Double and Quadruple Zeta Contracted Gaussian Basis Sets for Hydrogen through Neon

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Abstract

Koga and Thakkar's reoptimized (9s5p) and (12s7p) Gaussian basis sets for the atoms Li to Ne are contracted to [4s2p] and [7s4p], respectively, and their (4s) and (6s) sets for H and He are contracted to [2s] and [4s], respectively. The basis sets are tested by performing self-consistent-field (SCF) geometry optimizations on LiH, BeH$_2$, B$_2$H$_6$, CH$_4$, NH$_3$, H$_2$O, and HF. The equilibrium geometries of hydrogen peroxide and hydrazine are determined at both the SCF and fourth-order many-body perturbation theory level. © 1993 John Wiley & Sons, Inc.

Introduction

Most contemporary quantum chemical calculations use basis sets of Gaussian-type functions (GTF). There are many good reviews and compendia [1–8] of GTF basis sets. Dunning's double zeta [4s2p/2s] contractions [9] of Huzinaga's variationally optimized (9s5p/4s) GTF sets [10] are among the most popular basis sets for hydrogen and the first row atoms from B through F. Huzinaga's basis sets for H to Ne were variationally reoptimized and larger sets for Li to Ne were constructed [11] and contracted [12] by van Duijneveldt; these have also been widely used.

Recently, Koga and Thakkar [13] obtained further variational improvements in (9s5p) and (12s7p) GTF sets for Li to Ne, and (4s) and (6s) sets for H and He. Their (9s5p) basis sets [13] for Li to Ne are in complete agreement with the very recent work of Schafer et al. [14], who independently reoptimized Huzinaga's (9s5p) sets. Koga and Thakkar's basis sets for Li to Ne yield atomic energies lower than those of van Duijneveldt [11] by amounts ranging from 6.1×10^{-6} to 1.5×10^{-4} E_H. These energy improvements are rather small in the context of molecular calculations. However, the reoptimized exponents of the tight GTF differ by as much as 25% from the previous ones [11], and this may be of some significance for properties other than the energy. We report double and quadruple zeta contractions of Koga

TABLE I.   Atomic energies, with signs reversed, from various GTF basis sets.

	HD[a]	VD[b]	B0[c]	B1[c]	B2[c]	(9s5p)[d]
Li (^{2}P)			7.3647293	7.3647293	7.3647293	7.3647293
Be (^{3}P)			14.509918	14.510791	14.510812	14.510815
B (^{2}P)	24.526415	24.52687	24.526304	24.527471	24.527527	24.527546
C (^{3}P)	37.684508	37.68519	37.684687	37.685561	37.685665	37.685700
N (^{4}S)	54.394392	54.39535	54.395093	54.395655	54.395829	54.395885
O (^{3}P)	74.798837	74.80040	74.800333	74.800635	74.800912	74.800995
F (^{2}P)	99.393300	99.39557	99.395769	99.395937	99.396285	99.396402
Ne (^{1}S)		128.52711	128.52752	128.52793	128.52811	128.52827

[a] HD is Dunning's [4s2p] contraction [9] of Huzinaga's (9s5p) set [10].
[b] VD is (9s5p)/[4s2p] set of van Duijneveldt [11,12].
[c] B0, B1, and B2, respectively, are [4s2p] contractions of Koga and Thakkar's (9s5p) set [13] using 0, 1, and 2 repeated primitives.
[d] (9s5p) is the uncontracted set from Ref. [13].

and Thakkar's basis sets [13] for use in molecular calculations. The contraction procedure is described in the next section, and the basis sets are tested in the third section. Hartree atomic units are used except where explicitly stated otherwise.

Contraction of the Basis Sets

Basis sets of contracted Gaussian type functions (CGTFs) can be of either the segmented [9] or generalized [15] type. In the elegant general contraction scheme of Raffenetti [15], the CGTFs can be constructed from atomic calculations in the parent uncontracted GTF basis set without any further complications. However, a "primitive" GTF will generally appear in many CGTFs, and this will lead to many

TABLE II.   Atomic energies, with signs reversed, from various GTF basis sets.

	C0[a]	C1[a]	(12s7p)[b]	NHF[c]
Li (^{2}P)	7.3650363	7.3650363	7.3650363	7.3650697
Be (^{3}P)	14.511439	14.511443	14.511444	14.511502
B (^{2}P)	24.528939	24.528953	24.528953	24.529061
C (^{3}P)	37.688397	37.688422	37.688423	37.688619
N (^{4}S)	54.400561	54.400602	54.400603	54.400934
O (^{3}P)	74.808783	74.808842	74.808846	74.809398
F (^{2}P)	99.408404	99.408490	99.408492	99.409349
Ne (^{1}S)	128.54573	128.54584	128.54584	128.54710

[a] C0 and C1, respectively, are [7s4p] contractions of Koga and Thakkar's (12s7p) set [13] using 0 and 1 repeated primitives.
[b] (12s7p) is the uncontracted set from Ref. [13].
[c] NHF is the Hartree-Fock limit from Ref. [21].

TABLE III.   Exponents (α) and contraction coefficients (c) of the (4s)/[2s] CGTF basis sets for H and He.[a]

H		He	
α	c	α	c
13.011	0.033484	38.355	0.040183
1.9623	0.234719	5.7689	0.261395
0.44454	0.813774	1.2399	0.793038
--------		--------	
0.12195	1.000000	0.29758	1.000000

[a] Dashed lines separate the contracted functions. A scale factor of 1.2 should be used for H in molecular calculations by multiplying the α by 1.44.

unnecessary integral evaluations unless the integral program specifically takes this into account. Unfortunately, many popular integral programs do not have the capability to use generalized contractions efficiently.

The alternative is segmented contraction [9] in which primitive GTFs, with the possible exception of one or two crucial ones, appear in only one CGTF. Ideally, one should variationally optimize the contraction coefficients, the exponents, and the grouping pattern. We are not aware of any such work. Segmented CGTF basis sets with both exponents and contraction coefficients variationally optimized for a predetermined contraction pattern can be found in Refs. [14,16], for example. More common are segmented basis sets in which the contraction pattern (splitting)

TABLE IV.   Exponents (α) and contraction coefficients (c) of the (6s)/[4s] CGTF basis sets for H and He.[a]

H		He	
α	c	α	c
82.921	0.022940	234.06	0.024379
12.452	0.175491	35.174	0.184036
2.8330	0.864756	7.9911	0.857623
--------		--------	
0.80001	1.000000	2.2124	1.000000
--------		--------	
0.25859	1.000000	0.66707	1.000000
--------		--------	
0.089969	1.000000	0.20895	1.000000

[a] Dashed lines separate the contracted functions. No scaling of the H basis set is recommended for molecular calculations.

TABLE V. Exponents (α) and contraction coefficients (c) of the (9s5p)/[4s2p] CGTF basis sets for Li, Be, B, and C.[a]

	Li		Be		B		C	
	α	c	α	c	α	c	α	c
s	1.4990(+3)	0.001042	2.9330(+3)	0.001046	4.7108(+3)	0.001133	6.7799(+3)	0.001222
	2.2491(+2)	0.008024	4.4002(+2)	0.008066	7.0674(+2)	0.008740	1.0172(+3)	0.009430
	5.1184(+1)	0.040590	1.0015(+2)	0.041001	1.6088(+2)	0.044488	2.3157(+2)	0.048023
	1.4453(+1)	0.150484	2.8304(+1)	0.154551	4.5518(+1)	0.168530	6.5547(+1)	0.182197
	4.6303	0.393278	9.1146	0.416999	1.4724(+1)	0.458573	2.1253(+1)	0.496064
	1.5900	0.529439	3.1694	0.499759	5.1823	0.440665	7.5339	0.385105
		-------		-------		-------		-------
	1.5900	0.217740	3.1694	0.316393	5.1823	0.409712	7.5339	0.471311
	5.6547(−1)	0.812720	1.1439	0.721799	1.9068	0.632099	2.8031	0.571296
		-------		-------		-------		-------
	7.3410(−2)	1.000000	1.8648(−1)	1.000000	3.3302(−1)	1.000000	5.2151(−1)	1.000000
		-------		-------		-------		-------
	2.8042(−2)	1.000000	6.5912(−2)	1.000000	1.0434(−1)	1.000000	1.5957(−1)	1.000000
p	3.2665	0.012169	7.4498	0.014399	1.2053(+1)	0.017293	1.8734(+1)	0.018170
	6.5119(−1)	0.067015	1.5796	0.084345	2.6120	0.105484	4.1362	0.112687
	1.6963(−1)	0.295830	4.3604(−1)	0.332582	7.4689(−1)	0.365660	1.2004	0.376170
	5.5778(−2)	0.745417	1.4436(−1)	0.701899	2.3873(−1)	0.663256	3.8346(−1)	0.648667
		-------		-------		-------		-------
	2.0500(−2)	1.000000	5.0195(−2)	1.000000	7.7218(−2)	1.000000	1.2129(−1)	1.000000

[a] Dashed lines separate the contracted functions. $A(\pm n)$ means $A \times 10^{\pm n}$.

is optimized by trial and error, and the contraction coefficients are either taken from atomic calculations in the parent set as in Ref. [9], or variationally optimized as in Ref. [17].

In this work, we examined up to 11 contraction patterns for each basis set, and the use of 0, 1, and 2 primitive GTFs appearing in two CGTFs. For each pattern, the contraction coefficients were variationally optimized to minimize the spin-restricted Roothaan–Hartree–Fock (RHF) atomic energy [18]. The contraction pattern leading to the lowest energy was chosen with *no attempt* to impose a uniform pattern for all first-row atoms. All atomic self-consistent-field (SCF) calculations were done with the ATOM program [19] modified to allow the optimization of contraction coefficients by the conjugate direction algorithm of Powell [20].

The lightest atoms pose a few special problems. Hydrogen and helium have only one occupied atomic orbital (AO), and hence contraction imposes no penalty on the atomic RHF energy. Thus the contraction coefficients are simply taken from uncontracted calculations and renormalized. The contraction pattern is chosen so that the tightest GTFs are grouped in one CGTF and all the other primitive GTFs are left uncontracted. This procedure is, of course, equivalent to a generalized contraction scheme for H and He.

Lithium and beryllium have only s-type AOs occupied in their ground states but a basis set without p-type GTF would be useless for meaningful molecular calculations. This problem is solved for Be by contracting wave functions [13] for the

TABLE VI. Exponents (α) and contraction coefficients (c) of the (9s5p)/[4s2p] CGTF basis sets for N, O, F, and Ne.[a]

	N		O		F		Ne	
	α	c	α	c	α	c	α	c
s	9.1556(+3)	0.001327	1.1852(+4)	0.001445	1.4846(+4)	0.001915	1.8135(+4)	0.001966
	1.3736(+3)	0.010240	1.7782(+3)	0.011147	2.2274(+3)	0.014770	2.7210(+3)	0.015165
	3.1273(+2)	0.052146	4.0486(+2)	0.056764	5.0714(+2)	0.075268	6.1951(+2)	0.077257
	8.8547(+1)	0.197926	1.1466(+2)	0.215473	1.4364(+2)	0.285328	1.7548(+2)	0.292825
	2.8756(+1)	0.538041	3.7279(+1)	0.584655	4.6740(+1)	0.710267	5.7133(+1)	0.701811
	1.0246(+1)	0.320789	1.3334(+1)	0.246860	-------	-------	-------	-------
	-------	-------	-------	-------	4.6740(+1)	0.032103	5.7133(+1)	0.045089
	1.0246(+1)	0.524498	1.3334(+1)	0.569590	1.6766(+1)	0.634574	2.0538(+1)	0.633958
	3.8443	0.517846	5.0385	0.471791	6.3699	0.379011	7.8363	0.368695
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	7.4650(−1)	1.000000	1.0136	1.000000	1.3164	1.000000	1.6548	1.000000
	-------	-------	-------	-------	-------	-------	-------	-------
	2.2475(−1)	1.000000	3.0250(−1)	1.000000	3.9009(−1)	1.000000	4.8755(−1)	1.000000
p	2.6667(+1)	0.018796	3.4493(+1)	0.020236	4.3907(+1)	0.021053	5.4752(+1)	0.021555
	5.9557	0.117689	7.7562	0.126799	9.9298	0.132049	1.2440(+1)	0.135355
	1.7440	0.383034	2.2820	0.394680	2.9313	0.400866	3.6819	0.404588
	5.5629(−1)	0.638961	7.1691(−1)	0.624014	9.1433(−1)	0.615513	1.1444	0.610111
	-------	-------	-------	-------	-------	-------	-------	-------
	1.7315(−1)	1.000000	2.1461(−1)	1.000000	2.6783(−1)	1.000000	3.3084(−1)	1.000000

[a] Dashed lines separate the contracted functions. $A(\pm n)$ means $A \times 10^{\pm n}$.

$1s^2 2s2p$ (^3P) state. The problem is a bit more subtle for Li because the excited $1s^2 2p$ (^2P) state has no occupied valence s-type AO. In previous work, such as Ref. [1], the s-GTFs were taken from the ground $1s^2 2s$ (^2S) state and the p-GTFs from the ^2P state. We follow a similar method. The exponents of the s- and p-GTF were taken from the ^2S and ^2P states, respectively, and the contraction coefficients and pattern of the resulting basis set were optimized for the ^2P state.

Results and Discussion

Atomic Energies

Consider the (9s5p)/[4s2p] double zeta sets first. Table I compares atomic RHF energies predicted by the Huzinaga–Dunning (HD) basis sets [9,10], the van Duijneveldt (VD) basis sets [11,12], and our B0, B1 and B2 basis sets which are contractions of the Koga–Thakkar sets [13] allowing 0, 1, and 2 primitive GTFs to occur in two different CGTFs. Despite the fact that the uncontracted basis sets of Koga and Thakkar always predict lower energies than the uncontracted sets of Huzinaga [10] and van Duijneveldt [11], the B0 sets do not always yield the lowest atomic energy. The HD set for B and the VD sets for B, C, N, O, and F predict lower energies than B0. Perhaps this is because the lower energy in the uncontracted sets of Ref. [13] is achieved by more efficient sharing of the primitive GTFs between AOs. The B1 sets

TABLE VII. Exponents (α) and contraction coefficients (c) of the (12s7p)/[7s4p] CGTF basis sets for Li, Be, B, and C.[a]

	Li		Be		B		C	
	α	c	α	c	α	c	α	c
s	7.2056(+3)	0.001377	1.4726(+4)	0.000649	2.3831(+4)	0.000677	3.5088(+4)	0.000670
	1.0797(+3)	0.010690	2.2064(+3)	0.005039	3.5706(+3)	0.005258	5.2574(+3)	0.005202
	2.4575(+2)	0.055804	5.0211(+2)	0.026338	8.1263(+2)	0.027495	1.1965(+3)	0.027207
	6.9591(+1)	0.229711	1.4216(+2)	0.108941	2.3012(+2)	0.113855	3.3884(+2)	0.112759
	2.2677(+1)	0.774239	4.6333(+1)	0.372164	7.5026(+1)	0.390462	1.1048(+2)	0.387704
	--------		1.6653(+1)	0.584765	2.7001(+1)	0.561959	3.9785(+1)	0.565654
	8.1342	0.399797	--------		--------		--------	
	3.1007	0.638965	1.6653(+1)	0.175059	2.7001(+1)	0.190582	3.9785(+1)	0.188092
	--------		6.3909	0.847351	1.0405(+1)	0.833209	1.5366(+1)	0.835353
	3.1007	0.136977	--------		--------		--------	
	1.2284	0.880219	2.5611	1.000000	4.2062	1.000000	6.2406	1.000000
	--------		--------		--------		--------	
	4.9392(−1)	1.000000	1.0431	1.000000	1.7351	1.000000	2.5893	1.000000
	--------		--------		--------		--------	
	9.3051(−2)	1.000000	2.6381(−1)	1.000000	4.7134(−1)	1.000000	7.4105(−1)	1.000000
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	4.5938(−2)	1.000000	1.1902(−1)	1.000000	1.9016(−1)	1.000000	2.9334(−1)	1.000000
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	2.1487(−2)	1.000000	4.9993(−2)	1.000000	7.4118(−2)	1.000000	1.1187(−1)	1.000000
p	1.1280(+1)	0.009365	2.5176(+1)	0.008491	3.9999(+1)	0.008421	6.1636(+1)	0.008244
	2.5963	0.059879	5.8681	0.058808	9.3406	0.059974	1.4444(+1)	0.060288
	7.4764(−1)	0.226884	1.7584	0.238068	2.8358	0.252929	4.4412	0.258479
	2.4245(−1)	0.807339	5.9700(−1)	0.793234	9.9115(−1)	0.776731	1.5716	0.770226
	--------		--------		--------		--------	
	9.0648(−2)	1.000000	2.2804(−1)	1.000000	3.7600(−1)	1.000000	5.9804(−1)	1.000000
	--------		--------		--------		--------	
	3.7362(−2)	1.000000	9.2477(−2)	1.000000	1.4581(−1)	1.000000	2.3019(−1)	1.000000
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	1.6037(−2)	1.000000	3.7652(−2)	1.000000	5.6094(−2)	1.000000	8.6596(−2)	1.000000

[a] Dashed lines separate the contracted functions. $A(\pm n)$ means $A \times 10^{\pm n}$.

with one duplicated primitive give consistently lower energies than the HD, VD, and B0 sets. The B1 energies are higher than the uncontracted ones by amounts ranging between 0.02 and 0.47 mhartrees. The B2 energies are lower still. We think the B1 sets are a good compromise and choose them to be our double zeta sets.

Consider the "quadruple" zeta sets next. Table II compares atomic RHF energies predicted by the C0 and C1 basis sets, which are our [7s4p] contractions of the Koga–Thakkar sets [13] allowing 0 and 1 primitive GTF to occur in two different CGTFs, with the uncontracted (12s7p) set [13] and the numerical Hartree–Fock limits [21]. The C1 energies are within 1 μhartree of the uncontracted ones, whereas the C0 energies can be as much as 0.11 mhartrees above the uncontracted ones. The C1 sets are our chosen quadruple zeta sets.

TABLE VIII. Exponents (α) and contraction coefficients (c) of the (12s7p)/[7s4p] CGTF basis sets for N, O, F, and Ne.[a]

	N		O		F		Ne	
	α	c	α	c	α	c	α	c
s	4.8335(+4)	0.001342	6.3655(+4)	0.000659	8.0955(+4)	0.001338	1.0024(+5)	0.000652
	7.2421(+3)	0.010419	9.5376(+3)	0.005115	1.2130(+4)	0.010395	1.5020(+4)	0.005062
	1.6482(+3)	0.054507	2.1707(+3)	0.026762	2.7606(+3)	0.054388	3.4184(+3)	0.026486
	4.6676(+2)	0.226001	6.1472(+2)	0.111012	7.8177(+2)	0.225664	9.6806(+2)	0.109907
	1.5220(+2)	0.778370	2.0045(+2)	0.382771	2.5493(+2)	0.778747	3.1569(+2)	0.379532
	--------		7.2230(+1)	0.572099			1.1379(+2)	0.576290
	5.4828(+1)	0.370936		--------	9.1880(+1)	0.372275		--------
	2.1209(+1)	0.665560	7.2230(+1)	0.183965	3.5612(+1)	0.664141	1.1379(+2)	0.181356
	--------		2.7972(+1)	0.838955		--------	4.4134(+1)	0.841240
	2.1209(+1)	0.106526		--------	3.5612(+1)	0.111996		--------
	8.6404	0.906538	1.1423(+1)	1.000000	1.4568(+1)	0.901547	1.8079(+1)	1.000000
	--------		--------		--------		--------	
	3.5990	1.000000	4.7730	1.000000	6.1013	1.000000	7.5847	1.000000
	--------		--------		--------		--------	
	1.0622	1.000000	1.4400	1.000000	1.8691	1.000000	2.3498	1.000000
	--------		--------		--------		--------	
	4.1529(−1)	1.000000	5.5984(−1)	1.000000	7.2310(−1)	1.000000	9.0531(−1)	1.000000
	--------		--------		--------		--------	
	1.5609(−1)	1.000000	2.0807(−1)	1.000000	2.6649(−1)	1.000000	3.3148(−1)	1.000000
p	8.7205(+1)	0.008156	1.1154(+2)	0.008325	1.4099(+2)	0.008401	1.7499(+2)	0.008433
	2.0478(+1)	0.060642	2.6206(+1)	0.062300	3.3151(+1)	0.063288	4.1180(+1)	0.063903
	6.3463	0.262389	8.1556	0.269698	1.0356(+1)	0.274073	1.2905(+1)	0.276881
	2.2624	0.765702	2.9196	0.757895	3.7182	0.753122	4.6434	0.750009
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	8.6191(−1)	1.000000	1.1047	1.000000	1.4022	1.000000	1.7483	1.000000
	--------		--------		--------		--------	
	3.2978(−1)	1.000000	4.1368(−1)	1.000000	5.1932(−1)	1.000000	6.4347(−1)	1.000000
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	1.2205(−1)	1.000000	1.4810(−1)	1.000000	1.8225(−1)	1.000000	2.2294(−1)	1.000000

[a] Dashed lines separate the contracted functions. $A(\pm n)$ means $A \times 10^{\pm n}$.

Molecular Tests

The double and quadruple zeta basis sets for H and He are listed in Tables III and IV. The double zeta (DZ) sets for the first row atoms are given in Tables V and VI whereas the quadruple zeta (QZ) sets are in Tables VII and VIII. Note that the contraction pattern is not uniform across the first row. Following Dunning [9], we recommend that in molecular calculations the double zeta set for H be scaled by factor of 1.2, that is, the exponents for H in Table III be multiplied by $(1.2)^2 = 1.44$. The quadruple zeta set for H is sufficiently flexible that we recommend it not be scaled.

TABLE IX.   Exponents of polarization functions: p-GTF for H,
spherical harmonic (five-membered) d-GTF for first-row atoms.

	Pa	Pb	Pc	2P
H	1.0	1.0	0.727	(1.05, 0.35)
Li	0.18	0.18		
Be	0.32	0.32		
B	0.70	0.388	0.343	(0.187, 0.822)
C	0.75	0.600	0.550	(0.288, 1.335)
N	0.80	0.864	0.817	(0.412, 1.986)
O	0.85	1.154	1.185	(0.535, 2.704)
F	0.90	1.496	1.640	(0.682, 3.559)
Ne		1.888	2.202	(0.852, 4.550)

Polarization functions are needed in molecular calculations. Dunning and Hay [1] recommended exponents for a p-GTF in H, and d-GTF in B to F, and d-GTF exponents for Li and Be can be obtained from a formula of Ahlrichs and Taylor [2]. This set of polarization functions is listed as Pa in Table IX. A different set of d-GTF for B to Ne [3], and the same polarization functions for H, Li, and Be are listed in Table IX as Pb. Dunning's [22] correlation consistent polarization functions, listed as Pc, are quite close to the Pb set. Any one of Pa, Pb, and Pc could be used with the DZ sets. The QZ sets can be supplemented by a pair of p-GTF for H, and two sets of d-GTF for B to Ne [3] as listed in Table IX under 2P, or by the (2d1f) or (3d2f1g) correlation consistent sets of Dunning [22].

As a test, self-consistent-field (SCF) geometry optimizations were performed with Gaussian 90 [23] for seven molecules: LiH, HF, BeH$_2$ in $D_{\infty h}$ symmetry, CH$_4$ in T_d symmetry, NH$_3$ in C_{3v} symmetry, H$_2$O in C_{2v} symmetry, and B$_2$H$_6$ in D_{2h} symmetry. The basis sets used are the Huzinaga-Dunning (HD) [9,10] double zeta sets and our DZ and QZ sets, with and without polarization functions. There are no HD double zeta sets for Li and Be, and the Dunning–Hay (9s5p)/[3s2p] split valence sets [1] were used instead.

In all cases, the molecular SCF energies (not tabulated) at the equilibrium geometry, both experimental and predicted, obeyed the following ordering: HD > DZ > QZ > HD + Pa > DZ + Pa > QZ + Pb > QZ + 2P. Table X compares the resulting geometries and dipole moments with experiment [24–29]. Our DZ sets give essentially the same results as the standard HD sets, although in most cases the DZ results are slightly closer to the largest basis results than the HD ones. As expected, polarization functions affect dipole moments and bond angles much more than bond lengths. In most cases, the QZ + 2P basis set predicts dipole moments noticeably closer to the experimental ones than either the HD + Pa or DZ + Pa sets.

Finally, as nontrivial tests of these basis sets, we consider the equilibrium geometries of hydrogen peroxide (H$_2$O$_2$) and hydrazine (N$_2$H$_4$) assuming C$_2$ symmetry. Both require the determination of dihedral angles that are very sensitive to details of the basis set, as Table XI shows clearly. Geometry optimizations were also carried

TABLE X. SCE equilibrium geometries and dipole moments μ for HF, LiH, CH$_4$, BeH$_2$, H$_2$O, NH$_3$, and B$_2$H$_6$.[a]

	HF		LiH		CH$_4$	BeH$_2$
	r(HF)	μ(HF)	r(LiH)	μ(LiH)	r(CH)	r(BeH)
HD	0.9196	2.383	1.6318	5.998	1.0834	1.3359
DZ	0.9218	2.391	1.6332	6.034	1.0829	1.3366
QZ	0.9174	2.373	1.6061	6.035	1.0810	1.3306
HD + Pa	0.9032	2.027	1.6236	5.949	1.0846	1.3357
DZ + Pa	0.9037	2.030	1.6265	5.984	1.0844	1.3358
QZ + Pb	0.8985	2.068	1.6061	6.013	1.0831	1.3308
QZ + 2P	0.9002	1.927	—	—	1.0819	—
Expt	0.9168	1.803	1.5957	5.829	1.085	—

	H$_2$O			NH$_3$		
	r(OH)	$\angle$HOH	μ(H$_2$O)	r(NH)	$\angle$HNH	μ(NH$_3$)
HD	0.9514	112.51	2.530	0.9944	116.28	1.368
DZ	0.9519	112.49	2.526	0.9939	116.26	1.367
QZ	0.9502	112.10	2.553	0.9935	115.15	1.429
HD + Pa	0.9439	106.71	2.177	1.0011	108.18	1.809
DZ + Pa	0.9438	106.72	2.174	1.0008	108.09	1.803
QZ + Pb	0.9410	106.93	2.246	0.9987	108.68	1.743
QZ + 2P	0.9414	106.38	2.010	0.9990	107.88	1.612
Expt	0.9575	104.51	1.847	1.0124	106.67	1.47

	B$_2$H$_6$			
	r(BB)	r(BH$_t$)	r(BH$_h$)	$\angle$H$_t$BH$_t$
HD	1.8303	1.1826	1.3402	123.00
DZ	1.8209	1.1831	1.3358	122.62
QZ	1.8003	1.1802	1.3213	122.30
HD + Pa	1.7944	1.1865	1.3284	122.48
DZ + Pa	1.7901	1.1866	1.3263	122.28
QZ + Pb	1.7809	1.1839	1.3209	122.04
QZ + 2P	1.7773	1.1833	1.3180	121.99
Expt	1.743	1.184	1.314	121.5

[a] Bond lengths (r) are in Å, bond angles in degrees, and dipole moments in debyes. The bridging and terminal hydrogens in B$_2$H$_6$ are denoted H$_b$ and H$_t$, respectively. Experimental data are from Refs. [24–29].

out using fourth-order many-body perturbation theory with triple substitutions neglected, that is, SDQ-MP4 [30].

First, consider hydrogen peroxide. Inclusion of polarization functions reduces the dihedral angle β by 30–45°! A previous complete MP4/HD + Pa calculation [31] gave r(OO) = 1.471 Å, r(OH) = 0.970 Å, $\angle$HOO = 99.3°, and β = 116.3° in reasonable agreement with our SDQ − MP4/DZ + Pa results. An MP2/6-311G(3d,2p)

TABLE XI.   SCF and SDQ − MP4 geometries for H_2O_2 and N_2H_4.[a]

	H_2O_2			
	r(OO)	r(OH)	$\angle$HOO	β
SCF/HD	1.4438	0.9564	102.77	144.3
SCF/DZ	1.4461	0.9571	102.72	142.9
SCF/QZ	1.4396	0.9542	102.06	163.1
SCF/HD + Pa	1.3922	0.9467	102.73	112.5
SCF/DZ + Pa	1.3931	0.9466	102.69	112.1
SCF/QZ + Pb	1.3888	0.9431	102.74	118.2
SCF/QZ + $2P$	1.3966	0.9431	102.68	111.2
SDQ − MP4/DZ + Pa	1.4615	0.9688	99.74	114.2
SDQ − MP4/QZ + $2P$	1.4652	0.9630	99.77	113.8
Expt [33]	1.4645	0.965	99.4	111.8

	N_2H_4						
	r(NN)	r(NH$_a$)	r(NH$_b$)	$\angle$H$_a$NH$_b$	$\angle$H$_a$NN	$\angle$H$_b$NN	β(H$_a$NNH$_b$)
SCF/HD	1.4064	0.9952	0.9984	115.13	113.01	116.67	92.1
SCF/DZ	1.4044	0.9947	0.9978	115.14	113.08	116.72	92.0
SCF/QZ	1.4099	0.9933	0.9967	114.15	112.07	115.77	92.1
SCF/HD + Pa	1.4117	0.9989	1.0015	108.94	108.53	112.67	89.8
SCF/DZ + Pa	1.4107	0.9986	1.0013	108.87	108.48	112.64	89.7
SCF/QZ + Pb	1.4111	0.9963	0.9993	109.25	108.71	112.73	90.2
SCF/QZ + $2P$	1.4166	0.9957	0.9984	108.67	108.24	112.17	90.1
SDQ − MP4/DZ + Pa	1.4419	1.0152	1.0185	106.99	106.51	111.37	89.6
SDQ − MP4/QZ + $2P$	1.4476	1.0091	1.0119	107.44	106.58	111.05	90.9
Expt [35]	1.449	1.021	1.021	(106.6)	106	112	91

[a] Bond lengths are in Å and angles in degrees. β is a dihedral angle. The hydrogens on each N in hydrazine are nonequivalent and are denoted by H$_a$ and H$_b$, respectively.

calculation [32] led to r(OO) = 1.450 Å, r(OH) = 0.962 Å, $\angle$HOO = 99.5°, and β = 111.1°. Good agreement with an experimental geometry of Koput [33] is obtained by our SDQ − MP4/QZ + $2P$ calculation: The bond distances agree within 0.002 Å, the $\angle$HOO to 0.4°, and the dihedral angle to 2°.

Next consider hydrazine. All calculations show that the two hydrogens, labelled H$_a$ and H$_b$, on each nitrogen are nonequivalent. A CISD(Q), configuration interaction with all single and double substitutions approximately corrected for unlinked clusters, calculation [34] in a 6 − 31G* basis led to r(NN) = 1.448 Å, r(NH$_a$) = 1.018 Å, r(NH$_b$) = 1.021 Å, $\angle$H$_a$NH$_b$ = 106.64°, $\angle$H$_a$NN = 105.94°, $\angle$H$_b$NN = 110.82°, and β(H$_a$NNH$_b$) = 90.05°. An experimental equilibrium structure is not known but a thermally averaged r_g structure has been determined by Kohata et al. [35]. They were unable to match the nonequivalent NH bonds with the corresponding angles and therefore reported an average r(NH). Moreover, they fixed $\angle$HNH at 106.6° from the CISD(Q) calculation [34]. Our SDQ − MP4/QZ + $2P$ calculation may be the best equilibrium geometry available to date.

We hope the basis sets presented in this paper will be generally useful to the quantum chemistry community.

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