with nonlocal Hartree−Fock (HF) exchange as justified by the adiabatic connection theory.[8] Functionals containing HF exchange are usually called hybrid functionals, and they are often more accurate than local functionals for main-group thermochemistry. HF exchange would be exact if the Kohn−Sham orbitals were the accurate ones determined by the exact XC functional, which is unknown. We do, however, know some properties of the exact XC functional, for example, it is nonlocal,[9] and these properties can serve as constraints during functional development.

In the last six years, the development of new functional forms for meta-GGAs and hybrid meta-GGAs and their validation against diverse databases have yielded powerful new density functionals with broad applicability to many areas of chemistry. There has also been much interest in including noncovalent interactions in DFT.[10−17] This Account focuses on the research of our group in these exciting areas. For coverage of the functional development work of others, we recommend an excellent 2005 review by Scuseria and Staroverov.[2]

This Account is organized as follows. In section II, we describe the motivation of our research, and we discuss the deficiencies of widely used density functionals. Section III presents our strategies for the development of new density functionals that overcome these deficiencies, and in section IV, the performance for several databases is presented. Section V gives examples that illustrate the improvement of the newly developed density functionals as compared with some previous functionals, both for ground-state properties and for electronic spectroscopy. Section VI concludes this Account and gives recommendations.

II. Motivation and Development

For ease of discussion, we loosely define three types of XC energies according to the distance between two fragments in a molecule, namely, short-range ($\lesssim$2 Å), medium range ($\sim$2−5 Å), and long range ($\gtrsim$5 Å). Short-range XC energy is responsible for the formation of chemical bonds, whereas medium-range XC energy determines the properties of noncovalent interactions and barrier heights to chemical reactions.

Although the B3LYP[8,18−20] functional, which is a hybrid GGA, is largely responsible for DFT becoming one of the most popular tools in computational chemistry, it does have unsatisfactory performance issues, notably the following:

1. Barrier heights: B3LYP was found[21] to underestimate barrier heights by an average of 4.4 kcal/mol for a database of 76 barrier heights. This underestimation is usually ascribed to the self-interaction error (unphysical interaction of an electron with itself) in local DFT.

2. Noncovalent interactions: B3LYP is unable to describe van der Waals complexes bound by medium-range interactions, such as the interactions in methane dimers and benzene dimers. This inability of B3LYP (and most other popular functionals) to accurately describe medium-range XC energy limits their applicability for biological systems and soft materials where medium-range dispersion-like interactions play vital roles. Moreover, some recent studies have shown that inaccuracy for the medium-range XC energies leads to large systematic errors in the prediction of heats of formation of organic molecules[22−29] and incorrect trends in the bond energies of organometallic catalytic systems.[30,31]

3. Transition metal chemistry: B3LYP and many other hybrid functionals have been found to give unreliable results for transition metal chemistry,[32–35] where better performance is often obtained with local functionals that are poor for main-group organic chemistry. For example, popular functionals containing Hartree−Fock exchange often overestimate the spin polarization of systems containing transition metals.

We started our work on problem 1 in 2000, when MPW1K,[36] a hybrid GGA, was optimized against a database of barrier heights of 22 reactions by using the adiabatic connection method. In 2004, BB1K[37] was developed to have better performance than MPW1K when both thermochemistry and kinetics are considered. Next we developed MPWB1K,[38] which also has very good performance for problem 2.[39] In 2005, PWB6K[40] was developed for attacking both problems 1 and 2, and it has greatly improved performance for noncovalent interactions.[41–43] In the same year, we also developed two databases for attacking problem 3; TMAE9[33] is a database of bond energies in nine transition metal dimers, and MLBE21[34] is a metal−ligand database. From extensive assessments, we found a conflict between problems 1 and 3, that is, to obtain more accurate barrier heights, one needed to mix in a high percentage of HF exchange, whereas transition metal chemistry favors low percentages of HF exchange.[33,34] By taking account of all three problems, M05[3,44] ("Minnesota 2005") was developed, and it gives good performance for transition metal chemistry[45] as well as main-group thermochemistry, barrier heights, and noncovalent interactions. With the same functional form as M05, we also developed a functional, M05-2X,[3] that focuses on problems 1 and 2 and performs even better than M05 or other previous functionals for main-group kinetics, thermochemistry, and noncovalent interactions.[26,46–50] In 2006, building on all this experience, we developed a suite of four new functionals called the M06 suite, which essentially supersedes our previous functionals. The rest of this Account is focused on the most recently developed functionals, namely, the M06 suite.

III. Strategies, Constraints, and Databases

There are several strategies[2] for functional development including (i) constraint satisfaction, (ii) modeling the XC hole, (iii) empirical fits, and (iv) mixing HF and local DFT exchange. Our M06-L functional is constructed via strategies i, ii, and iii. Our M06-HF,[51] M06,[4] and M06-2X[4] functionals also involve strategy iv.

TABLE 1. Training Sets and Constraints of the M06 Suite of Functionals

functional	constraints[a]	training sets[b]
M06-L	UEG, SCorF, no HF	TC, BH, NC, TM
M06	UEG, SCorF	TC, BH, NC, TM
M06-2X	UEG, SCorF, 2X[c]	TC, BH, NC
M06-HF	UEG, SCorF, full HF	TC, BH, NC

[a] UEG = uniform electron gas limit; SCorF = one-electron self-interaction free; HF = Hartree−Fock exchange. [b] TC = thermochemistry; BH = barrier heights; NC = noncovalent interactions; TM = transition metal chemistry. [c] Constrained to have twice as much HF exchange as M06.

Although the mathematical forms of the density functionals are too complicated to include here, we note that key design elements in all four functionals include enforcing the constraint of being exact for a uniform electron gas, requiring the functional to be free of one-electron self-correlation error, and designing the τ_σ dependence to minimize numerical instabilities[39,52] that sometimes plagued earlier work. Furthermore we tried to take advantage of the ability[53] of the exchange functional to include some near-degeneracy correlation[54] energy (the correlation functional includes only dynamical correlation energy) while developing functional forms for the exchange and correlation components of the XC functional that can be consistent with variable HF exchange, in particular, a high percentage of HF exchange in M06, M06-2X, and M06-HF or no HF exchange in M06-L. Table 1 lists the constraints and training sets for all four M06-class functionals. The differences in the constraints and training sets distinguish them for different applications.

M06-L is a local functional, and its locality allows one to use highly efficient algorithms to reduce the cost for large systems. M06 is a hybrid functional for general-purpose applications, and both M06-L and M06 are very suitable for applications in transition metal chemistry; both of them also give better performance than B3LYP for main-group thermochemistry, barrier heights, and noncovalent interactions. M06-2X has improved performance for main-group thermochemistry, barrier heights, and noncovalent interactions as compared with M06-L and M06, but it is not suitable for describing transition metal chemistry.
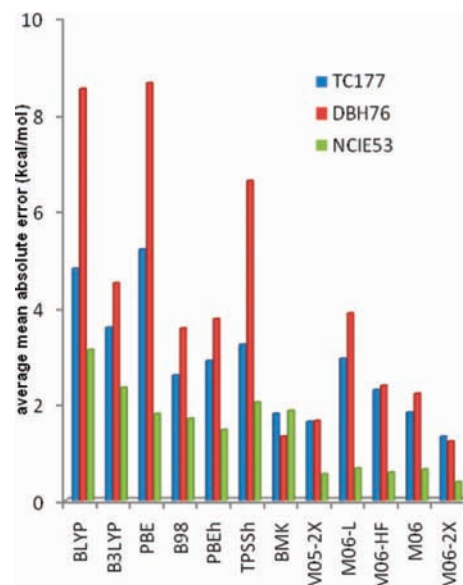
The M06-HF functional is designed to have full HF exchange because that provides the correct asymptotic behavior of the XC potential, which is important for long-range charge transfer excitations in electronic spectroscopy and some response properties such as polarizabilities of large conjugated molecules. Due to this full-HF constraint, it is not suitable for transition metal chemistry, and it is less accurate than M06 and M06-2X for general application in main-group chemistry. Nevertheless it is a very interesting functional

TABLE 2. Database for Ground-State Properties

databases	refs
A. Thermochemistry (TC177)	
1. atomization energies (109)	3
2. ionization potentials (13)	3,40,44,56
3. electron affinities (13)	3,40,44,56
4. proton affinities of small molecules (8)	46
5. alkyl bond dissociation energies (4)	3,27,57
6. π system isomerization energies (3)	28,46
7. proton affinities of conjugated polyenes (5)	46
8. proton affinities of conjugated Schiff bases (5)	46
9. hydrocarbon thermochemistry (7)	4,26
10. difficult cases (10)	4
B. Diverse Barrier Heights (DBH76)	
1. heavy-atom transfer (12)	21
2. nucleophilic substitution (16)	21
3. unimolecular and association (10)	21
4. hydrogen transfer (38)	3,21,58
C. Noncovalent Interaction Energies (NCIE53)	
1. hydrogen bonding (6)	39
2. charge-transfer complexes (7)	39
3. dipole-interaction complexes (6)	39
4. weak interaction complexes (7)	40
5. $\pi-\pi$ stacking (5)	40
6. biological hydrogen bonding (7)	50,59
7. biological predominantly dispersion-like (8)	50,59
8. biological mixed (7)	50,59
D. Electronic Spectroscopy	
electronic spectra (49)	4,51
E. Transition Metal Reaction Energies (TMRE48)	
1. transition metal atomization energies (9)	33
2. metal−ligand bond energies (21)	34
3. 3d transition metal reaction energies (18)	45,60
F. Structure Data	
1. bond lengths (40)	4,57
2. vibrational frequencies (38)	4
3. zero point energies (15)	4,75

FIGURE 1. Average mean unsigned errors for three databases.[4]

well as those in section IV are Born−Oppenheimer electronic energies including nuclear repulsion (i.e., zero-point exclusive, as in D_e rather than D_0).

IV. Performance on Diverse Databases

Figure 1 compares the performance on the TC177, DBH76, and NCIE53 databases. For the purpose of comparison, we also present results for several older functionals of various types, namely, the GGAs BLYP[18,19] and PBE;[61] the hybrid GGAs B3LYP, B98,[62] and PBEh (also called PBE0);[63] and the hybrid meta-GGAs TPSSh,[64] BMK,[65] and M05-2X.[3] For main-group thermochemistry, M06-2X, M05-2X, and BMK are the best performers, and they are also the best functionals for barrier heights. M05-2X and the M06 suite of functionals give the best performance for noncovalent interactions. One way to gauge the recent progress of DFT is to compare the recent functionals to B98. In 2005, Curtiss et al.[66] used a new test set, G3/05, with 454 energies, to test seven density functionals and found B98 to be the most accurate. The errors of M06-2X in Figure 1 are 1.3, 1.2, and 0.37 kcal/mol, whereas those for B98 are 2.6, 3.6, and 1.7 kcal/mol, factors of 2−5 larger. The errors for the popular B3LYP are even larger, 3.6, 4.5, and 2.3 kcal/mol, factors of 3−6 larger than those for M06-2X.

Figure 2 compares performance on the TMRE48 database. In all bar graphs, we compare with the same previous density functionals, exept that in Figure 2, M05-2X, M06-2X, and M06-HF are not included because functionals with more than 28% HF exchange are not recommended for transition metals; the functionals are listed in chronological order. Figure 2

because full HF exchange combined with a self-correlation-free correlation functional totally eliminates self-interaction at long range, which has been a bane of DFT. It has long been thought that one cannot obtain accurate results with full HF exchange because one must cancel the long-range error in the parallel-spin local correlation functionals with an opposite-sign long-range error in the exchange;[55] M06-HF is the first counterexample to this expectation.

Table 2 presents the databases developed in our group in the course of developing functionals. They are very important for designing and validating new functionals (and also WFT methods). TC177 is a composite database consisting of 177 data[3,4,26−28,40,44,46,56,57] for main-group thermochemistry. DBH76 is database of 76 diverse barrier heights.[3,21,58] NCIE53 is a database of 53 diverse noncovalent interactions energies,[39,40,50,59] and TMRE48 is a database[4,33,34,45,60] of 48 bond energies and reaction energies for transition metal chemistry. In section IV, we discuss the performance of the M06 suite of functionals as well as some other popular functionals for these databases. All energies in these databases as
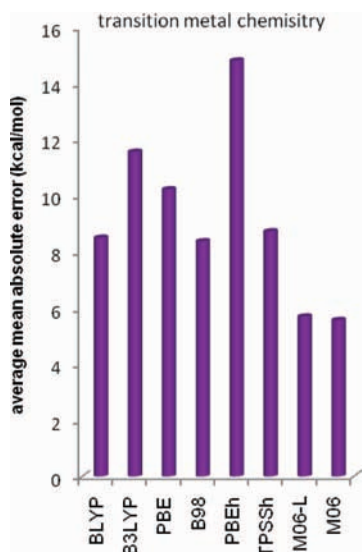
FIGURE 2. Average mean unsigned errors for the TMRE48 database.[4]

FIGURE 3. Isomerization energy of octane. The MG3S basis[56] and MP2/6-311+G(d,p) geometries are employed. The best estimate is from Grimme.[23]
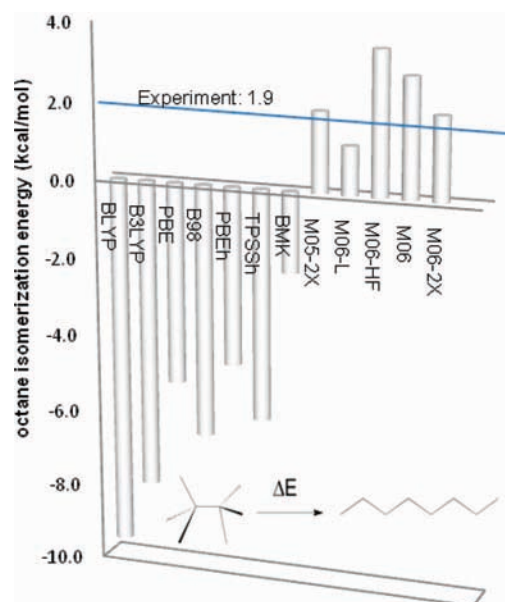
shows that M06-L and M06 give the best performance. M06 is the functional with broadest applicability, and it has errors of 1.8, 2.2, and 0.63 kcal/mol in Figure 1, which are 1.4−3 times smaller than B98 and 2−4 times smaller than B3LYP. Furthermore the error of M06 for transition metals (Figure 2) is only 5.6 kcal/mol, a factor of 1.5 smaller than B98 and a factor of 2 smaller than B3LYP.

Recent tests of density functionals against databases developed for testing WFT thermochemical predictions are published elsewhere.[2,66,67]
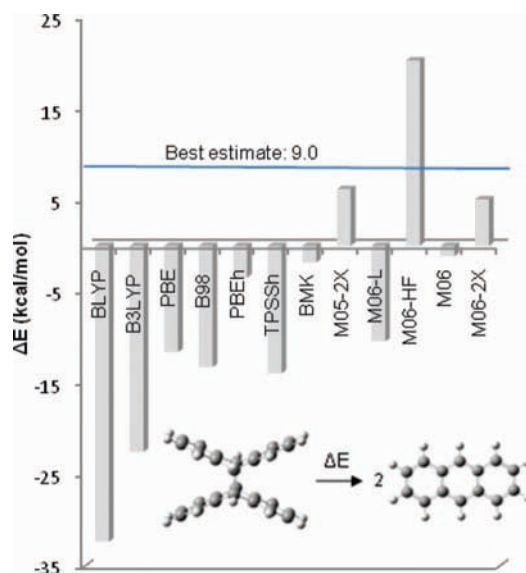
V. Case Studies

Although the databases in section III provide the most thorough assessment, the wellspring of our enthusiasm is best illustrated by troublesome cases for which the popular functionals fail, whereas our functionals give improved results. We group these cases into five categories, namely, main-group thermochemistry, noncovalent interactions, kinetics, electronic spectroscopy, and transition metal chemistry. None of the cases in this section is in the training set of any of the M06 suite of functionals.

V.A. Main-Group Thermochemistry. V.A.1. Isomerization Energy of Octane. Alkane isomerization involves "seemingly simple" stereoelectronic effects, but none of the previous functionals gives the right sign for the isomerization energy from 2,2,3,3-tetramethylbutane to *n*-octane.[23,26] Figure 3 shows that B3LYP gives an error of 10 kcal/mol. Only M05-2X and the M06 suite of functionals predict the right sign. This results because these functionals give a better description of medium-range XC energies, which are mani-


FIGURE 4. Reaction energies of a retro [4 + 4] cycloaddition reaction. The MG3S basis set and M06-2X/6-31+G(d,p) geomerties are employed. The best estimate is from Grimme.[68]

fested here as attractive components of the noncovalent interaction of geminal methyl and methylene groups.

V.A.2. Anthracene Dimer. The photodimerization of anthracene is a well-studied [4 + 4] cycloaddition that yields a covalently bound polycyclic dimer. There is a striking discrepancy between condensed-phase experiments and high-level correlated WFT calculations, which is apparently due to a delicate balance of noncovalent interactions.[68] Figure 4 shows that BLYP and B3LYP give large errors of 41 and 32 kcal/mol, respectively, for the gas-phase reaction. Only M05-
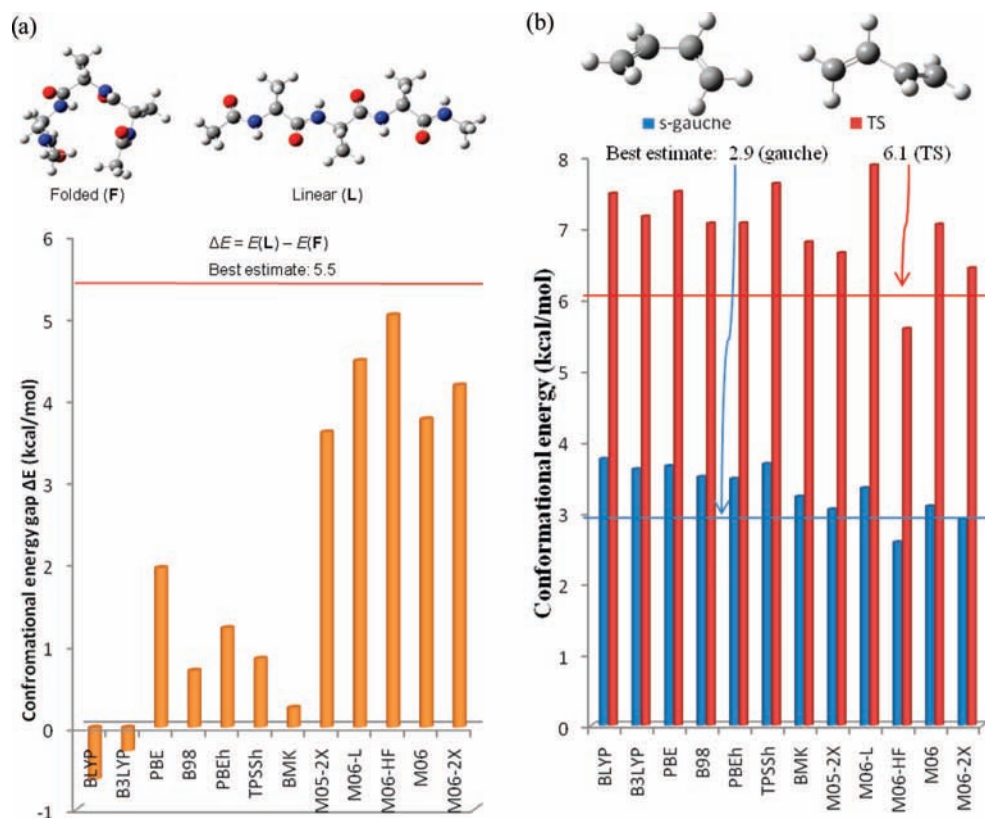
FIGURE 5. (a) Conformational energy difference of alanine tetrapeptide. The 6-31+G(d,p) basis set was employed with RI-MP2/cc-pVTZ geometries.[76] The best estimate was derived by RI-MP2/CBS + ΔCCSD(T)/6-31(0.25)G, where CBS denotes complete basis set. (b) Torsional energies of two conformers of 1,3-butadiene relative to the global *s-trans* minimum. The best estimates are from Karpfen and Parasuk.[77]

2X, M06-2X, and M06-HF give the correct sign of the fragmentation energy.

V.B. Noncovalent Interactions. V.B.1. Conformational Energies. Conformational energies are critical determinants of protein folding. Figure 5a shows that BLYP and B3LYP give the wrong sign of the conformational difference between the folded and unfolded alanine tetrapeptide. The M06 suite of functionals give the best performance.

Figure 5b presents the torsional energetics of two nonplanar conformers of 1,3-butadiene relative to the planar *s-trans* global minimum. The *s-gauche* conformer is a local minimum, and other is a transition state connecting it to the global minimum. Sancho-Garcia[69] has shown that most DFT functionals overestimate the conjugation effect and overstabilize the *s-trans* conformer. Figure 5b confirms this by showing that M06-L, BLYP, PBE, and TPSSh overestimate the torsional barrier by 20−30%, and B98, B3LYP, and PBEh also give errors greater than 1 kcal/mol. Among the tested functionals, M06-2X gives best accuracy as compared to the reference data, followed by M06-HF and M05-2X.

V.B.2. Adenine···Thymine Dimers. Hydrogen bonding and $\pi \cdots \pi$ stacking between nucleic acid base pairs play vital roles in the structure of biopolymers and the design of new

drugs. Figure 6 presents binding energies in the hydrogen bonded and $\pi \cdots \pi$ stacked adenine···thymine dimers. Figure 6 shows that all functionals give reasonable agreement for hydrogen bonding; however, for $\pi \cdots \pi$ stacking, BLYP and B3LYP give a repulsive interaction, and PBE, B98, PBEh, TPSSh, and BMK underestimate the binding energy by a large margin. The best performers for stacking are M06-2X and M06-HF, followed by M05-2X, M06, and M06-L.

V.B.3. Amino Acid Residue Dimer. Figure 7 presents the interaction energy of an amino acid residue pair[70] in the hydrophobic core of a small FeS protein, rubredoxin. Note that this interaction between the side chains of phenylalanine and tyrosine and their associated amide groups involves both electrostatics and $\pi \cdots \pi$ stacking. BLYP, B3LYP, and TPSSh give repulsive interactions, and PBE, B98, PBEh, and BMK considerably underestimate the binding energy. The M06 suite of functionals and M05-2X give much better agreement with experiments.
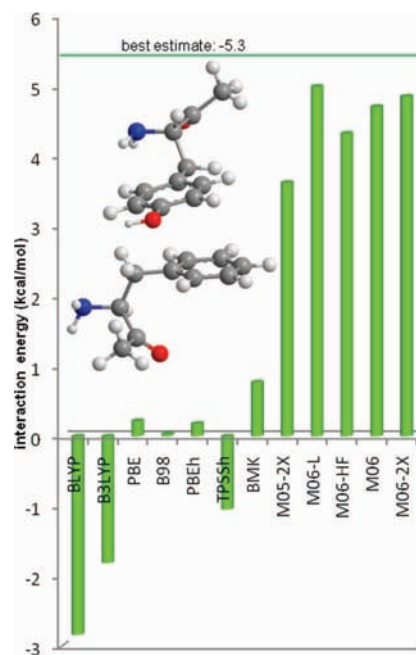
V.B.4. S22 Test Set and Rationale for the Success of DFT for Noncovalent Interactions. Forty-five density functionals have been tested[4,50] using the very affordable 6-31+G(d,p) basis set, against the S22 database of noncovalent interaction energies of biological importance proposed by
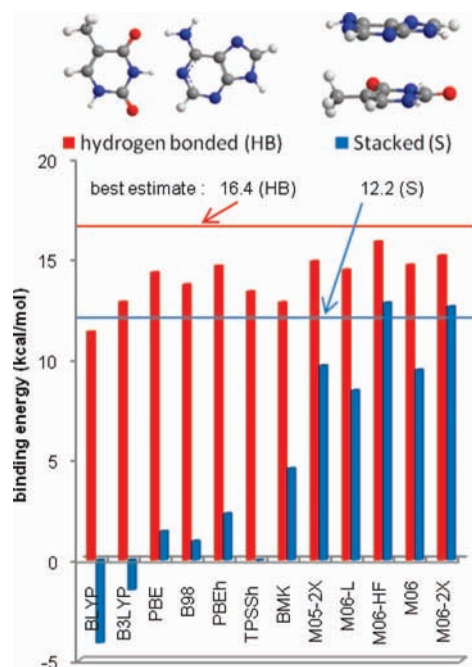
FIGURE 6. Interaction energies of the hydrogen-bonded and stacked adenine···thymine dimers (kcal/mol). The 6-31+G(d,p)[78] basis and counterpoise-corrected MP2/TZVP geometries[59] were employed for all calculations. The best estimates are from Jurecka et al.[59] The methods are listed in the same order as the order of the predicted potentials at 4.5 Å.

FIGURE 7. Interaction energies of an amino acid residue pair in the hydrophobic core of a small FeS protein, rubredoxin.[70] The 6-31+G(d,p) basis was employed. Geometries are from Vondrasek et al.[70] The best estimate was derived using MP2/CBS + side chain ΔCCSD(T).[70]

Jurecka et al.[59] The five smallest mean unsigned errors were obtained with M05-2X and the four M06 functionals, ranging from 0.47 kcal/mol for M06-2X to 0.85 kcal/mol for M06.[4] In contrast, the most popular method for noncovalent interactions, namely, Møller–Plesset second-order perturbation theory[71] (MP2, a WFT method), has a mean unsigned error of 1.6 kcal/mol with the same basis, more than a factor of three higher than the error of M06-2X with this basis.

There are some common misunderstandings about the performance of DFT for noncovalent interactions. Most DFT functionals cannot describe the $-C_6/R^6$ long-range interaction of nonoverlapped densities with no permanent multipole moments, where C_6 is a coefficient, and R is the distance between the monomers, but equilibrium structures of noncovalent complexes are dominated by medium-range exchange and correlation energies.[39,41,43,50] In order to better understand the range of distances over which the M06 suite of functionals is suitable for treating noncovalent interactions, Figure 8 compares WFT results[72] for the intermolecular potential of the $C_6H_6–CH_4$ complex to curves calculated by 12 density functionals. MP2 overestimates the strength of the $C_6H_6–CH_4$ complex as compared with the accurate CCSD(T) results; BLYP, B3LYP, and TPSS give repulsive potentials for this van der Waals complex; and PBE, PBEh, and B98 give a shallow well

with a minimum around 4.0 Å. M05-2X, M06-2X, and M06-HF give the best agreement with the CCSD(T) results; M06-L and M06 are slightly worse than these best three functionals, but they are better than other popular functionals. Figure 8 shows that the M06 suite of functionals can be useful out to 5.4 Å.

Even though the MP2 method leads to an interaction with the correct kind of long-range behavior, i.e., R^{-6}, it need not be quantitatively accurate, especially with practical basis sets (the results in Figure 8 involve the MG3S basis set for DFT but a complete basis set for WFT). For example, at 5 Å, the MP2/MG3S result deviates from CCSD(T)/CBS by 166 cal/mol, whereas the four M06-class results, with the same basis, have deviations of 3−99 cal/mol. For the study of dispersion-dominated noncovalent interactions at long range, one should probably use very-large-basis WFT or functionals[13−15,17] that parametrize in the correct asymptotic value of C_6.

V.C. Kinetics. Accurate prediction of chemical reaction barrier heights is essential for modeling kinetics. Due to their partially stretched bonds, transition states are harder to model than equilibrium structures. Figure 9 illustrates the barrier heights for two degenerate rearrangements. The first is an open-shell hydrogen transfer reaction with multireference[54] character. Even our local functional M06-L performs better than B3LYP, and the best performer is M06-2X. The second is a
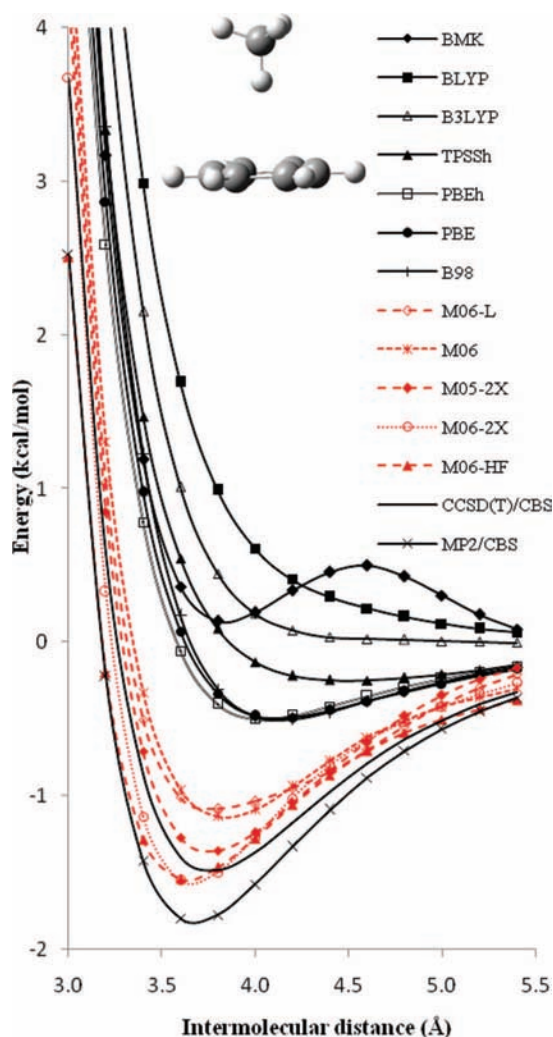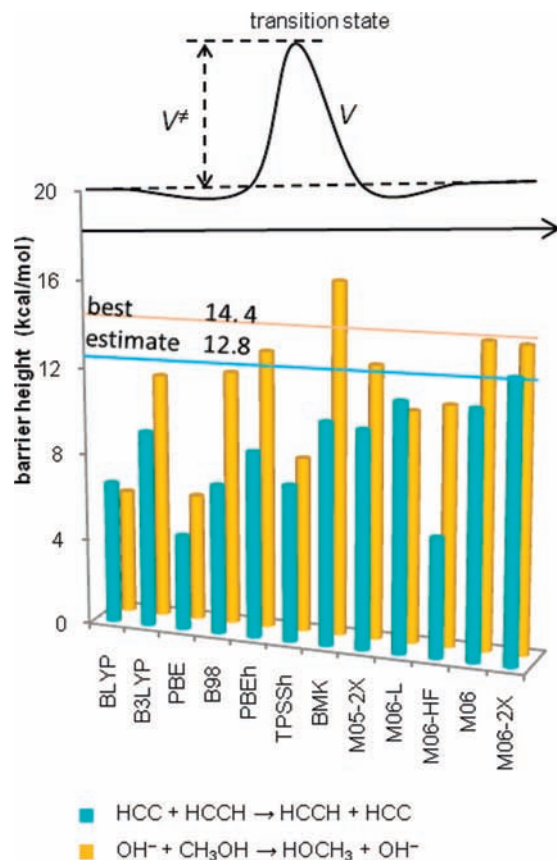
FIGURE 8. Binding energy curves for the C_6H_6–CH_4 complex with the 6-311+G(2df,2p) basis as functions of the distance between the carbon atom in CH_4 and the C_6H_6 plane. The CCSD/CBS and MP2/CBS results are from Shibasaki et al.[72]

FIGURE 9. Barrier heights. The MG3S basis set is employed with geometries optimized at each level of theory. The best estimate for HCC + HCCH is based on a W1//BMC-CCSD calculation, whereas the best estimate for OH^- + CH_3OH is from Gonzales et al.[79]

TABLE 3. Mean Unsigned Errors (eV) in Electronic Excitation Energies

functionals	valence and Rydberg[a]	charge transfer[b]	Be, Mg[c]
BLYP	1.16	5.9	0.20
B3LYP	0.66	4.4	0.17
PBE	1.12	5.9[d]	0.26
B98	0.57	4.3	0.16
PBEh	0.57	4.1	0.32
TPSSh	0.77	4.9	0.24
BMK	0.33	3.1	0.24
M05-2X	0.34	2.4	0.34
M06-L	0.95	5.4	0.24
M06-HF	0.55	0.09[e]	0.33
M06	0.95	4.1	0.14
M06-2X	0.35	2.5	0.17

[a] Forty-one valence and Rydberg transitions in N_2, CO, formaldehyde, and tetracene. [b] Three charge transfer excitations in tetracene, $NH_3 \cdots HF$, and $C_2H_4 \cdots C_2F_4$. [c] Lowest excitation energy in two main-group metal atoms. [d] Largest error in the table: 135 kcal/mol. [e] Smallest error in the table: 2 kcal/mol.

closed-shell S_N2 reaction, and M06-L again performs reasonably well. M06 and M06-2X are the best performers, followed by PBEh and M05-2X, Figure 1 provides a broader assessment of barrier height accuracy.

V.D. Electronic Spectroscopy. Although the discussion above has been solely concerned with the ground electronic state, there is increasing interest in using time-dependent DFT for electronic spectroscopy. Table 3 shows some mean errors[4] for electronic excitation energies. Both BMK and M06-2X perform quite well, provided one excludes long-range charge transfer states, which are handled well only by M06-HF.

V.E. Transition Metal Chemistry. Recently, Tsipis et al.[30] reported that some popular functionals fail to predict the trend of the phosphine binding energies between the first- and second-generation Grubbs' ruthenium precatalysts for olefin metathesis. Experiments show that the phosphine dissocia-

tion (Figure 10) in $(PCy_3)_2Cl_2Ru=CHPh$ (**1**) is faster than that in $(H_2IMes)(PCy_3)Cl_2Ru=CHPh$ (**2**),[73,74] where Cy, Ph, and IMes are cyclohexyl, phenyl, and 1,3-dimesitylimidazol-2-ylidene. Since the reverse association reaction is believed to be barrierless,[30] the relative dissociation rates are attributed to a smaller Ru–P bond dissociation energy (BDE) in **1** than in **2**.
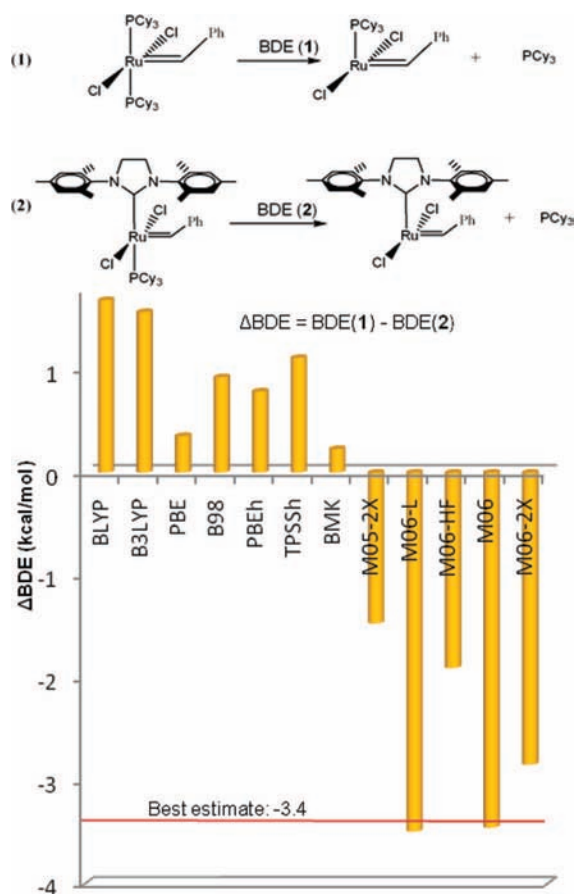
FIGURE 10. Difference of phosphine dissociation energies of precatalysts. The DZQ basis[33,34] was employed. The best estimate was inferred from experiment.[30,31,73]

As shown in Figure 10, only M05-2X and the M06 suite of functionals predict the right trend of BDE. Perhaps even more important than the quantitative results is the qualitative insight gained. Interpretations in experimental papers on ligand design for catalysts are focused essentially exclusively on coordinate covalency strength and steric effects, whereas the M06-L calculations show[31] that the trend studied here is dominated by attractive noncovalent interactions.

VI. Concluding Remarks

We have found that the newly developed M06 suite of density functionals enable computational modeling of diverse chemical phenomena more reliably than was possible previously. On the basis of tests for 496 data in 32 databases (Table 2[4]), we recommend (1) the M06-2X, BMK, and M05-2X functionals for main-group thermochemistry and kinetics; (2) M06-2X, M05-2X, and M06 for systems where main-group thermochemistry, kinetics, and noncovalent interactions are all important; (3) the M06-L and M06 functionals for transition metal thermochemistry; (4) M06 for problems involving rear-

rangements of both organic and transition metal bonds; (5) M06-2X, M05-2X, M06-HF, M06, and M06-L for the study of noncovalent interactions; (6) M06-HF when the use of full Hartree–Fock exchange is important, for example, to avoid the error of self-interaction at long range; and (7) M06-L when a local functional is required, because a local functional has much lower cost for large systems. The availability of functionals developed in our group is described on our Web site, http://comp.chem.umn.edu/info/DFT.htm.

BIOGRAPHICAL INFORMATION

Yan Zhao was born in Sichuan, China, in 1971. He received a B.A. from Fudan University in 1993, and a M.E. from Sichuan University in 1996. In 2005, he received a Ph.D. in Chemistry from the University of Minnesota, where his advisor was Donald Truhlar. He is currently an ONR project manager and research associate of the Truhlar group at the University of Minnesota.

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