

Functional Group Basis Sets

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Abstract: The electronic properties of molecular functional groups (methyl, benzyl, etc.) are generally conserved across different molecules. However, atomic basis sets use the same electronic variational space on an element regardless of the functional group it is in. The computational expense of ab initio calculations on molecules may be reduced by constructing functional-group-specific basis sets. Our functional group (FG) basis functions are contractions over a “parent” atomic basis on all atoms in the functional group of interest. Contraction coefficients are obtained by calculating the functional group’s electron density in a set of representative molecules and performing principle component analysis of the results. When the functional group’s chemical identity is maintained (e.g. no bonds are broken in the group), FG basis sets provide accuracies similar to the parent basis while using a smaller number of basis functions. We demonstrate our methods by parametrizing FG basis sets for the –OH and –CH– functional groups and testing them in DFT calculations on several molecules. The results suggest that FG basis sets may be useful in many contexts, especially for treating spectator groups in mixed basis calculations.

1. Introduction

Ab initio quantum chemistry is practical because of basis sets, which turn the integro-differential Schroedinger’s equation into a linear algebra problem over a finite variational space.¹

A primary challenge to modern theoretical chemistry is accurately treating large systems. Accuracy requires both a large variational space and high-level approximations for effects such as electron correlation. Unfortunately, large variational spaces are computationally expensive. Canonical ab initio calculations in an N -orbital variational space scale from $\mathcal{O}(N^2)$ – $\mathcal{O}(N^3)$ for Hartree–Fock and DFT methods² to $\mathcal{O}(e^N)$ for full inclusion of electron correlation. Several authors have developed physically motivated $\mathcal{O}(N)$ approximations in order to reduce this expense.^{2–5} Here we develop a complimentary approach: physically motivated reductions of the variational space itself.

We suggest that exploiting molecular similarity can reduce the variational spaces needed for molecular calculations. “Molecular similarity” is the familiar assumption that the

properties of molecular functional groups (methyl, benzyl, hydroxy, etc.) are similar in different molecules. It is a natural consequence of the “nearsightedness” of electronic structure. Nearsightedness, which underlies many of the $\mathcal{O}(N)$ approximations cited above, is the observation that distant regions of a large molecule have a weak influence on each other.⁶ Molecular similarity implies that electrons in a particular functional group will explore a well-defined variational space. The relevant variational spaces will differ in different functional groups. Molecular similarity is often a good approximation and underlies the success of molecular mechanics methods.⁷ However, existing atomic orbital (AO) basis sets do not use this approximation. Such basis sets treat each element with the same variational space, independent of what functional group it is in.

We parametrize basis sets to describe the most important components of a particular functional group’s electronic variational space. In systems where the assumption of molecular similarity holds, these functional group (FG) basis sets should provide accuracies comparable to AO basis sets, while leading to a significant dimensional reduction. They will not work where molecular similarity breaks down, e.g. where a bond breaks in a functional group.

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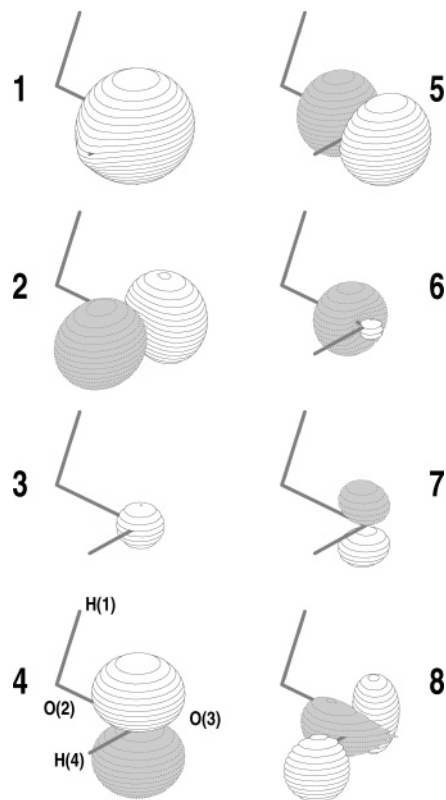


Figure 1. Surface plots of the first eight $-OH$ group basis functions obtained from the FG(HOOH,HOH) training set (Table 1). Contour is at 0.15 au. The basis functions are shown on one OH group of an H_2O_2 molecule (gray lines).

Functional group basis functions are obtained as contractions over a “parent” atomic orbital basis. Let $\{\phi_i^A\}$ be the set of parent AO basis functions located on atom A and indexed by i . FG basis functions for a group F (Φ_j^F) are obtained from the parent basis functions on all atoms A in F :

$$\Phi_j^F = \sum_{A \in F} \sum_i C_{j,i}^{F,A} \phi_i^A \quad (1)$$

For example, our $-OH$ group basis functions (section 3) are linear combinations of the 42 6-311G++(3d,p) AO basis functions on oxygen and hydrogen. Figure 1 plots⁸ the first eight functions from one of our $-OH$ group basis sets.

In quantum chemistry, basis functions are typically constructed from the eigenfunctions of simple systems such as isolated atoms. We use a very different approach to parametrize FG basis sets. This approach entails calculating the electronic structure of a functional group in many different environments and extracting the electronic degrees of freedom (basis functions) that are most important in these environments. This process is referred to as feature extraction.⁹ To construct an FG basis for functional group F , we build a training set of F -containing molecules and perform ab initio calculations in the parent basis set on each molecule. These molecules are designed to (a) contain sufficient diversity to explore the behavior of F in all molecules of interest and (b) be small enough to permit ab initio calculations in the parent basis set. For example, an FG basis set for amino acid A in proteins might be trained on $R -$

$A - R'$ trimers, with R and R' selected from the 20 biologically important amino acids. We add diversity to the training sets by applying random geometric and electrostatic perturbations to each molecule.

We next use principle component analysis (PCA) to extract the most important electronic degrees of freedom from the training set calculations. Consider a set of data vectors $\{v_i\}$ that are defined in a variational space of dimension N_0 . PCA of $\{v_i\}$ returns N_0 basis vectors, ordered according to their importance in describing the training set.⁹ In our case, N_0 is the number of parent AO basis functions on a group F and $\{v_i\}$ come from F 's calculated electron density in the training set molecules (see section 7 for details). The first $N \leq N_0$ vectors returned by PCA can be used as an N -orbital FG basis set. For example, Figure 1 shows the eight most important $-OH$ group basis functions obtained from PCA of 42 parent basis functions. We can use the first 6 of these functions to give an $-OH$ basis set of minimal-basis size, the first 11 functions to give an $-OH$ basis of valence-double- ζ size, and so forth.

The remainder of this paper is as follows. Section 2 presents a discussion of related work. Section 3 presents information on the parametrization and testing of FG basis sets for two functional groups, $-OH$ and $-CH-$. The results from section 3 are discussed in section 4, with a focus on the benefits and limitations of the approach. Section 5 demonstrates the potential utility of this approach for hybrid electronic structure calculations. Section 6 gives the conclusions, and section 7 presents details of the method and implementation.

2. Related Work

To our knowledge, the current work is unique in constructing a transferable set of functional-group-specific basis functions by analyzing variation across a set of molecules. Some related methods attempt to transfer functional groups' electronic structures (electron densities^{10–13} or localized, occupied molecular orbitals^{14–19}) between different calculations. One difficulty faced by these methods is that the transferred electronic structures should be both localized to a functional group and orthogonal to the rest of the system.²⁰ Ab initio valence bond calculations²¹ can use nonorthogonal occupied orbitals, but the complexity of the resulting Hamiltonians limits this method's generality. Approximately orthonormal monomer orbitals can be used for calculations^{22–24} and interpretations^{25–27} of intermolecular interactions. Orthogonality can also be treated by transferring occupied orbital energies^{28–30} or localized properties³¹ rather than the orbitals themselves or by constructing transferable models of functional groups from ab initio densities.^{32,33} Finally, some methods treat orthogonality issues by using the transferred orbitals as a basis set for SCF calculations.^{19,24} Our methods differ from these in that we focus entirely on transferable variational spaces and in our parametrization to a set of representative molecules. In our view, this is a promising alternative to the complexities inherent in the wholesale transfer of electronic structures between calculations. Other relevant reduced-variational-space methods include dual basis set methods,^{34,35} polarized atomic orbit-

Table 1: Data Sets Used To Train the $-OH$ and $-CH-$ Functional Group Basis Sets

data set	molecule(s)	groups ^a	perturbations
FG(HOH)	H ₂ O	320	Rand ^b
FG(HOOH)	H ₂ O ₂	320	Rand
FG(HOOH,HOH)	H ₂ O, H ₂ O ₂	320	Rand
FG(ROH) ^c	R-OH	5	none
propene	propene	200	

^a Number of $-OH$ or $-CH-$ functional groups in the training set. Both $-OH$ groups are used from each H₂O₂ molecule. ^b A unique set of random electrostatic and geometric perturbations is applied to each molecule. Geometric perturbations vary bond lengths, angles, and dihedrals by ≤ 0.2 Å, ≤ 3 degrees, and ≤ 360 degrees, respectively. Electrostatic perturbations randomly place 10 fractional charges in a 14.0 Å square box around the molecule, with ≥ 0.7 Å charge-atom separations. ^c Trained on R-OH molecules with R = H, F, OH, COH, O⁻, and Li; at their RHF/6-31G optimized geometries.

als,^{36,37} molecule intrinsic minimal basis sets,³⁸ and mixed basis sets (see section 5).

Our PCA-based parametrization differs considerably from the standard methods for generating basis sets. As mentioned above, electronic basis functions are typically constructed from the eigenfunctions of simpler systems such as isolated atoms.^{39–43} Exceptions include molecular fragment⁴⁴ and atomic natural orbital⁴⁵ AO basis sets.

Other uses of PCA in computational chemistry include PCA of ab initio calculations to predict the crystal structures of binary metallic alloys⁴⁶ and PCA of molecular dynamics trajectories to determine condensed-phase vibrational spectra.^{47,48} PCA has also been extensively applied in analysis of experimental data.^{49,50} We have previously used PCA of calculated electron densities in constructing a functional group based model for electron correlation.⁵¹

3. Results

3.1. Parametrization. We parametrized functional group basis sets for the $-OH$ functional group to singlet and triplet B3LYP/6-311G++(3d,p) calculations on the first four training sets in Table 1. The 6-311G++(3d,p) parent basis has 42 basis functions per $-OH$ group. FG basis sets for $-CH-$ were parametrized to singlet and triplet B3LYP/6-31G(d) calculations on the last training set in Table 1. The 6-31G(d) parent basis has 17 basis functions per $-CH-$ group. $-CH-$ training sets included both orientations of the $-CH-$ group ($CH_2 = CH - CH_3$ and $CH_3 - CH = CH_2$) to avoid bias in treating the substituents. Details of the parametrization procedure are discussed in section 7. Unperturbed geometries are from experimental data.⁵² Systematic analysis of FG basis set properties as a function of the parametrization variables (training set size and composition, thresholds in selecting vectors for PCA, etc.) is left for later work.

3.2. Testing. The $-OH$ and $-CH-$ functional group basis sets were tested by performing B3LYP/(FG basis) calculations on various molecules and comparing the results to B3LYP in the parent basis. Calculations for functional group F ($-OH$ or $-CH-$) used the first N FG basis functions on each F group and the parent basis on the remainder of the molecule. (For example, the “FG(HOH)” points in Figure 2 are B3LYP calculations on H₂O where one $-OH$ group is

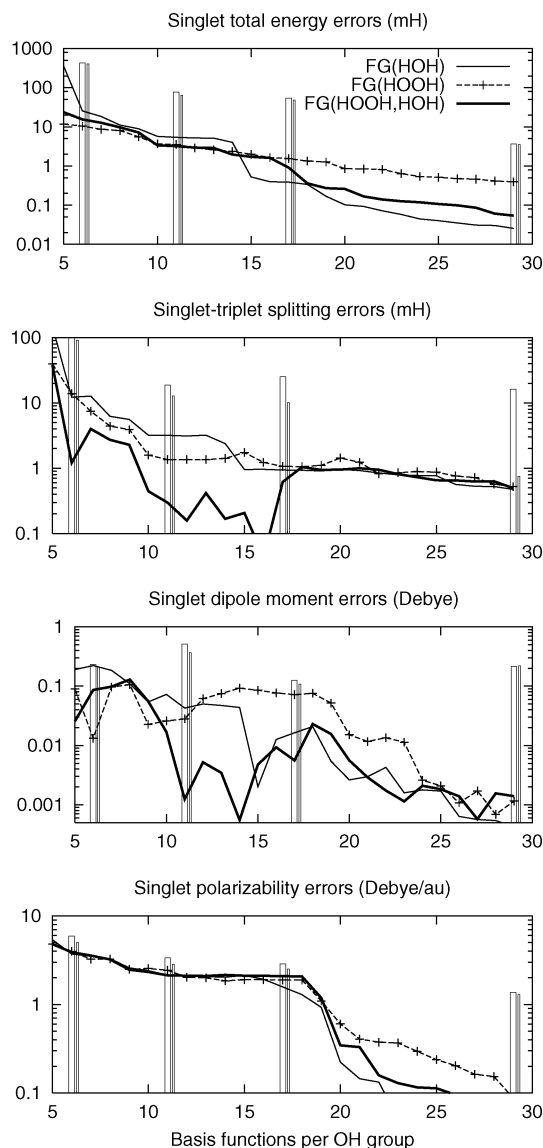


Figure 2. Errors relative to B3LYP/6-311G++(3d,p) in the energy and properties of unperturbed H₂O. Results are plotted vs the number of basis functions on the $-OH$ group. Lines are the results of B3LYP calculations that use an FG basis on the $-OH$ group and the parent basis on the remainder (see section 3.2). Columns are the results of B3LYP calculations that use small AO basis sets on the $-OH$ group: 6-311G+(d,p) at 29, 6-31G(d) at 17, 6-31G at 11, and STO-6G at 6 basis functions per $-OH$ group. Narrow and wide columns correspond to treating the rest of the molecule with the small AO basis (uniform basis set) or the parent basis (mixed basis set), respectively. The FG basis sets are obtained from the training sets in Table 1.

treated using the first 5, 6, 7, etc. $-OH$ basis functions obtained from the FG(HOH) training set and the remaining H atom is treated using 6-311G++(3d,p).) The results are compared to calculations in smaller AO basis sets as well as hybrid-basis calculations that use a small AO basis on all F groups and the parent basis on the remainder. The results of these tests are listed below and discussed in section 4.

The $-OH$ basis sets were tested on H₂O and H₂O₂ in their equilibrium geometries (Figures 2 and 3), on the dihedral rotational barrier of H₂O₂ (Table 2 and Figure 6), and on 90

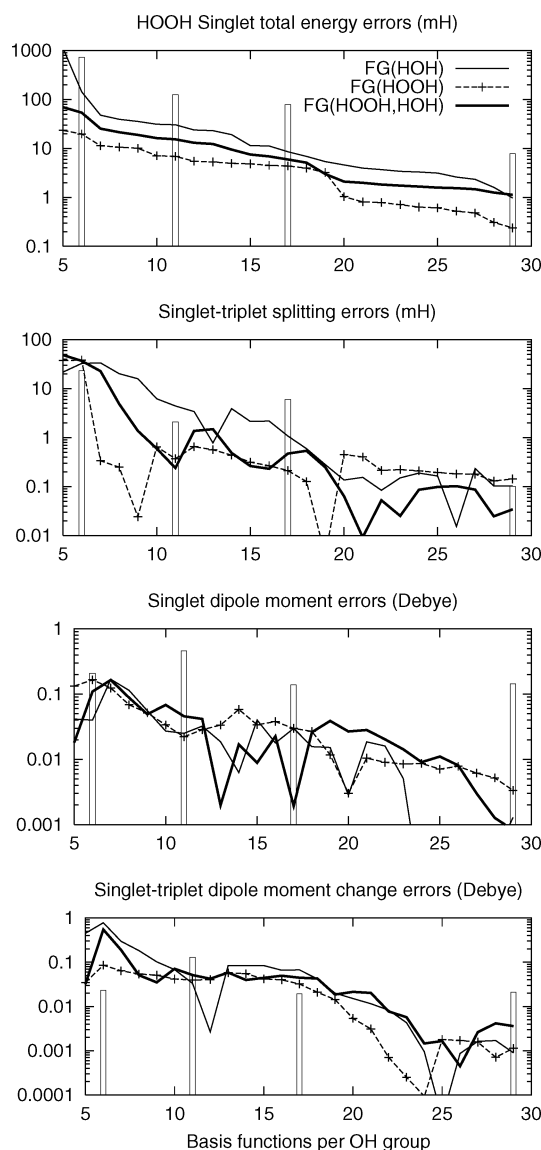


Figure 3. Errors in the energy and properties of unperturbed H_2O_2 , plotted as in Figure 2. The same basis set (FG or small AO) is used for both $-\text{OH}$ groups.

H_2O_2 molecules with perturbations as in Table 1 (Figure 4). The H_2O_2 molecules in Figure 4 were not included in the FG(HOOH) training set. The results in Figure 4 are similar to those for perturbed H_2O (data not shown). Basis functions from the FG(HOOH,HOH) and FG(ROH) training sets were tested in calculations on a set of eight R-OH molecules (Table 3). FG(HOOH,HOH) was also tested on the potential energy surfaces for the water O-H bond stretch (Figure 7). Figure 5 shows the highest occupied molecular orbitals (MOs) from FG and AO basis calculations on triplet H_2O . All errors are calculated versus B3LYP/6-311G++(3d,p) and plotted vs the number of basis functions per $-\text{OH}$ group.

The $-\text{CH}-$ basis sets were tested on 43 propene molecules with perturbations as in Table 1 (Figure 8) and on unperturbed benzene (Figure 9). The molecules in Figure 8 were not in the propene training set. Errors are calculated relative to B3LYP/6-31G(d) and plotted vs the number of basis functions per $-\text{CH}-$ group.

Table 2: B3LYP Rotational Barriers and Minimum-Energy Dihedral Angle for the Dihedral Rotation of Singlet H_2O_2

N^a	basis set	rotational barrier (mH)	minimum dihedral (deg) ^b
42	6-311G++(3d,p)	17.19	121
29	6-311G+(d,p)	18.83	131
29	FG(HOH)	16.96	121
29	FG(HOOH)	17.22	121
17	6-31G(d)	19.86	131
17	FG(HOH)	17.06	121
17	FG(HOOH)	17.40	127
11	6-31G	27.65	178
11	FG(HOH)	16.89	127
11	FG(HOOH)	17.10	140
6	STO-6G	19.03	180
6	FG(HOH)	16.95	127
6	FG(HOOH)	18.27	131

^a Number of basis functions per $-\text{OH}$ group. ^b Sampled in 1-degree increments, with other geometry parameters frozen at equilibrium values.

An alternative to extracting basis functions from molecules in different environments is to extract them from single molecules. Table 3 contains results from two such basis sets. The “One” results are an $-\text{OH}$ functional group basis set that was parametrized to B3LYP/6-311G++(3d,p) singlet and triplet calculations on a single unperturbed H_2O molecule (section 7.1). The “Orb” results use $-\text{OH}$ basis functions obtained from the Kohn–Sham orbitals of a B3LYP/6-311G++(3d,p) calculation on singlet H_2O . Here, the orbitals are sorted by orbital energy, projected onto one OH group of H_2O , and renormalized before use. Results from the latter set of basis functions are included in Figure 5 as “ H_2O Orb”.

4. Discussion

This section considers the results in section 3 and argues that the functional group basis sets can treat a wide range of systems at useful levels of theory. The results highlight the potential utility of FG basis sets and suggest further work.

The most important result in section 3 is that small functional group basis sets can reliably reproduce the parent basis results. Calculations using 29 of the 42 $-\text{OH}$ group basis functions always return small errors in total energies, singlet–triplet splittings, rotational barriers, and dipole moments (energy errors < 1.5 mH, dipole errors < 0.01 D for results in Figures 2, 3, 4 and 6 and Tables 2 and 3). Calculations using 12 of the 17 $-\text{CH}-$ group basis functions also return small errors (Figure 8).

Another important result is that the first N functional group basis functions from a particular training set are generally better than an N -orbital AO basis set at reproducing the parent basis results. The FG basis sets are better than AO basis sets at reproducing the parent basis total energy (upper panels of Figures 2, 3, 4, 8, and 9, and first section of Table 3). The FG basis sets are also better than AO basis sets at treating most of the properties tested. Notable examples include the polarizability (Figure 2) of unperturbed H_2O , the energies and properties of R-OH molecules (Table 3), and the average properties of perturbed molecules (Figures 4 and

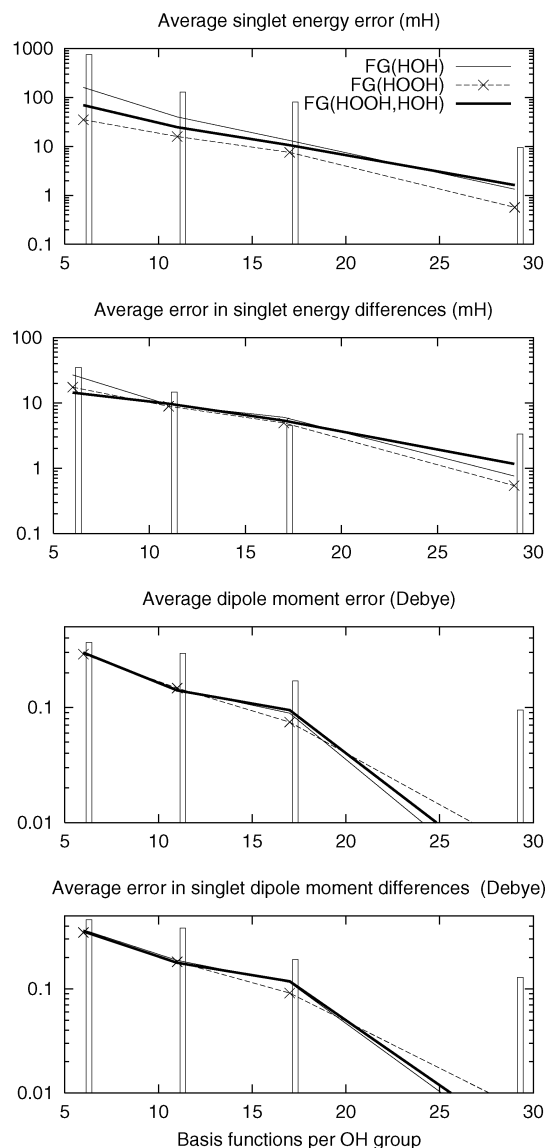


Figure 4. Average errors, relative to B3LYP/6-311G++-(3d,p), in the energies and properties of 90 perturbed singlet H_2O_2 molecules. Perturbations are as in Table 1 and results are plotted as in Figure 2. “Differences” correspond to the average error in the differences between the energies and properties of pairs of the H_2O_2 molecules (panels 2 and 4).

8). The only tested properties that are not well-treated by the FG basis sets are the singlet–triplet energy splitting and dipole moment changes of unperturbed H_2O_2 (Figure 3).

Another important result is that functional group basis sets can extrapolate to systems that are outside of their training sets. The results in Figures 4 and 8 show that the FG basis sets can extrapolate to different geometries and electrostatic environments. Table 3 shows extrapolations to entirely novel systems: a chemically diverse set of R–OH molecules. The FG basis sets in Table 3 clearly outperform equivalently sized atomic basis sets. Average errors in energy, singlet–triplet splitting, and dipole moment are generally smaller for these functional group basis sets than for the AO or hybrid AO basis sets. The functional group basis sets also usually return better values for the *difference* between the properties of a pair of R–OH molecules. The results are especially notable

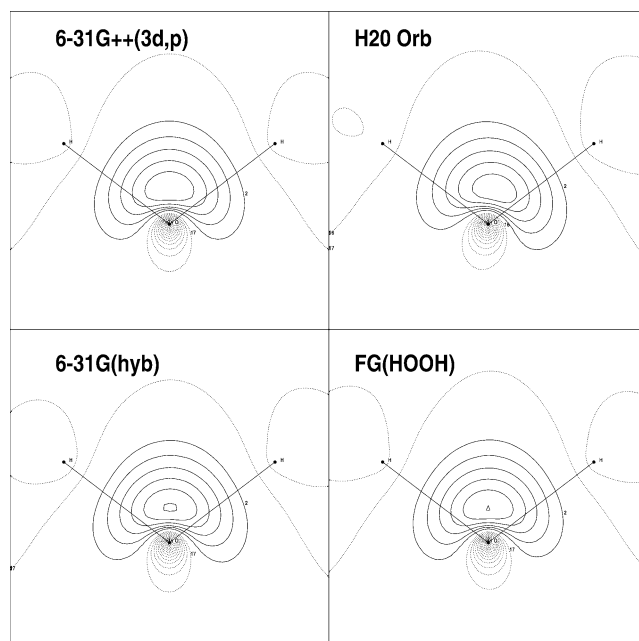


Figure 5. B3LYP HOMO of unperturbed triplet H_2O . Contours are 0.05 au, 0.10 au, 0.15 au, etc. All results other than “6-31G++(3d,p)” use the parent basis on the left H atom and eleven basis functions on the remaining OH group. The “6-31G(hyb)” and “FG(HOOH)” results treat this OH group with the 6-31G AO basis set and the first 11 –OH basis functions from the FG(HOOH) training set, respectively. The “H2O Orb” results treat this OH group with the first 11 –OH basis functions obtained from the Kohn–Sham orbitals of singlet H_2O (section 3.2).

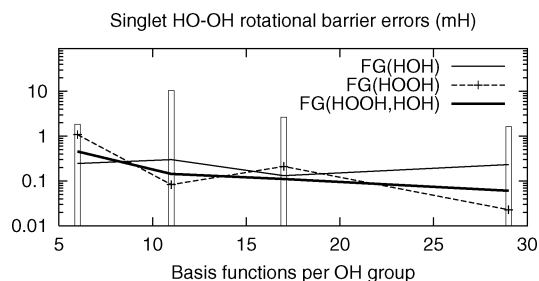


Figure 6. Errors in the dihedral rotational barrier of singlet H_2O_2 , plotted as in Figure 2. Selected rotational barrier values are in Table 2.

in that none of the R–OH groups in Table 3 were used in the FG basis training sets.

Table 3 contains results from two basis sets (“One” and “Orb”) that were extracted from a single molecule rather than molecules in different environments. These basis sets are parametrized to the electron density and Kohn–Sham orbitals of unperturbed H_2O (section 3.2). While these basis sets are generally better than similarly sized AO basis sets, they are not as good as the large-training-set basis sets. The “Orb” and “One” basis sets are comparable to FG(HOOH,HOH) and generally worse than FG(ROH). This is especially true for larger basis set sizes: while the “Orb” results give the best minimal –OH basis set, the FG(ROH) basis generally gives the best results for larger basis sizes. This result is not surprising, as only a chemically diverse training

Table 3: B3LYP Energy and Property Errors for R–OH Molecules, R = COO[−], Na, OCH₃, Cl, CN, CH₃, CFH₂, NH₃⁺

Prop ^c	N ^d	average error ^a						average difference error ^b					
		AO ^e	Hyb ^f	One ^g	Orb ^h	FG ⁱ	FG(ROH) ^j	AO	Hyb	One	Orb	FG	FG(ROH)
E	6	1028.	297.5	17.17	20.39	23.81	21.98	510.0	11.48	18.97	24.39	23.94	19.97
	11	132.1	51.90	11.66	14.07	14.55	8.70	47.20	2.55	14.85	16.69	15.25	4.04
	17	83.06	35.90	8.41	8.69	8.02	4.86	26.09	1.27	10.29	11.24	9.34	0.77
	29	8.36	2.92	3.76	1.94	1.09	2.12	2.20	1.26	3.97	2.92	1.06	0.27
ΔE	6	49.08	11.66	8.94	12.12	6.05	10.27	61.39	10.18	5.72	6.43	15.32	9.93
	11	20.19	4.47	4.84	5.37	2.30	1.90	27.47	6.32	3.92	3.86	5.75	1.88
	17	22.39	3.69	3.61	1.74	0.66	0.57	28.89	5.38	3.15	1.75	1.59	0.76
	29	4.85	2.77	2.60	0.61	0.35	0.25	7.47	3.95	2.33	0.72	1.07	0.28
μ	6	0.802	0.419	0.168	0.174	0.202	0.354	0.927	0.486	0.239	0.262	0.277	0.474
	11	0.525	0.283	0.076	0.128	0.111	0.071	1.262	0.321	0.111	0.200	0.163	0.082
	17	0.326	0.130	0.062	0.072	0.079	0.033	1.055	0.174	0.091	0.108	0.117	0.040
	29	0.096	0.043	0.017	0.009	0.007	0.009	0.265	0.039	0.022	0.014	0.011	0.012

^a Errors are relative to B3LYP/6-311G++(3d,p), all calculations except “AO” use 6-311G++(3d,p) on the R group and a small AO or FG basis on the OH group. ^b Average error in the difference between the energies and properties of pairs of different R–OH molecules. ^c Properties tested: E and ΔE are errors in total energy and singlet–triplet splitting (mH), μ is error in total singlet dipole (Debye). ^d Number of basis functions on the OH group. ^e Small AO basis set (STO-6G, 6-31G, 6-31G(d), or 6-311G+(d,p) for 6, 11, 17, and 29 basis functions per OH, respectively) used on the entire molecule. ^f OH basis is a small AO basis. ^g OH basis is an FG basis parametrized to unperturbed H₂O. ^h OH basis is the first N orbitals from a B3LYP/6-311G++(3d,p) calculation on H₂O (section 3.2). ⁱ OH basis is FG(HOOH, HOH) (Table 1). ^j OH basis is FG(ROH) (Table 1).

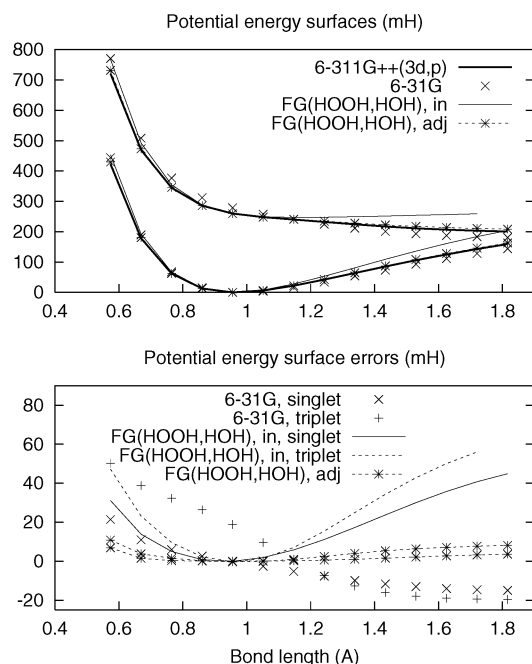


Figure 7. Testing –OH basis sets on bond dissociation. Results are singlet and triplet B3LYP potential energy surfaces (energy in mH vs bond length in Å) for stretching an O–H bond in H₂O, with the other O–H bond and the H–O–H angle frozen at their equilibrium values. Upper and lower panels are the potential energy surfaces and the energy errors (mH) relative to B3LYP/6-311G++(3d,p). Calculations in the functional group basis used the first 11 –OH basis functions from the FG(HOOH,HOH) training set (Table 1) on one OH group and the parent basis on the remaining H atom. These calculations have the dissociating H–OH bond either within (“in”) or adjacent to (“adj”) the OH group treated with the FG basis. Potential energy surfaces are normalized such that the singlet energy at 0.956 Å is zero.

set will contain information about which basis functions are most important for describing the response to different R groups.

FG basis sets from molecules in different environments also generally have better symmetry properties than those obtained from single molecules. For example, Figure 5 contains results from the “Orb” basis set discussed above (“H₂O Orb”). The highest-occupied Kohn–Sham orbital calculated with this basis set is asymmetric, unlike the one obtained from the FG(HOOH) basis. These results are representative, both for other basis sizes and for the “One” basis in Table 3 (data not shown).

FG basis sets have the useful property of converging smoothly with basis size. Smooth convergence can be seen, for example, in using the first 5, 6, 7, etc. –OH group basis functions from the FG(HOOH,HOH) training set to describe unperturbed H₂O₂ (top panel of Figure 3). Smooth convergence is desirable as it enables extrapolation of large-basis results from a series of small-basis calculations. Several atomic basis sets, including the correlation-consistent,⁵³ polarization-consistent,⁵⁴ and correlation-consistent pseudopotential⁵⁵ basis sets, have been explicitly designed to give smooth convergence. We find that FG basis set convergence is smoothest for total energies and averaged properties (Figures 4 and 8 and Table 3). Convergence is generally smoother for FG basis sets than for the small AO basis sets tested (see e.g. H₂O₂ rotational barrier errors in Figure 6).

Some of the functional group basis set results in Figures 2 and 3 do not appear to converge smoothly with basis size. This is partly an artifact of the logarithmic scale. For example, the large apparent variations in the FG(HOOH,HOH) singlet–triplet splittings are all < 1.5 mH when using 10 or more FG basis functions. The rough convergence is also partly due to symmetry effects. The individual functional group basis functions do not (and cannot) all have the same symmetry as the functional group (see Figure 1). We are currently experimenting with partitioning the FG basis functions into properly symmetrized groups.

It is perhaps counterintuitive that functional group basis functions can work for multiple group geometries (see Table

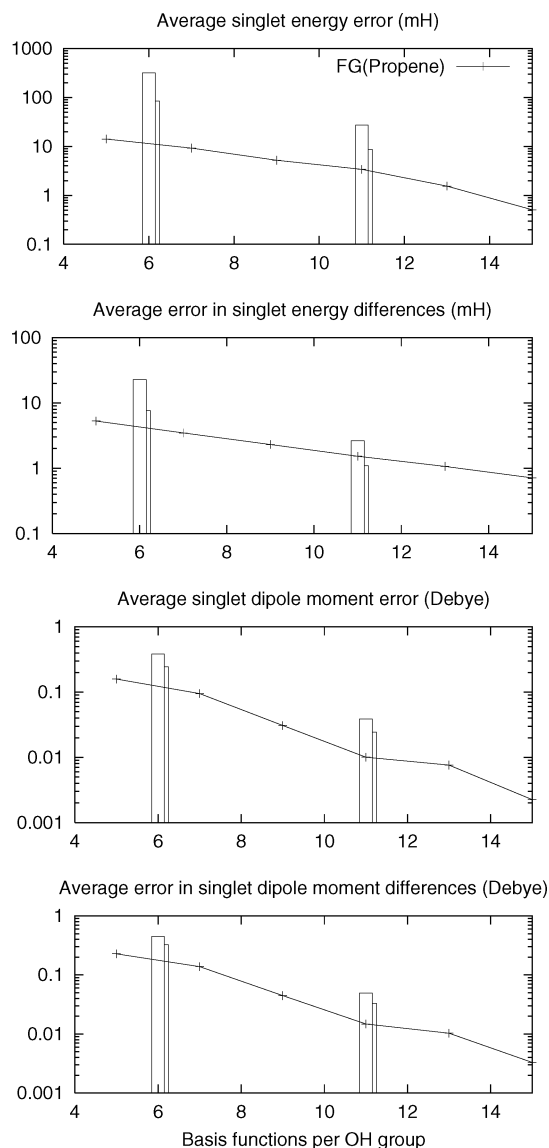


Figure 8. Average errors, relative to B3LYP/6-31G(d), in the energies and properties of 43 perturbed singlet propene molecules. Perturbations are as in Table 1, and results are plotted as in Figure 2. AO-basis results use 6-31G and STO-6G (11 and 6 basis functions per $-\text{CH}-$ group, respectively). “Differences” correspond to the average error in the differences between the energies and properties of pairs of the propene molecules (panels 2 and 4).

3 and Figures 4 and 8). This is possible because our FG basis functions are contractions over atomic basis functions and can therefore change shape with molecular geometry. Consider a simple example: an FG basis set for H_2 , where the parent AO basis has one s orbital on each atom. The FG basis functions will be the bonding and antibonding combination of the two atomic orbitals. The first (bonding) FG basis function will be the singlet RHF ground state for all H–H bond lengths.

Figure 7 presents a detailed test of geometry variations in a functional group basis set. As expected, the FG basis set gives large errors for large bond variations. However, it does better than an equivalently sized AO basis over the range of bond lengths included in its training set ($0.956 \pm 0.3 \text{ \AA}$, see Table 1). In this regime, the 6-31G energy errors change

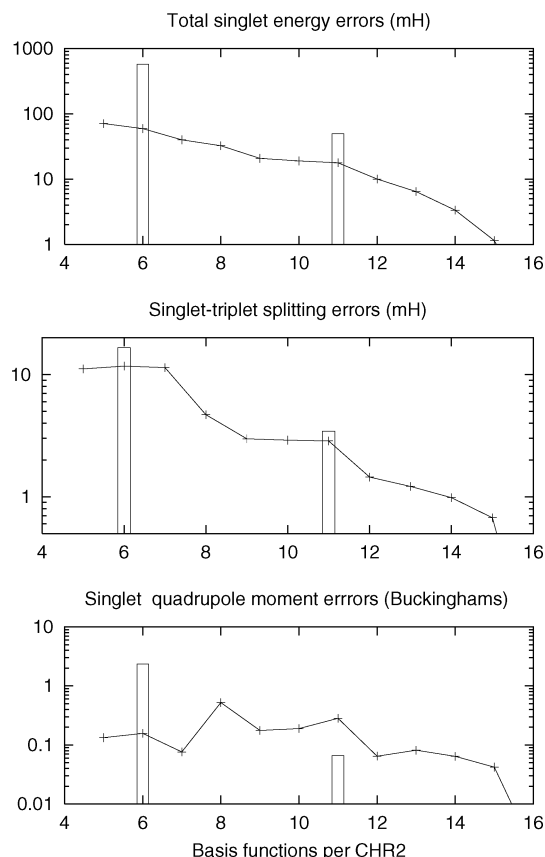


Figure 9. Errors relative to B3LYP/6-31G(d) in the energy and properties of unperturbed benzene. $-\text{CH}-$ basis sets are from the training set in Table 1, and results are plotted as in Figure 8. Quadrupole moments are measured perpendicular to the plane of the benzene ring.

dramatically with bond length, while the $-\text{OH}$ basis errors are approximately constant. These results are representative of the other basis set sizes tested (data not shown). We also consider a situation where the parent basis is used on the dissociating H atom and the FG basis is used on the remaining $-\text{OH}$ fragment. Since the functional group retains its identity in this situation, we expect that the errors will be small. The “FG(HOOH,HOH), adj” results in Figure 7 show that this is the case.

The results in section 3 show that functional group basis sets work for useful levels of theory (B3LYP density functional theory). These results are representative for self-consistent field methods, including Hartree–Fock theory and DFT with other functionals (data not shown). While the electron density implicitly describes electron correlation via the Hohenberg–Kohn theorem,⁵⁶ we expect that FG basis sets for explicitly correlated methods will need to be parametrized to explicit information about electron–electron interactions. We are currently using ideas from our electron-pair-density methods⁵¹ to develop such basis sets.

5. Hybrid Electronic Structure Methods

Functional group basis sets may be particularly useful for hybrid electronic structure calculations. Many large systems, such as protein catalysts and solvated molecules, have a relatively small region of chemical interest. Such systems

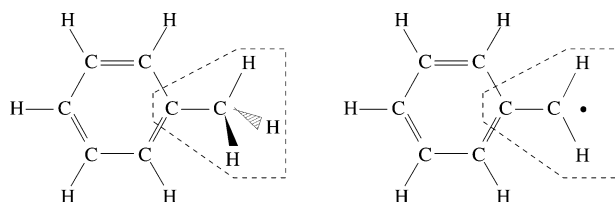


Figure 10. Reactant (left) and product (right) of the toluene $\text{PhCH}_2\text{-H}$ bond dissociation. The active region, which requires treatment with a large variational space, is enclosed with dotted lines.

can be treated using hybrid methods. These methods combine a high-level treatment of the active region with a lower-level treatment of the remaining spectator groups.^{57–60} Semiempirical or molecular-mechanics treatments of spectator groups is problematic for systems with complex interactions between the active and spectator regions.^{60–63} The $\text{PhCH}_2\text{-H}$ bond dissociation of toluene (Figure 10) is one such system, as the product PhCH_2^* radical can delocalize onto the C_5H_5 spectator group.

Systems with complex interactions between active and spectator groups may be treated with mixed basis set methods. This hybrid method involves an *ab initio* calculation on the entire system, with a large basis set on the active region and a smaller basis elsewhere.^{64–68} Like all hybrid methods, mixed basis sets require care in treating the high-level/low-level interface. Inappropriate choice of basis sets can produce inaccuracies due to basis set imbalance. A simple example of basis set imbalance is a homonuclear diatomic with a minimal basis on one atom and a large basis on the other. Electron density will tend to move onto the atom with the large basis, giving the molecule a spurious dipole moment.

We have tested FG basis sets vs atomic basis sets in a series of hybrid calculations. These tests, detailed below, use the parent AO basis on the active region and a functional group or small atomic basis on the remainder. We find that FG basis sets have smaller basis set imbalance effects than equivalently sized atomic basis sets. We believe that this is because the FG basis functions are contracted over the parent basis set and so are likely to be more compatible with the full parent basis.

Table 3 in section 3 gives errors for mixed basis calculations on several R-OH molecules. Here, R is treated with the parent basis, and OH is treated with either a small AO basis (“Hyb”) or an -OH functional group basis (“FG”, “FG-(ROH)”). The average errors in energy, singlet–triplet splittings, dipole moment, and the difference between these properties for pairs of R-OH molecules, are almost always lower for the functional group basis sets.

Table 4 presents calculated dipole moments for trans H_2O_2 . This molecule is analogous to a homonuclear diatomic and has zero dipole moment when treated with a balanced basis set. Here, one OH group is treated with either a FG basis set or a small AO basis. The other group is treated with the parent AO basis. The FG basis sets have much lower dipole moments than the equivalently sized AO basis sets, indicating less basis set imbalance.

Table 4: Hybrid-Basis Dipole Moments (Debye) for trans H_2O_2

N^a	AO ^b	FG ^c
6	0.938	0.204
11	0.258	0.118
17	0.179	0.072
29	0.075	0.004

^a Number of basis functions on the second OH group. ^b The second OH group is treated with a small AO basis (STO-6G, 6-31G, 6-31G(d), or 6-311G+(d,p) for 6, 11, 17, and 29 basis functions per OH, respectively). ^c The second OH group is treated with the first N basis functions from the FG(HOOH,HOH) training set (Table 1).

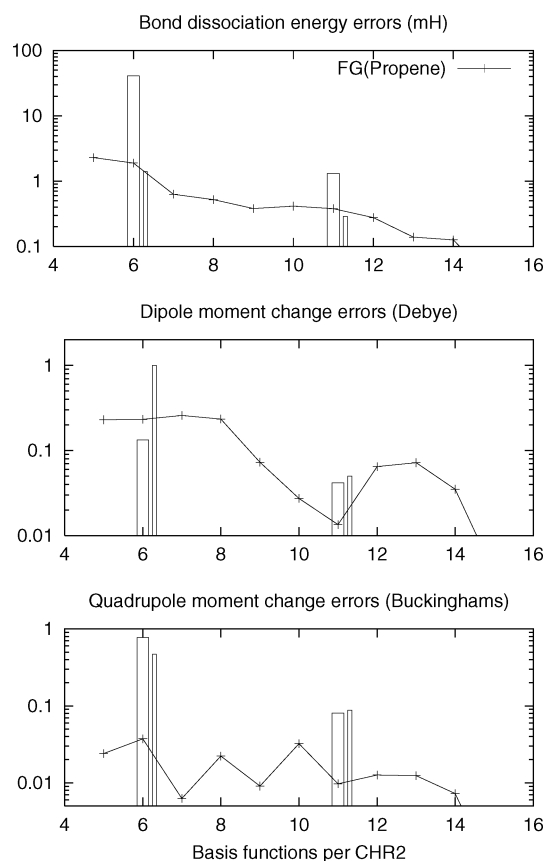


Figure 11. Errors in $\text{PhCH}_2\text{-H}$ bond dissociation energy and $\text{PhCH}_3 \rightarrow \text{PhCH}_2^*$ dipole and out-of-plane quadrupole moment change, relative to B3LYP/6-31G(d), plotted vs number of basis functions per -CH- group. Lines use 6-311G(d) on the active region (Figure 10) and the -CH- functional group basis sets from section 3 on the remainder. Narrow columns use 6-31G(d) on the active region and a small AO basis set (STO-6G at 6 and 6-31G at 11 basis functions per -CH- , respectively) on the remainder. Wide columns use a small AO basis set on the entire molecule.

Finally, we consider mixed basis calculations on the $\text{PhCH}_2\text{-H}$ bond dissociation shown in Figure 10. Figure 11 presents errors in the calculated dissociation energy and $\text{PhCH}_2\text{-H} \rightarrow \text{PhCH}_2^*$ change in total dipole moment and out-of-plane quadrupole moment, relative to B3LYP/6-31G(d). The active region (see Figure 10) is treated with the parent 6-31G(d) basis, and the C_5H_5 spectator group is treated with either a small AO basis set or a -CH- FG basis set. The functional group basis sets perform about the same as equivalently sized atomic basis sets for the dissociation

energy and somewhat better for the change in multipole moments. Figure 11 also presents results obtained using a small atomic basis on the entire molecule (wide columns). The use of a balanced but small basis reduces the error in the multipole moment changes, at the expense of a substantially increased error in the dissociation energy. Hybrid-basis calculations with the $-\text{CH}-$ FG basis have the advantage of giving reasonable results for both dissociation energy and multipole moments.

6. Conclusions

This paper presents a new approach to reducing the variational space needed for ab initio calculations on molecules. The electronic structures of molecular functional groups are largely conserved across different molecules. However, existing atomic orbital basis sets treat each element with the same variational space, regardless of what functional group it is in. We generate basis sets for functional groups in molecules ($-\text{OH}$ groups, $-\text{CH}-$ groups, and so forth). The functional group (FG) basis sets are designed to describe the electronic variational space that is most important for electrons in the group of interest. FG basis functions for a functional group F are generated by contracting over a “parent” AO basis on all atoms in F . The contraction coefficients are determined via feature extraction (principle component analysis)⁹ of the calculated electronic structures of a “training set” of F -containing molecules. This approach differs considerably from the standard methods of constructing basis sets.

In the current work, we generate basis sets for the $-\text{OH}$ and $-\text{CH}-$ functional groups. Our results demonstrate that these basis sets enable substantial dimensional reduction with minimal loss of accuracy relative to the parent basis. The FG basis sets always give lower energy errors, and usually give lower property errors, than comparably sized atomic basis sets. They are able to extrapolate to chemically diverse sets of molecules. In addition, their convergence with basis size is generally fairly smooth, allowing one to extrapolate more readily to the large-basis limit. The FG basis sets are especially suited for mixed-basis calculations, due to the reduced effects of basis set imbalance.

One interesting aspect of this method is that we can tailor the dimensional reduction to specific instances. For example, one might parametrize an FG basis set for electronic polarizability by applying electric fields to the training set molecules and doing PCA on the difference between the calculated electron densities in the presence and absence of applied fields. We intend to explore such methods in future work.

The results presented here suggest that FG basis sets may be useful for ab initio calculations on large systems, especially for treating spectator groups in mixed-basis calculations. However, a number of aspects are left to future work. These include FG basis sets for explicitly correlated methods and a complete implementation into a production quality electronic structure package.

7. Implementation Details

7.1. Parametrization Method. Basis functions for a functional group F are parametrized as follows. First, we define

a set of local coordinates for F (section 7.2). We select a parent atomic orbital basis set and a set of small R groups and build a training set of molecules from $\{R\}$ and F (e.g. $R = \text{OH}$ for $-\text{OH}$ groups and $R = \text{CH} - R'$ for $-\text{CH}-$ groups). We usually add diversity to the training set by generating $\mathcal{O}(100)$ conformers for each molecule, each with a different set of geometric and electrostatic perturbations (“Rand” in Table 1). Geometric perturbations are generated by randomly changing all bond lengths, angles, and dihedrals. Electrostatic perturbations are generated by randomly placing point charges in a box around the molecule and discarding those that are too close to the nuclei.

Next we perform ab initio calculations, in the parent basis set, on all molecules in the training set. Each calculation yields a one-electron density matrix in the parent AO basis (1D) and the overlap matrix of the parent basis functions (S). We extract the sub-blocks that correspond to functional group F : all matrix elements ${}^1D_{ij}$ and S_{ij} where AO basis functions i and j are on atoms in F . Each density matrix sub-block is rotated into F 's local coordinates (section 7.2) and diagonalized. The eigenvectors, referred to here as “group natural orbitals”, provide a representation of how the electrons in F are distributed across the parent basis functions. We save all group natural orbitals with eigenvalues (occupancies) > 0.1 electrons and perform PCA on the saved group natural orbitals from the entire training set. The vectors returned by PCA are the functional group basis functions in the parent AO basis. FG basis sets that are parametrized to very small training sets (e.g. results labeled “One” in Table 3) have the input group natural orbitals weighted by their occupancies before doing the PCA. We have experimented with using this technique for large training sets but have not found it to improve the results.

Principle component analysis on vectors in an orthonormal basis returns a set of orthogonal vectors. We minimize the overlap of the FG basis functions by performing the PCA in an approximately orthogonal basis set. This basis is obtained by averaging the saved overlap matrix sub-blocks from the entire training set and performing Schmidt orthogonalization on the result. The saved group natural orbitals are projected into this basis before PCA, and the resulting PCA vectors are projected back into the parent AO basis.

7.2. Orienting Functional Group Basis Functions. Since functional groups are generally not spherically symmetric, our FG basis functions must be oriented with respect to the geometry of each molecule of interest. Consider, for example, the H_2O_2 molecules in Figure 1. Here, the FG basis functions are plotted on the $-\text{OH}$ group containing atoms O(3) and H(4). Let the z axis be vertical, such that basis function 4 is mostly composed of the p_z orbitals on O(3). If the basis functions were transferred without rotation to the other $-\text{OH}$ group, basis function 4 would be composed of the p_z orbitals on O(2) and would have the wrong orientation with respect to the H(1)–O(2) bond. Rotation ensures that this basis function is composed of the linear combinations of p orbitals on O(2) that are perpendicular to the plane defined by atoms 1–3.

We orient our FG basis functions by defining them relative to an internal coordinate system. For example, the internal

coordinates of the R–OH group have the x -axis along the R–O bond and the O–H group in the x – y plane. The basis functions are oriented by calculating the Cartesian rotation matrix between a group's local coordinates and its orientation in the molecule of interest. This rotation matrix is used to rotate each p- and d-orbital shell from the local orientation to the correct global orientation.^{69,70}

7.3. GAMESS Implementation and Timing Tests. A complete implementation of functional group basis sets would calculate the one- and two-electron operators in the parent AO basis, rotate each group's FG basis functions into the correct orientation (section 7.2), project the operators into the FG basis, and use the transformed operators in the ab initio calculation. The time savings would be similar to those for contracted vs uncontracted AO basis sets.³⁹ Initial one- and two-integral evaluations would scale as the number of Gaussian primitives, and all subsequent steps (dimension of Fock matrix, number of possible determinants) would scale as the number of FG basis functions.

The results presented here use a preliminary implementation of FG basis sets built into GAMESS.⁷¹ This implementation builds the Fock matrices in the parent AO basis and diagonalizes them in the FG basis. Transformations into the FG basis are performed by exploiting the methods in GAMESS for removing linearly dependent combinations of basis functions. Our initial implementation used GAMESS for the parent-basis operator evaluations and home-built code for ab initio calculations in the FG basis. Test calculations showed that the two implementations return identical results (data not shown).

GAMESS removes linearly dependent combinations of basis functions as follows.⁷² Consider a system with an N -orbital parent AO basis. Let S be the overlap matrix of the AO basis functions. SCF calculations in the parent basis diagonalize the transformed Fock matrix $Q^\dagger F Q$, where F is the AO-basis Fock matrix and Q is an orthonormal basis set generated by diagonalizing S ($Q^\dagger S Q = 1$). Linear dependencies are removed by discarding eigenvectors of S with negligible eigenvalues, such that a basis with $N' < N$ linearly independent vectors yields a rectangular Q matrix and a transformed Fock matrix of dimension $N' \times N'$.

We implement FG basis functions as follows. Consider calculations using $N_{\text{used}} < N$ FG basis functions U , where U_{ji} is the projection of the i th FG basis function onto the j th parent AO basis function. We replace S with the $N \times N$ matrix $R^\dagger S R$ in the GAMESS routine for calculating Q . Matrix R zeros out the degrees of freedom that are outside of the FG basis, such that $R^\dagger S R$ has $N - N_{\text{used}}$ negligible eigenvalues. R is defined as $U \sigma^{-1} U^\dagger S$ where $\sigma = U^\dagger S U$ is the FG basis functions' overlap matrix. Finally, we replace Q with RQ , such that SCF calculations diagonalize the $N_{\text{used}} \times N_{\text{used}}$ matrix given by $Q^\dagger R^\dagger F R Q$. The FG basis functions are rotated from their internal coordinates outside of GAMESS (section 7.2).

Figure 12 presents a timing test of our GAMESS implementation of functional group basis sets. The figure plots the total calculation times for RHF/6-311G++(3d,p) calculations on 10 noninteracting H₂ molecules. The FG basis set is the RHF/6-311G++(3p) molecular orbitals of a single H₂,

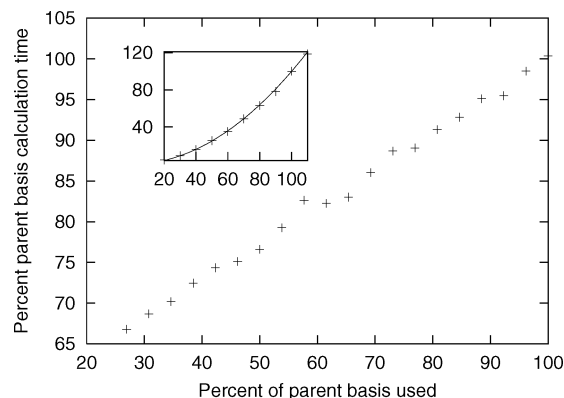


Figure 12. Timing tests for functional group basis calculations on a model system of 10 noninteracting H₂ molecules. X axis is basis size as a percent of the parent AO basis. Y axis is RHF calculation time as a percent of the time for a calculation in the parent AO basis. Inset is calculation time vs total basis size for N H₂ molecules, percentages relative to $N=10$, and a quadratic fit to the data.

and all FG basis calculations return the parent-basis wave function. The FG basis sets have a clear computational savings and a relatively small overhead (calculation time 100.4% of parent basis at basis size 100%). The computational savings of our FG basis implementation will depend on the linear-scaling approximations used in the calculation. In the systems tested here, we use a fast multipole moment approximation for the two-electron integrals. The total calculation time scales quadratically (Figure 12 inset) and the time savings scales linearly.

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