

Regular article

Small basis sets for calculations of barrier heights, energies of reaction, electron affinities, geometries, and dipole moments

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Abstract. Beginning with the MIDI! basis set (also called MIDIX), we introduce the MIDIX+, MIDIY, and MIDIY+ basis sets. Using correlated ab initio and hybrid density functional theory, we compare their performance to that of several existing basis sets for electronic structure calculations. The new basis sets are tested with databases of 358 energies of reactions, 44 barrier heights, 31 electron affinities, 18 geometries, and 29 dipole moments. The MIDI!, MIDIX+, MIDIY, and MIDIY+ basis sets are shown to be cost-efficient methods for calculating relative energies, geometries, and dipole moments. The MIDIX+ basis is shown to be particularly efficient for calculating electron affinities of large molecules.

Introduction

The MIDI! basis set [1, 2, 3] (also called MIDIX [3, 4, 5]) was developed for efficient calculations of partial charges and geometries of medium-sized neutral and charged molecules. It is a split-valence basis defined for H, Li, C, N, O, F, Si, P, S, Cl, Br, and I with d polarization functions on all atoms except H, Li, and C. As compared to the popular 6-31G(d) basis [6], MIDI! has fewer primitive Gaussians to make up the core and valence functions, and it does not have d polarization functions on C or Li. These features make calculations with MIDI! less expensive than those with 6-31G(d), especially in systems with a large number of carbon atoms. In fact, although typically the basis set is equally as accurate as or more accurate than the larger 6-31G(d) [6] for geometries and partial charges, it is smaller than the 3-21G basis

extended by d functions on non-hydrogenic atoms; compared to the latter basis set, it has the same number of primitive s and p functions (except for Li, for which MIDI! has a smaller p basis) but does not have d functions on Li or C. However, unlike MIDI!, the 3-21G basis uses sp shell functions, i.e., sets of s and p functions with the same orbital exponents, and this allows extra efficiencies in programs that use sp shell methods [7] to evaluate the integrals over basis functions. The reason for using different exponents for s and p functions in MIDI! is that it allows one to start with the very well optimized and well balanced MIDI-1 basis sets of Tatewaki and coworkers [8, 9]. The high quality of MIDI-1 is one reason for the success of MIDI!, and a second reason is that the d functions were specifically optimized [1, 2, 3] to provide good geometries and charge distributions at the Hartree–Fock (HF) level. This is a very unusual procedure since essentially all other basis sets are optimized for energy.

Since the MIDI! basis sets have proven to be so successful for geometries and charge distributions, the question arises of the quality of their energetic predictions, and in the present article we address this question for energies of reaction, barrier heights, and electron affinities (EAs). For energetic calculations, it is usually advisable to go beyond HF theory in order to include dynamical correlation energy [6], and so we will test the bases extensively with hybrid density functional theory [10] (hybrid DFT, in which exchange is treated by a linear combination of HF exchange operators and density functionals) and Møller–Plesset second-order perturbation theory (MP2) [6, 11] based on explicitly antisymmetrized and correlated wave functions. We also present a few tests with HF theory [6] and quadratic configuration interaction with single and double excitations (QCISD) [12].

Since energetic calculations are often improved by inclusion of p functions on H, we will also propose and test a new basis set (MIDIY) obtained by adding p functions on H to the MIDI! basis.

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It is well known that diffuse basis functions are important to calculate accurate EAs. Recently, it has also been shown [13] that a polarized double-zeta basis with diffuse functions on heavy atoms yields more accurate reactive barrier heights, isogyric energies of reaction, and conformational energies than a polarized triple-zeta basis without diffuse functions, as confirmed by using several hybrid DFT methods. Owing to the importance of diffuse functions for the calculation of EAs, barrier heights, energies of reaction, and conformational energies, we also propose and test new basis sets (to be called MIDIX+ and MIDIY+) obtained by adding diffuse functions on all elements with nuclear charges of 3 or larger to the cost-effective MIDI! and MIDIY basis sets. All four basis sets tested (MIDI!, MIDIY, MIDIX+, and MIDIY+) retain the cost advantage of having no d functions on Li or C.

In summary, three new basis sets are introduced, and they are named MIDIX+, MIDIY, and MIDIY+. These three new basis sets, plus MIDI! itself, will sometimes be called MIDI!-type basis sets for convenience in referring to all four of them at once. There are many systems of interest that are too large to be treated with state-of-the-art thermochemical methods such as CBS-APNO [14], G3SX [15], MCG3/3 [16], and W2 [17]. Even methods such as MP2 and hybrid DFT become expensive for large enough systems. As the systems of interest become larger, we would like to know what the most efficient basis sets are to treat large systems. For many systems, especially those with a large number of carbon atoms, the MIDI!-type basis sets tested here are good candidates to be considered, not only for the calculation of geometries and charge distributions, but also for the calculation of energies.

The methods used in this paper are discussed in Sect. 2, the results are presented in Sect. 3, and the conclusions are given in Sect. 4.

Methods and test sets

All electronic structure calculations in this paper were performed with Gaussian98 [4]. All calculations use the spin-restricted formalism for closed shells [18] and the spin-unrestricted formalism [19] for open-shell systems. The previously defined basis sets used in various calculations are the MIDI! (also called MIDIX) [1, 2, 3], 3-21G^(*) [6, 20, 21, 22] (3-21G with polarization functions only on second-row atoms), 3-21+G** [6] (3-21G^(*) with a diffuse sp set [23] added to atoms of nuclear charge 3 or larger and a p function [6] added to H), 6-31G [6], 6-31G(d) [6], 6-31+G(d,p) [6], 6-311G(d,p) [6, 24, 25], MG3 [13, 26], and MG3S [13, 26]. (For atomic numbers from H to Si, the MG3S basis is identical to 6-311+G(3d2f,2df,2p), and for P, S, and Cl it is improved as discussed elsewhere [27].) For open-shell systems with nonzero spin-orbit coupling, we add a spin-orbit contribution; all spin-orbit coupling contributions [28, 29, 30, 31] added to calculations on open-shell systems are listed in Table 1.

Programs such as Gaussian98 can take advantage of sp shell functions to reduce the time to calculate two-electron integrals [7]. In the present work, we used sp shell methods for integral evalu-

Table 1. Spin-orbit contributions (kcal/mol)

Species	E_{SO}	Species	E_{SO}
C	-0.09 ^a	Br	-3.51 ^a
O	-0.23 ^a	I	-7.25 ^a
F	-0.39 ^a	CH	-0.04 ^b
Si	-0.43 ^a	OH	-0.20 ^b
S	-0.56 ^a	BrO	-1.38 ^c
Cl	-0.84 ^a	IO	-2.99 ^d

^aRef. [28]

^bRef. [29]

^cRef. [30]

^dRef. [31]

ation for all basis sets that are defined as having the same orbital exponents for s and p functions. For example, the shells for valence and diffuse functions in MG3S use sp shells, whereas the MIDI basis uses separate s and p functions. To provide further insight into computational costs, some timings were performed in which all the sp shell functions were replaced with separate s and p functions.

The hybrid DFT methods used in the present work include B3LYP [32, 33], mPW1PW91 [34], and MPW1K [35]. The ab initio methods used include MP2 [11] and QCISD [12].

The test set used for comparisons involving H, C, N, O, F, Si, P, S, and Cl includes 44 reaction barrier heights that are the forward and reverse barriers from 22 isogyric reactions in Database/3 [13], which was introduced elsewhere. We also compare to 321 Born-Oppenheimer energies of reaction (ΔE) that were calculated from the zero-point-exclusive atomization energies in Database/3. The ΔE s consist of all 321 unique isogyric hydrogen-transfer reactions that can be determined from the D_e data in Database/3, and they are listed in the Appendix. We also include the ΔE s for 15 isomerization reactions involving molecules in Database/3. These reactions are listed in Table 2. We include 22 EAs; 13 of these are the EAs in Database/3, and the remaining nine can be found in Table 3. The experimentally determined [36] EAs are adjusted by the difference in zero-point energy between the neutral and the anionic species using frequencies calculated at the mPW1PW91/MG3 level and scaled [13] by 0.9758.

We note that MIDI! is defined for H, Li, C, N, O, F, Si, P, S, Cl, Br, and I, but the previous data are limited to molecules containing H, C, N, O, F, Si, P, S, and Cl. Therefore we created an auxiliary energetic data set for Li, Br, and I compounds. These data are given in Table 4; it has 22 isogyric energies of reaction and nine EAs. Each energy of reaction (ΔE) is calculated from the difference in total zero-point-exclusive atomization energy for reactants and products. The experimental [37] heats of formation are used to

Table 2. Energies of reaction of isomerization reactions (kcal/mol)

	ΔE^a
Unstrained	
C ₄ H ₆ (2-butyne) → C ₄ H ₆ (<i>trans</i> -1,3-butadiene)	-8.2
C ₄ H ₈ (cyclobutane) → C ₄ H ₈ (isobutene)	-9.6
C ₄ H ₁₀ (isobutane) → C ₄ H ₁₀ (<i>trans</i> -butane)	1.7
C ₃ H ₄ (propyne) → C ₃ H ₄ (allene)	1.6
C ₂ H ₄ O (oxirane) → CH ₃ CHO (acetaldehyde)	26.3
CH ₃ CH ₂ OH (ethanol) → CH ₃ OCH ₃ (dimethyl ether)	12.3
CH ₃ CCOOH (acetic acid) → HCOOCH ₃	17.4
Strained	
C ₄ H ₆ (bicyclobutane) → C ₄ H ₆ (cyclobutene)	-14.4
C ₄ H ₆ (cyclobutene) → C ₄ H ₆ (2-butyne)	-2.5
C ₄ H ₆ (<i>trans</i> -1,3-butadiene) → C ₄ H ₆ (bicyclobutane)	25.2
C ₄ H ₆ (cyclobutene) → C ₄ H ₆ (<i>trans</i> -1,3-butadiene)	-10.8
C ₄ H ₆ (2-butyne) → C ₄ H ₆ (bicyclobutane)	16.9
C ₃ H ₄ (cyclopropene) → C ₃ H ₄ (propyne)	-22.1
C ₃ H ₄ (allene) → C ₃ H ₄ (cyclopropene)	20.5
C ₃ H ₆ (propene) → C ₃ H ₆ (cyclopropane)	7.2

^aExcluding vibrational contributions

Table 3. Electron affinities (*EAs*) (kcal/mol)

	Exp ^a	Δ ZPE	EA ^b
C	29.11	0.00	29.11
O	33.69	0.00	33.69
F	78.44	0.00	78.44
Si	32.04	0.00	32.04
P	17.21	0.00	17.21
S	47.90	0.00	47.90
Cl	83.31	0.00	83.31
NH	8.53	-0.13	8.40
NH ₂	17.78	-0.26	17.52
OH	42.15	0.06	42.21
CN	89.06	-0.04	89.02
PH	23.71	-0.15	23.56
O ₂	10.40	-0.65	9.75
PH ₂	29.31	-0.33	29.98
SH	53.43	-0.05	53.38
PO	25.18	-0.30	24.88
SO	25.94	-0.37	25.57
PO ₂	78.87	-0.12	78.75
S ₂	38.51	-0.21	38.31
SO ₂	25.53	-0.76	24.77
Cl ₂	54.88	-0.48	54.40
C ₆ H ₅	25.27	-1.40	23.87

^aRef. [36]^bExcluding vibrational contributions**Table 4.** Accurate energies of reaction and adiabatic EAs (kcal/mol) for systems containing bromine and iodine

	ΔE
LiO + H ₂ → LiOH + H	-24.7
Li + HF → LiF + H	4.4
Li + HCl → LiCl + H	-4.7
LiO + HCl → LiOH + Cl	-25.4
Li ₂ + O ₂ → 2LiO	-7.1
LiC ₂ H ₅ + HCl → C ₂ H ₅ Cl + LiH	1.9
Li ⁻ → Li + e ⁻	11.6
LiH ⁻ → LiH + e ⁻	10.0
LiCl ⁻ → LiCl + e ⁻	15.7
HBr + H → H ₂ + Br	-19.1
CH ₃ Br + H → CH ₄ + Br	-40.0
CH ₃ Br + F → CH ₃ F + Br	-41.2
CH ₃ Br + Cl → CH ₃ Cl + Br	-14.4
C ₂ H ₅ Br + CH ₄ → C ₂ H ₆ + Br	3.5
C ₂ H ₅ Br + CH ₃ Cl → C ₂ H ₅ Cl + CH ₃ Br	0.2
CH ₃ COBr + CH ₄ → CH ₃ Br + CH ₃ COH	16.2
CH ₃ COBr + CH ₃ Cl → CH ₃ Br + CH ₃ COCl	-1.3
Br + e ⁻ → Br ⁻	77.6
HCBBr + e ⁻ → HCBBr ⁻	32.2
BrO + e ⁻ → BrO ⁻	54.0
HI + H → H ₂ + I	-35.8
CH ₃ I + H → CH ₄ + I	-53.2
CH ₃ I + F → CH ₃ F + I	-54.4
CH ₃ I + Cl → CH ₃ Cl + I	-27.6
C ₂ H ₅ I + CH ₄ → C ₂ H ₆ + CH ₃ I	1.7
C ₂ H ₅ I + CH ₃ Cl → C ₂ H ₅ Cl + CH ₃ I	-1.6
CH ₃ COI + CH ₄ → CH ₃ I + CH ₃ COH	11.0
CH ₃ COI + CH ₃ Cl → CH ₃ I + CH ₃ COCl	-6.5
I ⁻ → I + e ⁻	70.5
HCl ⁻ → HCl + e ⁻	35.8
IO ⁻ → IO + e ⁻	54.7

calculate the total atomization energy by using thermal and zero-point-energy contributions calculated using MP2/6-311G(d,p) frequencies scaled [38] by 0.95 and following the method described

earlier [39]. The adiabatic EAs from experiment [36] were adjusted to remove the effects of zero-point energy using MP2/6-311(d,p) frequencies scaled by 0.95.

All energies (discussed in later sections) calculated for comparison with the data in Tables 2, 3, 4 and in the Appendix were computed at geometries optimized by QCISD/MG3.

One question that arises is whether the additional basis functions in the MIDIX+, MIDYI, and MIDY+ basis sets allow one to retain good accuracy for geometries and charge distributions. We first checked this on a small set of 18 molecules in Table 5, called the geometry-dipole test set, by comparing mPW1PW91 geometries and dipole moments with MIDI!-type basis sets to those from mPW1PW91/MG3S calculations and from experiment [40, 41, 42]. Additional checks on dipole moments of Li-containing compounds are presented in Table 6, which will be discussed in Sect. 3.2.

As explained in the Introduction, all three of the new basis sets are modifications of the MIDI! basis set (also called MIDIX). MIDIX+ is defined as the MIDI! basis with a diffuse sp set of functions added to all atoms except hydrogen and lithium; separate s and p functions are used for lithium and no diffuse functions are added to hydrogen. In the MIDI! basis, the smallest-exponent p functions are tighter (larger exponent) than the smallest-exponent s functions for all atoms except silicon and phosphorus, where they are equal, and smaller, respectively. The exponent used for the diffuse sp set in MIDIX+ and MIDYI+ is one fourth of the exponent of the most diffuse p function for each atom in MIDI! with the exceptions of phosphorus and lithium. For phosphorus the diffuse sp exponent is set to one fourth the exponent of the most diffuse s function. Lithium is often treated as a special case [3, 8, 9] in the first row. Polarized basis sets for Li do not always include d functions [3], and nonpolarized basis sets do not always include p functions [8, 9]. The MIDI! basis defines Li as having a single p function. For MIDIX+ and MIDYI+, it was decided to add a more diffuse p function as well as a more diffuse s function. The exponent for the diffuse s function was set to be a factor of 4 smaller than the most diffuse valence s function in MIDI!. The diffuse p function is set to the same exponent as the most diffuse valence s function in MIDI!. A result of the manner in which the

Table 5. Test set of molecules for which geometries and dipole moments were calculated

Molecule	Bond distances	Bond angles	Source of accurate data
H ₂ O	1	1	Ref. [41]
H ₃ COH	4	3	mPW1PW91/MG3S ^b
H ₃ CC(O)NH ₂	7	6	mPW1PW91/MG3S ^b
H ₃ CNH ₃ ⁺	3	2	mPW1PW91/MG3S ^b
H ₃ CCO ₂ ⁻	5	3	mPW1PW91/MG3S ^b
CH ₃ SiH ₃	3	2	Ref. [41]
HPO	2	1	mPW1PW91/MG3S ^b
H ₂ PO ₄ ⁻	3	5	mPW1PW91/MG3S ^b
H ₃ CSH	4	3	Ref. [41]
HC(S)NH ₂	5	4	Ref. [41]
CH ₃ F	2	1	Ref. [41]
CHFCHCl	5	4	mPW1PW91/MG3S ^b
CH ₂ Cl ₂	2	2	mPW1PW91/MG3S ^b
LiC ₂ H ₃	4	4	mPW1PW91/MG3S ^b
LiOH	2	0 ^a	mPW1PW91/MG3S ^b
CH ₃ Br	2	1	Ref. [40]
CH ₃ I	2	1	Ref. [40]
Pyridine	6	6	mPW1PW91/MG3S ^b
Total	62	50	

^aThe LiOH bond angle was not included because it is very sensitive to basis set and level of theory and is not representative of the bond angles of interest

^bOptimized structure

Table 6. Comparison of mPW1PW91 dipole moments (debye) for lithium compounds

Molecule	Accurate ^a	3-21G ^(*)	6-31G(d)	MIDI!	MIDIX+	MIDIY	MIDIY+
LiCH ₃	5.68	4.88	5.18	4.96	5.69	5.03	5.75
LiC ₂ H ₃	5.95	5.49	5.56	5.84	6.08	5.86	6.10
LiC ₃ H ₅	3.77	3.55	3.42	4.44	4.28	4.43	4.28
LiNH ₂	4.86	3.19	4.09	5.54	5.18	5.53	5.22
LiO	6.84 ^c	5.49	6.20	6.20	7.17	6.20	7.17
LiOH	4.75 ^d	2.73	3.82	5.82	4.82	5.79	4.84
LiOCH ₃	5.26	3.83	4.89	5.44	5.29	5.44	5.34
LiS	7.06	7.07	7.07	7.32	7.80	7.32	7.80
LiSH	6.96	7.01	7.00	7.30	7.63	7.31	7.61
LiF	6.33 ^e	5.08	5.73	5.94	6.75	5.94	6.75
LiCl	7.13 ^f	7.28	7.23	7.60	7.93	7.59	7.92
Mean unsigned error		0.90	0.48	0.55	0.42	0.54	0.43
Energy cost (LiC ₂ H ₃)		2.63	3.91	2.31	3.25	2.69	3.80

^a For all calculations in this table, the geometry was optimized by mPW1PW91 with the same basis set used to calculate the dipole moment.

^b Calculated with mPW1PW91/MG3S except where indicated otherwise

^c Ref. [44]

^d Ref. [45]

^e Ref. [46]

^f Ref. [47]

diffuse sp functions are chosen, the spacing between neighboring s and p functions (in a list arranged in numerical order) is a factor of 4 or less for all atoms except Li.

The MIDIY basis is defined to be the same as the MIDIX basis but with a set of p functions added to hydrogen. The exponent used for the set of p functions is 1.100 (which is a popular standard value [6]). The MIDIY+ basis is defined as the MIDIX+ plus the same set of p functions on hydrogen. The exponents for the most diffuse s and p functions in the MIDI!-type basis sets are listed in Table 7. Complete details of the MIDI!-type basis sets are available in electronic form at <http://comp.chem.umn.edu/basissets>.

The MIDI!-type basis sets use sets of five d functions (spherical harmonic sets) for polarization of the atoms C–I. Some electronic structure programs cannot use spherical harmonic d functions, and so we will test the performance of the MIDI!-type basis sets using six d functions (Cartesian sets) as well. MIDI! with Cartesian d functions is called MIDI!6D or MIDIX6D, and the three new basis sets with Cartesian d sets will be called MIDIY6D, MIDIX+6D, and MIDIY+6D.

We compare costs of various methods using a standard cost function in Sect. 3. The cost function used in all tables and figures except Table 6 is the sum of the computer time to calculate an energy, gradient, or Hessian (as stated in each case) for the three molecules 1-phosphinopropane, *trans*-1,3-butadiene, and 2,2-dichloro-1-ethanol with a single 500 MHz R14000 processor on a Silicon Graphics Origin 3800 with the Gaussian98 [4] electronic structure package. In Tables 8 and 9, the times are normalized by dividing by the time for a MP2/6-31G(d) energy calculation on the same molecules on the same computer. Table 6 gives the costs for a single mPW1PW91 energy calculation on LiC₂H₃ normalized by the cost for an MP2/6-31G(d) energy calculation on the same

Table 7. Exponents of the outer s and p functions in MIDI!, MIDIX+, MIDIY, and MIDIY+ basis sets

	Valence s	Valence p	Diffuse s ^a	Diffuse p ^a
H	0.151398	1.100000 ^b		
Li	0.027350	0.027350 ^a	0.00683750	
C	0.147070	0.201350	0.05033750	0.05033750
N	0.210090	0.291450	0.07286250	0.07286250
O	0.278800	0.372510	0.09312750	0.09312750
F	0.358110	0.479370	0.11984250	0.11984250
Si	0.093339	0.093339	0.02333475	0.02333475
P	0.108854	0.086447	0.02721350	0.02721350
S	0.138786	0.318130	0.07953250	0.07953250
Cl	0.169958	0.396004	0.09900100	0.09900100
Br	0.164764	0.164764	0.04119100	0.04119100
I	0.115076	0.115076	0.02876900	0.02876900

^a These functions are only in the MIDIX+ and MIDIY+ basis sets

^b This function is only in the MIDIY and MIDIY+ basis sets

molecule. The number of basis functions and the number of primitive Gaussians that are in the MIDI!-type and two other basis sets for the four molecules that are used for timings in this paper are listed in Table 10.

Results

H, C–Cl

Of the 15 isomerization reactions in the ΔE database, eight reactions are treated poorly by the MIDI! family of basis sets. Because of this, we separated them from the other 328 ΔE s. These eight isomerization reactions all involve three-member or four-member rings (cyclopropane, cyclopropene, cyclobutene, bicyclobutane), which are highly strained and they have an average error of over 20 kcal/mol at the QCISD/MIDIY+ level. The suspected causes for the high error are an inadequate description of the wavefunction in the inner region of the valence space and the lack of d functions on carbon to treat the small bond angles. The MIDI!-type basis sets have only two primitive s Gaussians and two primitive p Gaussians for the tighter regions of the s and p valence spaces. To test the effect that this has on strained rings, we created an intermediate basis set where we modified the MIDIY+ basis for carbon by removing the contracted inner valence s and p functions and replacing them with the 3-Gaussian contracted sp set from the 6-31G basis. This has the net effect of removing four basis functions made from eight primitive Gaussians, and replacing them with four basis functions made from 12 primitive Gaussians. We label this modified MIDIY+ basis as 3-31+G. It can be seen in Table 11 that our simple modification has greatly reduced the error using QCISD for the eight strained isomerization reactions, confirming our suspicion of the cause for almost half of the error. The second cause of error is the lack of d functions on carbon, and this can be confirmed by comparing the error at the QCISD/6-31G level to the error with QCISD/6-31G(d). The addition of d functions reduces the error by 12 kcal/mol.

In the last three columns of Table 11 the error in the ΔE s for hydrogen-abstraction reactions is divided into the following three categories: reactions where the

Table 8. Costs and errors (kcal/mol) for 328 unstrained energies of reaction and 44 reactive barrier heights at QCISD/MG3 optimized geometries

	ΔE			Cost		
	Mean unsigned error	Mean signed error	Mean unsigned error	<i>E</i>	<i>G</i>	<i>H</i>
MPW1K/MIDI!	6.16	-3.97	4.55	1.6	2.2	19
MPW1K/MIDIY	4.72	-3.54	3.95	2.0	3.0	29
MPW1K/MIDIX+	4.81	-2.15	2.59	2.6	3.6	33
MPW1K/MIDIY+	3.51	-1.49	1.91	3.3	4.5	50
MPW1K/6-31G(d)	4.56	-0.71	2.48	2.3	3.3	33
MPW1K/6-31G(d,p)	3.39	-1.40	1.91	2.9	4.5	49
MPW1K/6-31+G(d)	3.82	-0.31	2.04	4.1	5.5	52
MPW1K/6-31+G(d,p)	2.64	-0.95	1.43	5.6	7.7	76
MPW1K/MG3S	2.40	-0.73	1.38	57	77	400
mPW1PW91/MIDI!	5.52	-6.98	6.98	1.6	2.2	19
mPW1PW91/MIDIY	4.12	-6.63	6.63	2.0	3.0	29
mPW1PW91/MIDIX+	3.95	-5.00	5.00	2.6	3.6	33
mPW1PW91/MIDIY+	2.80	-4.42	4.42	3.3	4.5	50
mPW1PW91/6-31G(d)	3.77	-3.68	3.68	2.3	3.3	33
mPW1PW91/6-31G(d,p)	2.75	-4.37	4.37	2.9	4.5	49
mPW1PW91/6-31+G(d)	3.00	-3.17	3.17	4.1	5.5	52
mPW1PW91/6-31+G(d,p)	2.07	-3.83	3.83	5.6	7.7	76
mPW1PW91/MG3S	2.11	-3.55	3.56	57	77	400
B3LYP/MG3S	2.50	-4.17	4.25	57	77	400
HF/6-31+G(d,p)	7.13	12.90	13.24	1.1	2.4	15
MP2/MIDI!	7.77	4.47	4.86	0.56	1.3	15
MP2/MIDIY	7.12	4.21	4.42	0.88	2.2	32
MP2/MIDIX+	6.37	5.35	5.35	0.93	2.2	31
MP2/MIDIY+	6.18	5.34	5.34	1.5	4.0	73
MP2/6-31G(d)	7.39	6.78	6.84	1.0 ^a	2.6	36
MP2/6-31G(d,p)	6.62	5.44	5.61	1.5	4.7	77
MP2/6-31+G(d)	6.81	6.89	7.01	1.5	4.4	77
MP2/6-31+G(d,p)	6.16	5.59	5.81	2.4	7.2	150
MP2/MG3S	5.87	4.01	4.39	77	140	3,000

^a Basis for cost comparisons in this table

reactants and products have only single bonds, reactions where a reactant or product has a double bond but no triple bonds, and finally, reactions that involve at least one triple bond. The reactions with triple bonds involve CO, C₂H, or CN. The hybrid DFT methods have an error 1.1–2.4 times larger (median factor of 1.6) for these reactions compared to the reactions involving only single and double bonds. At the MP2 level, reactions involving double bonds have around twice the error of reactions with only single bonds and reactions involving triple bonds have 4–8 times the error of reactions with only single bonds. At the MP2 level, this can be explained by spin contamination. The $\langle S^2 \rangle$ values (where S is the operator for total electron spin) obtained using the MG3S basis for the C₂H and CN radicals are 1.13 and 1.14, respectively, and are much larger than the accurate value of 0.75. It has been previously observed [43] that calculations using MP2 perform poorly for treating radicals, especially when there is significant spin contamination. Similarly to what was found in previous studies [43], we see that QCISD treats these spin-contaminated systems very well. Unlike the hybrid DFT and MP2 results, QCISD usually predicts energies of reaction more accurately when triple bonds are involved than when only lower bond orders are involved.

The error over 328 ΔE s (321 hydrogen abstraction and seven nonstrained isomerizations) and the cost of an energy, gradient, and Hessian calculation are given in Table 8. The results at the B3LYP/MG3S level are listed

for comparison; however, B3LYP is outperformed by both the mPW1PW91 and MPW1K methods with the same basis set. We draw several key conclusions from Table 8. First consider the energies of reaction. Hybrid DFT is much more accurate than HF or MP2 for energies of reaction. Within the hybrid DFT methods, adding p functions on H or diffuse sp shells on C to Cl improves the accuracy considerably, and adding both gives even greater improvement. The MIDIY+ basis is similar in accuracy to 6-31G(d,p) but at slightly higher cost if sp shell integral packages are available. Next consider the barrier heights. We see that HF and MP2 systematically overestimate barrier heights (positive mean signed error), whereas hybrid DFT systematically underestimates barrier heights. The mean unsigned error in barrier heights are, however, much lower for hybrid DFT than for HF or MP2. As expected from previous work, MPW1K is particularly accurate for barrier heights, especially with the MIDIY+, 6-31G(d,p), and 6-31+G(d,p) basis sets.

Table 9 contains the central results of this whole study; it gives the mean unsigned error over ΔE s, reactive barrier heights, and EAs. For energies of reaction and barrier heights, the MIDIY+ basis sets have similar performance and cost as 6-31G(d,p) and a better performance for a given cost than 6-31+G(d). Compared to 6-31+G(d) and 6-31+G(d,p), the new MIDIX+ and MIDIY+ basis sets are more cost efficient for predicting EAs. The 6-31+G(d) and 6-31+G(d,p) basis sets

Table 9. Costs and errors (kcal/mol) for 328 unstrained energies of reaction, 44 reactive barrier heights, and 22 EAs based on QCISD/MG3 optimized geometries

	Mean unsigned error			Cost of energy calculation	
	ΔE	ΔE^\ddagger	EA	Hybrid sp	No hybrid
MPW1K/MIDI!	6.16	4.55	28.71	1.6	1.6
MPW1K/MIDIY	4.72	3.95	28.71	2.0	2.0
MPW1K/MIDIX+	4.81	2.59	5.79	2.6	2.7
MPW1K/MIDIY+	3.51	1.91	5.72	3.3	3.4
MPW1K/6-31G(d)	4.56	2.48	19.06	2.3	2.4
MPW1K/6-31G(d,p)	3.39	1.91	19.02	2.9	3.1
MPW1K/6-31+G(d)	3.82	2.04	5.87	4.1	4.3
MPW1K/6-31+G(d,p)	2.64	1.43	5.73	5.6	6.3
mPW1PW91/MIDI!	5.52	6.98	29.66	1.6	1.6
mPW1PW91/MIDIY	4.12	6.63	29.59	2.0	2.0
mPW1PW91/MIDIX+	3.95	5.00	4.12	2.6	2.7
mPW1PW91/MIDIY+	2.80	4.42	3.87	3.3	3.4
mPW1PW91/6-31G(d)	3.77	3.68	19.51	2.3	2.4
mPW1PW91/6-31G(d,p)	2.75	4.37	19.40	2.9	3.1
mPW1PW91/6-31+G(d)	3.00	3.17	3.92	4.1	4.3
mPW1PW91/6-31+G(d,p)	2.07	3.83	3.72	5.6	6.3
HF/MIDI!	10.50	11.10	50.28	0.42	0.42
HF/MIDIY	9.22	11.26	50.24	0.54	0.54
HF/MIDIX+	9.22	12.09	25.74	0.70	0.73
HF/MIDIY+	7.89	12.84	25.70	0.74	0.78
HF/6-31G(d)	8.84	13.37	38.07	0.58	0.63
HF/6-31G(d,p)	7.66	12.98	38.07	0.90	0.99
HF/6-31+G(d)	8.19	13.59	25.80	0.78	0.86
HF/6-31+G(d,p)	6.95	13.24	25.73	1.1	1.3
MP2/MIDI!	7.77	4.86	46.46	0.56	0.56
MP2/MIDIY	7.12	4.42	46.32	0.88	0.88
MP2/MIDIX+	6.37	5.35	16.09	0.89	0.92
MP2/MIDIY+	6.18	5.34	15.98	1.5	1.6
MP2/6-31G(d)	7.39	6.84	33.77	1.0 ^a	1.1
MP2/6-31G(d,p)	6.62	5.61	33.63	1.5	1.7
MP2/6-31+G(d)	6.81	7.01	17.30	1.5	1.7
MP2/6-31+G(d,p)	6.16	5.81	17.12	2.4	2.8

^a Basis for cost comparisons

have around 7% less error than the MIDIX+ and MIDIY+ using the mPW1PW91 hybrid DFT functional but cost 58–70% more when sp shell integral packages are available and 59–85% more when they are not. At the MP2 and MPW1K levels of theory, the smaller MIDIX+ and MIDIY+ bases outperform the larger 6-31+G(d) and 6-31+G(d,p) basis sets in both cost and performance. In general, HF calculations are very inexpensive but have unacceptable accuracy for energy calculations.

Li, Br, and I

The dipole moments of 11 Li compounds calculated at the mPW1PW91 level of theory are listed and compared

to values calculated with a large basis set or other accurate values in Table 6. The new MIDI!-type basis sets have lower mean unsigned errors than the original MIDI! basis for calculating dipole moments. The addition of p functions on H atoms has very little effect; however, the diffuse functions reduce the error by about 20–25%.

A similar test for energetic quantities is provided by Table 12. We see that the MIDIX+ and MIDIY+ basis sets perform much better than MIDIX and MIDIY. They also have less than half the error of the larger 3-21+G** basis.

The energies of reaction and EAs of reaction for compounds containing bromine and iodine are listed in Table 13. Unlike lithium or the H, C, N, O, F, Si, P, S, and Cl data, the energies of reaction for bromine and

Table 10. Number of basis functions in typical molecules

	MIDI!		MIDIX+		MIDIY		MIDIY+		6-31G(d)		6-31+G(d,p)	
	N_{prim}	N_{con}	N_{prim}	N_{con}	N_{prim}	N_{con}	N_{prim}	N_{con}	N_{prim}	N_{con}	N_{prim}	N_{con}
PH ₂ CH ₂ CH ₂ CH ₃	104	63	120	79	131	90	147	106	172	82	215	125
C ₅ H ₈	99	61	119	81	123	85	143	105	172	91	216	135
Cl ₂ C ₂ H ₃ OH	126	76	146	96	138	88	158	108	204	91	236	123
LiC ₂ H ₃	48	30	60	42	57	39	69	51	96	51	117	72
Total	377	230	445	298	449	302	517	370	644	315	784	455

Table 11. Errors (kcal/mol) of ΔE values of strained cyclic isomerizations and hydrogen-abstraction reactions (QCISD/MG3 geometries)

	ΔE strained cycles (8)	Hydrogen abstractions		
		X^- (157)	$X =$ (106)	$X \equiv$ (58)
MPW1K/MIDI!	10.24	6.64	4.96	7.39
MPW1K/MIDIY	10.65	4.81	3.58	6.75
MPW1K/MIDIX+	11.01	4.22	4.51	7.23
MPW1K/MIDIY+	11.34	2.24	3.69	6.73
MPW1K/6-31G(d)	4.86	4.20	4.58	5.66
MPW1K/6-31G(d,p)	5.06	2.85	3.34	5.09
MPW1K/6-31+G(d)	4.06	3.20	3.88	5.52
MPW1K/6-31+G(d,p)	4.21	1.82	2.65	4.94
MPW1K/MG3S	2.82	1.89	1.95	4.72
mPW1PW91/MIDI!	10.36	5.95	4.47	5.95
mPW1PW91/MIDIY	10.77	4.40	3.11	5.33
mPW1PW91/MIDIX+	11.18	3.39	3.70	6.08
mPW1PW91/MIDIY+	10.51	1.86	2.77	5.45
mPW1PW91/6-31G(d)	3.77	3.55	3.83	4.32
mPW1PW91/6-31G(d,p)	3.91	2.42	2.69	3.81
mPW1PW91/6-31+G(d)	3.13	2.53	3.07	4.17
mPW1PW91/6-31+G(d,p)	3.25	1.57	1.97	3.66
mPW1PW91/MG3S	1.98	1.85	1.71	3.62
B3LYP/MG3S	4.00	2.28	2.06	3.96
MP2/MIDI!	18.66	4.77	6.96	17.59
MP2/MIDIY	19.00	3.98	6.50	16.82
MP2/MIDIX+	19.38	2.93	6.01	16.54
MP2/MIDIY+	19.58	2.94	5.83	15.72
MP2/6-31G(d)	2.10	3.37	7.55	18.54
MP2/6-31G(d,p)	2.16	2.87	6.68	17.20
MP2/6-31+G(d)	1.62	3.08	6.67	17.76
MP2/6-31+G(d,p)	1.62	2.83	5.82	16.44
MP2/MG3S	1.65	2.21	5.28	17.41
QCISD/MIDIY+	20.67	3.00	3.76	2.51
QCISD/3-31+G	11.65	2.90	3.94	2.53
QCISD/6-31G	13.33	8.50	8.62	6.27
QCISD/6-31G(d)	0.91	4.56	4.82	4.01
QCISD/6-31+G(d)	1.16	3.46	3.93	3.45
QCISD/6-31+G(d,p)	1.00	2.80	2.93	2.58
QCISD/6-311G(d,p)	1.13	3.26	2.46	2.61
QCISD/MG3S	1.91	1.65	1.65	2.36

iodine compounds show little improvement when diffuse functions are added. This is mostly because MIDI! already gives very accurate results. The EAs do, however, improve by a factor of about 9–10 when the diffuse functions are added.

Geometries and charge distributions

The mean unsigned errors in bond distances, bond angles, and dipole moments for the geometry-dipole set

are in Table 14, which (along with Table 9) is one of the two central tables of this study. In computing the mean unsigned errors, only unique (i.e., non-symmetry-identical) values were included. Thus H_3COH has four unique bond lengths and three unique bond angles (see Table 5). We see that the geometries calculated at the HF level remain relatively unchanged when diffuse functions are added to first-row atoms, or when polarization functions are added to hydrogen. The geometries calculated with mPW1PW91 improve significantly when diffuse functions are added. Furthermore we see that HF

Table 12. mPW1PW91 energies of reaction and EAs (kcal/mol) for lithium compounds

Basis functions on Li	MIDI!	MIDIY	MIDIX+	MIDIY+	3-21+G**	6-31+G(d,p)
	6	6	10	10	13	19
$\text{LiO} + \text{H}_2 \rightarrow \text{LiOH} + \text{H}$	-20.7	-25.0	-21.8	-27.0	-26.4	-23.6
$\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$	30.8	37.2	-3.9	2.4	3.5	6.7
$\text{Li} + \text{HCl} \rightarrow \text{LiCl} + \text{H}$	5.5	9.9	-6.5	-2.8	-2.3	-3.3
$\text{LiO} + \text{HCl} \rightarrow \text{LiOH} + \text{Cl}$	-22.4	-23.8	-26.1	-29.0	-28.7	-27.4
$\text{Li}_2 + \text{O}_2 \rightarrow 2\text{LiO}$	81.9	81.9	-10.4	-10.4	-38.6	-3.6
$\text{LiC}_2\text{H}_5 + \text{HCl} \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{LiH}$	-1.4	2.0	0.8	4.1	5.5	1.2
$\text{Li}^- \rightarrow \text{Li} + e^-$	8.2	8.2	11.8	11.8	11.9	10.9
$\text{LiH}^- \rightarrow \text{LiH} + e^-$	-13.3	-13.5	9.0	8.8	9.7	9.7
$\text{LiCl}^- \rightarrow \text{LiCl} + e^-$	-0.5	-0.5	17.4	17.4	18.3	17.1
Meanunsigned error(ΔE & EA)	19.8	20.2	2.3	2.0	5.2	1.5

Table 13. Energies of reaction, EAs, and mean unsigned errors for bromine and iodine

	MIDI!	MIDIY	MIDIX+	MIDIY+
HBr + H → H ₂ + Br	-14.6	-12.6	-14.8	-12.6
CH ₃ Br + H → CH ₄ + Br	-32.9	-34.9	-33.4	-35.3
CH ₃ Br + F → CH ₃ F + Br	-32.7	-34.2	-33.9	-34.7
CH ₃ Br + Cl → CH ₃ Cl + Br	-12.1	-12.6	-9.3	-9.3
C ₂ H ₅ Br + CH ₄ → C ₂ H ₆ + CH ₃ Br	3.6	3.6	4.2	4.2
C ₂ H ₅ Br + CH ₃ Cl → C ₂ H ₅ Cl + CH ₃ Br	-0.3	-0.1	0.0	0.1
CH ₃ COBr + CH ₄ → CH ₃ Br + CH ₃ COH	18.2	17.5	15.5	14.7
CH ₃ COBr + CH ₃ Cl → CH ₃ Br + CH ₃ COCl	-0.9	-0.4	-0.9	-0.9
HI + H → H ₂ + I	-27.6	-25.4	-27.8	-25.5
CH ₃ I + H → CH ₄ + I	-42.8	-44.9	-42.8	-44.9
CH ₃ I + F → CH ₃ F + I	-42.6	-44.2	-43.3	-44.2
CH ₃ I + Cl → CH ₃ Cl + I	-22.0	-22.6	-18.8	-18.8
C ₂ H ₅ I + CH ₄ → C ₂ H ₆ + CH ₃ I	2.7	2.8	3.4	3.5
C ₂ H ₅ I + CH ₃ Cl → C ₂ H ₅ Cl + CH ₃ I	-1.2	-0.9	-0.8	-0.6
CH ₃ COI + CH ₄ → CH ₃ I + CH ₃ COH	17.7	14.0	12.7	12.0
CH ₃ COI + CH ₃ Cl → CH ₃ I + CH ₃ COCl	-4.4	-3.8	-3.7	-3.6
Mean unsigned error (ΔE) ^a	1.9	1.8	1.9	1.8
Br ⁻ → Br + e ⁻	57.5	57.5	81.1	81.1
HCB ⁻ → HCB + e ⁻	19.7	20.1	35.8	36.2
BrO ⁻ → BrO + e ⁻	13.3	13.3	52.4	52.4
I ⁻ → I + e ⁻	64.8	64.8	76.5	76.5
HCl ⁻ → HCl + e ⁻	27.1	27.5	38.1	38.6
IO ⁻ → IO + e ⁻	16.0	16.0	53.6	53.6
Mean unsigned error (EA) ^a	23.6	23.5	2.4	2.5

^a Spin-orbit coupling contributions are added to all values listed before comparing to experiment

is more accurate than hybrid DFT for geometries when MIDI!-type basis sets are used. This striking result may be a consequence of the fact that the MIDI! basis was optimized for geometries and charge distributions at the HF level.

MIDI!6D basis sets

The ΔE and EA values and dipole moments obtained with the MIDI!-type basis sets using spherical (5D) and Cartesian (6D) functions are compared in Table 15. Up to this point, all calculations have been performed with 5D basis sets. As can be seen in Table 15, there is very

Table 14. Mean unsigned errors (angstroms, degrees, and debyes) in bond lengths, R , bond angles, θ , and dipole moments, μ , with Hartree-Fock(HF) and mPW1PW91

	Data set	HF			mPW1PW91		
		R	θ	μ	R	θ	μ
MIDI!	Full	0.012	0.9	0.36	0.016	1.2	0.38
MIDIY	Full	0.011	0.8	0.34	0.014	1.0	0.37
MIDIX+	Full	0.011	0.6	0.39	0.017	0.7	0.21
MIDIY+	Full	0.011	0.6	0.40	0.015	0.6	0.20
MIDI!	ExI ^a	0.011	0.9	0.37	0.016	1.2	0.40
MIDIY	ExI ^a	0.010	0.8	0.35	0.014	1.0	0.39
MIDIX+	ExI ^a	0.011	0.6	0.39	0.017	0.7	0.22
MIDIY+	ExI ^a	0.010	0.6	0.40	0.015	0.6	0.21
6-31G(d)	ExI ^a	0.008	0.5	0.22	0.006	0.5	0.24
6-31G(d,p)	ExI ^a	0.008	0.5	0.22	0.005	0.6	0.24
6-31+G(d)	ExI ^a	0.008	0.5	0.36	0.007	0.4	0.16
6-31+G(d,p)	ExI ^a	0.008	0.5	0.36	0.006	0.3	0.15

^a This set does not include CH₃I because I is not defined for 6-31+G(d,p)

little difference between the 5D and 6D forms of the MIDI!-type basis sets. A noticeable trend is that the MIDIX+6D and MIDIY+6D basis sets exhibit a slightly higher error in all three categories in Table 15.

Conclusions

We have introduced the MIDIY, MIDIY+, and MIDIX+ basis sets, which, along with MIDI! itself, give one a choice of four MIDI!-type basis sets. These basis sets have been shown to predict reasonably accurate energies of reaction, barrier heights, and EAs at a reasonable cost.

All of the MIDI!-type basis sets perform poorly for highly strained cyclic compounds involving carbon owing to the small number of primitive Gaussian functions that make up the tighter portion of the valence space and the lack of d functions on carbon. This limitation resulting from using a small number of basis functions is more

Table 15. Mean unsigned error in energies of reaction (kcal/mol), EAs (kcal/mol) and dipoles (debye) for the MIDI!-type and the MIDI!6D-type basis sets using mPW1PW91

	ΔE (328)	EA (22)	Dipole moments (18)
MIDI!	5.52	29.66	0.38
MIDIY	4.12	29.59	0.37
MIDIX+	3.95	4.12	0.21
MIDIY+	2.80	3.87	0.20
MIDI!6D	5.56	29.13	0.38
MIDIY6D	4.43	29.05	0.37
MIDIX+6D	4.11	4.15	0.23
MIDIY+6D	3.10	4.07	0.22

substantial in explicitly correlated methods (MP2 and QCISD) than in the hybrid DFT methods tested. The core and inner valence space are also the probable cause for the slightly larger error in bond distances using the MIDI!-type basis sets compared to the 6-31G-type basis sets.

For both the MIDI and the 6-31G(d) basis sets, the addition of p functions on hydrogen, diffuse functions on heavy atoms, or both yields large improvements in the accuracy in all hybrid DFT and ab initio methods. The error in ΔE s and barrier heights does not decrease much when going to basis sets larger than 6-31+G(d,p) when using the mPW1PW91, MPW1K, and MP2 levels of theory. Hybrid DFT calculations with 6-31+G(d,p) have a mean unsigned error for predicting the 328 ΔE s within 2% of that for the much more expensive, heavily polarized triple-zeta basis MG3S. The more efficient MIDIY+ and MIDIX+ basis sets have mean unsigned errors that are larger than mPW1PW91/MG3S by 33 and 87% respectively, but they are less expensive than 6-31+G(d,p) by factors of 1.7 and 2.1, respectively.

The MIDIX+ basis set is highly recommended for calculating EAs of large molecules. It performs similarly to, or better than, the more expensive 6-31+G(d) basis set.

All MIDI!-type basis sets are available in electronic form at <http://comp.chem.umn.edu/basissets>.

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Appendix

The isogyric reaction data set is given in Table 16.

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