

Figure 15.2 Shows that increasing the diversity of the basis set lowers The HF-SCF energy considerably, but comes *nowhere near* the exact experimental energy, regardless of the basis set size

TABLE 15.2 H₂O Hartree–Fock Calculations^a

Reference ^b	Basis Set ^c	Energy/ <i>E_h</i>	μ /D	θ	<i>R_{OH}</i> /Å
CCCBDB	STO-3G, 7	-74.966	1.71	100.0°	0.989
CCCBDB	3-21G, 13	-75.586	2.39	107.7°	0.967
Pitzer, Merrifield	Minimal STO, 7	-75.705	1.92	100.3°	0.990
CCCBDB	6-31G*, 19	-76.011	2.20	105.5°	0.947
CCCBDB	6-31G**, 25	-76.024	2.15	106.0°	0.943
CCCBDB	cc-pVDZ, 24	-76.027	2.04	104.6°	0.946
K. S. Kim et al.	6-311++G(2d,2p), 47	-76.057	2.02	106.3°	0.940
CCCBDB	cc-pVTZ, 58	-76.058	1.99	106.0°	0.941
CCCBDB	aug-cc-pVTZ, 92	-76.061	1.93	106.3°	0.941
Dunning et al.	[6s5p2d/3s1p], 43	-76.062	2.08	106.6°	0.941
Rosenberg et al.	(5s4p2d/3s1p) _{STO} , 39	-76.064	2.00	106.1°	0.940
CCCBDB	cc-pVQZ, 115	-76.0655	1.97	106.2°	0.940
CCCBDB	aug-cc-pVQZ, 172	-76.0667	1.94	106.3°	0.940
Amos	[8s6p4d2f/6s3p1d], 112	-76.0675		106.3°	0.940
K. S. Kim et al.	(13s8p4d2f/8s4p2d), 131	-76.0676	1.94	106.3°	0.940
Bakken et al.	cc-pV5Z, 201	-76.0678	1.96	106.33°	0.9396
Bakken et al.	aug-cc-pV5Z, 287	-76.0680	1.94	106.34°	0.9396
Cortez et al.	cc-pV6Z, 322	-76.06810	1.95	106.34°	0.9396
	aug-cc-pV6Z, 443	-76.06815	1.94	106.34°	0.9396
Pahl, Handy	special ^c	-76.06817		106.34°	0.9396
Estimated Hartree–Fock energy ^d		-76.068 ₃			
Nonrelativistic fixed–nuclei energy ^e		-76.438			
Experimental values		-76.480 ^c	1.85	104.5 ^{of}	0.9578 ^f

Estimated Hartree–Fock energy ^d	-76.068 ₃
Nonrelativistic fixed–nuclei energy ^e	-76.438
Experimental values	-76.480 ^c

This proves that electrons are particles, not clouds!

CCCBDB= Computational Chemistry Comparison Benchmark Data Base
Other properties get WORSE as basis increased!

Estimated Hartree–Fock energy ^d	-76.068 ₃
Nonrelativistic fixed–nuclei energy ^e	-76.438
Experimental values	-76.480 ^c 1.85 104.5 ^{of} 0.9578 ^f

^aEnergy/*E_h* is the total electronic energy including nuclear repulsion in hartrees at the calculated equilibrium geometry; μ , θ , and *R_{OH}* are the calculated electric dipole moment, equilibrium bond angle, and equilibrium bond length.

^bCCCBDB is the Computational Chemistry Comparison and Benchmark DataBase (Section 15.1); R. M. Pitzer and D. P. Merrifield, *J. Chem. Phys.*, **52**, 4782 (1970); K. S. Kim et al., *J. Chem. Phys.*, **97**, 6649 (1992); T. H. Dunning, R. M. Pitzer, and S. Aung, *J. Chem. Phys.*, **57**, 5044 (1972); B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.*, **63**, 2162 (1975) and B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.*, **65**, 4072 (1976); R. D. Amos, *J. Chem. Soc. Faraday Trans. 2*, **83**, 1595 (1987); K. S. Kim et al., op. cit; V. Bakken et al., *Mol. Phys.*, **96**, 653 (1999); M. H. Cortez et al., *J. Chem. Theory Comput.*, **3**, 1267 (2007); F. A. Pahl and N. C. Handy, *Mol. Phys.*, **100**, 3199 (2002).

^cThe number of basis functions is given. All the basis sets are GTFs except the Pitzer–Merrifield, Rosenberg et al., and Pahl–Handy sets. Brackets denote CGTF sets and parentheses denote an uncontracted set. A slash separates the oxygen and hydrogen basis functions. The Pahl–Handy set consists of plane waves and radial polynomials.

^dThis estimate is for the calculated Hartree–Fock equilibrium geometry. See D. Feller, C. M. Boyle, and E. R. Davidson, *J. Chem. Phys.*, **86**, 3424 (1987).

^eA. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997).

^fP. Jensen et al., *J. Mol. Spectrosc.*, **168**, 271 (1994); A. Császár et al., *J. Chem. Phys.*, **122**, 214305 (2005).

TABLE 16.1 H₂O Calculations That Include Correlation^a

Reference ^b	Method ^c / Basis Set	Energy / E _h	μ / D	θ	R _{OH}	α
Harrison, Handy	CISD/DZ	-76.150				
Harrison, Handy	FCI/DZ	-76.158				
CCCBDB	MP2(FC)/6-31G*	-76.197	2.24	104.0°	0.969	
CCCBDB	CISD(FC)/6-31G*	-76.198	2.24	104.2°	0.966	
CCCBDB	MP2(full)/6-31G*	-76.199	2.24	104.0°	0.969	
CCCBDB	CCSD(FC)/6-31G*	-76.206	2.25	103.9°	0.969	
CCCBDB	MP4(FC)/6-31G*	-76.207	2.25	103.8°	0.970	
CCCBDB	CCSD(T)(FC)/6-31G*	-76.208	2.25	103.8°	0.971	
CCCBDB	MP2(FC)/6-31G**	-76.220	2.20	103.8°	0.961	
CCCBDB	CISD(FC)/6-31G**	-76.221	2.19	104.2°	0.958	
CCCBDB	MP2(FC)/cc-pVDZ	-76.229	2.10	101.9°	0.965	
CCCBDB	CCSD(T)(FC)/cc-pVDZ	-76.241	2.10	101.9°	0.966	
Scuseria, Schaefer	CISDTQ/DZP	-76.270	2.13	104.5°	0.965	
Schaefer et al.	CISD/TZ2P	-76.312	1.94	104.9°	0.952	
CCCBDB	CISD(FC)/cc-pVTZ	-76.314	2.03	104.2°	0.955	
CCCBDB	MP2(FC)/6-31+G(3df,2p)	-76.318	2.02	104.5°	0.959	
CCCBDB	MP2(FC)/cc-pVTZ	-76.319	2.04	103.5°	0.959	
CCCBDB	CCSD(T)(FC)/cc-pVTZ	-76.332	2.04	103.6°	0.959	
Cortez et al.	CCSD(T)(FC)/cc-pV6Z	-76.372		104.4°	0.958	
Kim et al.	CISD(full)/(13s...2d) ^d	-76.382		104.8°	0.952	
Kim et al.	MP2(full)/(13s...2d)	-76.391		104.2°	0.959	
Kim et al.	CCSD(full)/(13s...2d)	-76.396		104.4°	0.956	
Kim et al.	CCSD(T)(full)/(13s...2d)	-76.406		104.1°	0.959	
Kim et al.	MP4(full)/(13s...2d)	-76.407		104.1°	0.960	
CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969	
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965	
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	0.969	
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 ^e				
Gurtubay, Needs	FN-DQMC	-76.428 ^e				
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	0.961	
<i>Nonrelativistic fixed-nuclei energy</i>		-76.438				
<i>Experimental values</i>		-76.480	1.85	104.5°	0.958	

^aSee footnote a to Table 15.2 in Section 15.6.

^bR. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983); cccbdb.nist.gov; G. E. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.*, **146**, 23 (1988); H. F. Schaefer, III et al., in *Yarkony*, Chapter 1; M. H. Cortez et al., *J. Chem. Theor. Comput.*, **3**, 1267 (2007); J. Kim et al., *J. Chem. Phys.*, **102**, 310 (1995); A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997); I. G. Gurtubay and R. J. Needs, *J. Chem. Phys.*, **127**, 124306 (2007).

^cFC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.

^d(13s...2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.

^eCalculated at a geometry close to the experimental geometry.

If electron-correlation is added to the wavefunction, all properties converge to experimentally observed values.

CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	0.969
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 ^e			
Gurtubay, Needs	FN-DQMC	-76.428 ^e			
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	0.961
<i>Nonrelativistic fixed-nuclei energy</i>		-76.438			
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^aSee footnote a to Table 15.2 in Section 15.6.

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^cFC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.

^d(13s...2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.

^eCalculated at a geometry close to the experimental geometry.

B3LYP is the most popular DFT method;
B3LYP/cc-pVTZ
99.87% of experiment;
Takes 5 sec on a PC

Basis Sets

<http://gaussian.com/glossary/g09/>
<http://gaussian.com/basissets/>

For all methods, choice of basis set must be done:

$MO_i = \varphi_i =$ linear combination of STOs or Gaussian type functions (GTFs)
(LC-STO, LC-GTF)

This includes Density Functional Theory (DFT) in which one does not have a wave function, yet works with Kohn-Sham orbitals, which are a fictitious reference system of non-interaction electrons of no physical significance allow one to construct the exact density (if and when someone learns how). There is no wavefunction in DFT

Diatomic basis functions are STOs

Typically use Gaussian Type Functions for non-linear larger triatomic and larger linear combinations of LC-GTF, because of the large number of e-e repulsion integrals that are very time-consuming for STOs.

a “primitive” GTF on atom b: $g_{ijk} = N x_b^i y_b^j z_b^k e^{-\alpha r_b^2}$

If $i + j + k = 0$, it is an **s** GTF

If $i + j + k = 1$, it is a **p** GTF only **3**

If $i + j + k = 2$, it is a **d** GTF typically **6** (6 ways $i+j+k=2$

If $i + j + k = 3$, it is an **f** GTF typically **10** (10 ways $i+j+k=3$)

etc.

e.g., the 6 d functions are : $x^2, y^2, z^2, xy, xz, yz$
used to seeing $5 = xy, xz, yz, x^2-y^2, r^2-3z^2$ i.e., "dz²"
which are all linear combinations of the 6 GTFs

The 6th wheel is $x^2 + y^2 + z^2 = r^2$, i.e., another s type (not d)

Requires more GTFs than STOs, but no 4-center e-e repulsion
(rs|tu) to calculate because product of 2 Gaussians is another Gaussian centered in at
different place.

In practice **contracted GTFs** (CGTFs) are used as the basis functions.

$$\text{A CGTF} = \chi_{\mu} = \sum_p d_{\mu p} g_p \quad \text{MO}_i = \varphi_i = \sum_{\mu} c_{\mu i} \chi_{\mu}$$

and the $d_{\mu p}$ are constants previously optimized for the given basis set and never change.

Some TERMS

minimal basis e.g., STO-3g

double zeta DZ (DZ stands for double zeta; what's zeta? ζ Often used as the orbital exponent instead of α); **DZ means two different sizes of everything; TZ =triple zeta= 3 different sizes, etc.**

quadruple QZ

5Z

6Z

split valence VDZ, VTZ, etc. inner shells are typically a single function
but valence shell gets multiple zeta

Examples: 3-21g : inner shells 1 contracted GTF (CGTF) made of 3 primitive GTFs
Valence shell is double zeta: 1 CGTF made of 2 primitive GTFs
and one made of 1 primitive GTF

6-31g : inner shells 1 contracted GTF (CGTF) made of 6 primitive GTFs
Valence shell is double zeta: 1 CGTF made of 3 primitive GTFs
and one made of 1 primitive GTF

Alpha	A α	Iota	I ι	Rho	Ρ ρ
Beta	B β	Kappa	Κ κ	Sigma	Σ σ
Gamma	Γ γ	Lambda	Λ λ	Tau	Τ τ
Delta	Δ δ	Mu	Μ μ	Upsilon	Υ υ
Epsilon	Ε ε	Nu	Ν ν	Phi	Φ φ
Zeta	Ζ ζ	Xi	Ξ ξ	Chi	Χ χ
Eta	Η η	Omicron	Ο ο	Psi	Ψ ψ
Theta	Θ θ	Pi	Π π	Omega	Ω ω

More TERMS

Polarization Basis sets

The previous page was about changing the size of orbitals without change in shape. But when in a molecule, the electron density on an atom is not the same as an isolated atom. This is accomplished by adding orbitals that have d character in the first row, and p character for H.

Examples: 6-31g* = 6-31g(d) adds 6 d-type GTFs for the atoms Li-Ca, and 10 f-type GTFs for Sc-Zn.

6-31g** = 6-31g(d,p) adds p character to H, in addition.

Diffuse Basis Sets

Anions particularly benefit from include large basis functions. e.g, 6-31+g includes extra large s and p functions on heavy atoms, and 6-31++g in addition at a diffuse s orbital to H

Even Larger Basis sets

For example 6-311++G(3df,3pd) is triple zeta set defined for H-Ar, that provides diffuse functions on all atoms, 3 sets of d and 1 set of f functions to non-H atoms, and 3 sets of p functions, 1 set of d functions for H. This also called a VTZ3PD, meaning valence triple zeta with triple polarization and diffuse on all atoms.

The above were developed by Pople.

Dunning and co-workers developed as series of basis functions denoted cc-pVnZ: i.e., cc-pVDZ, cc-pVTZ...,cc-pV6Z, which stand for *correlation-consistent, polarized valence double-zeta*, etc.

These basis sets were specifically designed to be used with methods that introduce electron correlation. Each set increases the orbital types as follows:

cc-pVDZ,	cc-pVTZ	cc-pVQZ,	cc-pV5Z	cc-pV6Z
[3s2p1d]	[4s3p2d1f]	[5s4p3d2f1g]	[6s5p4d3f2g1h]	[7s6p5d4f3g2h1i]

The number and degree of polarization (angular momentum) function increases rapidly from left to right, meaning more nodes, which is what is needed to introduce fine-grained correlation (**better dodging**). Doing a series of calculations with these basis sets on a molecule allow smooth extrapolation to what may be considered a near exact value.

If diffuse functions are added to the cc-pVnZ sets, they are called **aug- cc-pVnZ**.

Some General Terms

<http://gaussian.com/keywords/>

Names

key words

method/basis

for example:

hf/6-31g*

single point

geometry optimization

opt

vibrational frequency (must be opt first)

freq

transition state search

reaction path following

potential energy surface

solvation

Open Shell Calculations (some MOs have only 1 electron)

ROHF (restricted open shell) means electrons with opposite spin in same MO have the same spatial orbital.

UHF (unrestricted HF) means alpha and beta spins may have different spatial functions, thereby giving a slightly lower energy. (but, will not usually be eigenfunctions of the S^2 operator (i.e., neither singlet or triplet, for example)