

Chem 564

## CHMY 564 Reading #4 and Lecture 16

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**Basis Sets**

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The next approximation involves expressing the molecular orbitals as linear combinations of a pre-defined set of one-electron functions known as basis functions. These basis functions are usually centered on the atomic nuclei and so bear some resemblance to atomic orbitals. However, the actual mathematical treatment is more general than this, and any set of appropriately defined functions may be used.

An individual molecular orbital is defined as:

$$\phi_i = \sum_{\mu=1}^N c_{\mu i} \chi_{\mu} \quad [23]$$

where the coefficients  $c_{\mu i}$  are known as the *molecular orbital expansion coefficients*. The basis functions  $\chi_1 \dots \chi_N$  are also chosen to be normalized. We follow the usual notational convention of using roman subscripts on molecular orbital functions and Greek subscripts on basis functions. Thus,  $\chi_{\mu}$  refers to an arbitrary basis function in the same way that  $\phi_i$  refers to an arbitrary molecular orbital.

*Gaussian* and other ab initio electronic structure programs use gaussian-type atomic functions as basis functions. Gaussian functions have the general form:

$$g(\alpha, \vec{r}) = c x^n y^m z^l e^{-\alpha r^2} \quad [24]$$

where  $\vec{r}$  is of course composed of  $x$ ,  $y$  and  $z$ .  $\alpha$  is a constant determining the size (radial extent) of the function. In a gaussian function,  $e^{-\alpha r^2}$  is multiplied by powers (possibly 0) of  $x$ ,  $y$ , and  $z$ , and a constant for normalization, so that:

$$\int_{\text{all space}} g^2 = 1 \quad [25]$$

Thus,  $c$  depends on  $\alpha$ ,  $l$ ,  $m$  and  $n$ .

The following table summarizes the most commonly-used basis sets and provides some recommendations as to when each is appropriate:

Some Recommended Standard Basis Sets

Basis Set [Applicable Atoms]	Description	# Basis Functions		Default Function Types <sup>†</sup>
		1st row atoms	hydrogen atoms	
STO-3G [H-Xe]	Minimal basis set (stripped down in the interest of performance): use for more qualitative results on very large systems when you cannot afford even 3-21G.	5	1	6D
3-21G [H-Xe]	Split valence: 2 sets of functions in the valence region provide a more accurate representation of orbitals. Use for very large molecules for which 6-31G(d) is too expensive.	9	2	6D
6-31G(d) 6-31G* [H-Cl]	Adds polarization functions to heavy atoms: use for most jobs on up to medium/large sized systems. (This basis set uses the 6-component type d functions.)	15	2	6D 7F
6-31G(d,p) 6-31G** [H-Cl]	Adds polarization functions to the hydrogens as well: use when the hydrogens are the site of interest (for example, bond energies) and for final, accurate energy calculations	15	5	6D 7F
6-31+G(d) [H-Cl]	Adds diffuse functions: important for systems with lone pairs, anions, excited states.	19	2	6D 7F
6-31+G(d,p) [H-Cl]	Adds p functions to hydrogens as well: use when you'd use 6-31G(d,p) and diffuse functions are needed.	19	5	6D 7F
6-311+G(d,p) [H-Br]	Triple zeta: adds extra valence functions (3 sizes of s and p functions) to 6-31+G(d). Diffuse functions can also be added to the hydrogen atoms via a second +.	22	6	5D 7F
6-311+G(2d,p) [H-Br]	Puts 2 d functions on heavy atoms (plus diffuse functions), and 1 p function on hydrogens.	27	6	5D 7F
6-311+G(2df,2p) [H-Br]	Puts 2 d functions and 1 f function on heavy atoms (plus diffuse functions), and 2 p functions on the hydrogen atoms.	34	9	5D 7F
6-311++G(3df,2pd) [H-Br]	Puts 3 d functions and 1 f function on heavy atoms, and 2p functions and 1 d function on hydrogens, as well as diffuse functions on both.	39	15	5D 7F

<sup>†</sup> 6D denotes Cartesian, 6-component d functions, 5D and 7F denote "pure," 5-component d functions and 7-component f functions, respectively.

Here are three representative gaussian functions (s, p<sub>y</sub> and d<sub>xy</sub> types, respectively):

$$\begin{aligned} g_s(\alpha, \vec{r}) &= \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} \\ g_y(\alpha, \vec{r}) &= \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} y e^{-\alpha r^2} \\ g_{xy}(\alpha, \vec{r}) &= \left(\frac{2048\alpha^7}{\pi^3}\right)^{1/4} xy e^{-\alpha r^2} \end{aligned} \quad [26]$$

Linear combinations of *primitive gaussians* like these are used to form the actual basis functions; the latter are called *contracted gaussians* and have the form:

$$\chi_\mu = \sum_p d_{\mu p} g_p \quad [27]$$

where the  $d_{\mu p}$ 's are fixed constants within a given basis set. Note that contracted functions are also normalized in common practice.

All of these constructions result in the following expansion for molecular orbitals:

$$\phi_i = \sum_\mu c_{\mu i} \chi_\mu = \sum_\mu c_{\mu i} \left( \sum_p d_{\mu p} g_p \right) \quad [28]$$

## The Variational Principle

The problem has now become how to solve for the set of molecular orbital expansion coefficients,  $c_{\mu i}$ . Hartree-Fock theory takes advantage of the variational principle, which says that for the ground state of any antisymmetric normalized function of the electronic coordinates, which we will denote  $\Xi$ , then the expectation value for the energy corresponding to  $\Xi$  will always be greater than the energy for the exact wavefunction:

$$E(\Xi) > E(\Psi); \quad \Xi \neq \Psi \quad [29]$$

In other words, the energy of the exact wavefunction serves as a lower bound to the energies calculated by any other normalized antisymmetric function. Thus, the problem becomes one of finding the set of coefficients that minimize the energy of the resultant wavefunction.

# Basis Set Effects

In This Chapter:

**Split Valence Basis Sets**

**Polarized Basis Sets**

**Diffuse Functions**

**Pseudopotentials**

A basis set is the mathematical description of the orbitals within a system (which in turn combine to approximate the total electronic wavefunction) used to perform the theoretical calculation. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of the electrons in space. In the true quantum mechanical picture, electrons have a finite probability of existing anywhere in space; this limit corresponds to the infinite basis set expansion in the chart we looked at previously.

Standard basis sets for electronic structure calculations use linear combinations of gaussian functions to form the orbitals. *Gaussian* offers a wide range of pre-defined basis sets, which may be classified by the number and types of *basis functions* that they contain. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbitals. These basis functions themselves are composed of a linear combination of gaussian functions; such basis functions are referred to as *contracted functions*, and the component gaussian functions are referred to as *primitives*. A basis function consisting of a single gaussian function is termed *uncontracted*. These concepts are illustrated in detail in Advanced Exercise 5.5.

## Minimal Basis Sets

*Minimal basis sets* contain the minimum number of basis functions needed for each atom, as in these examples:

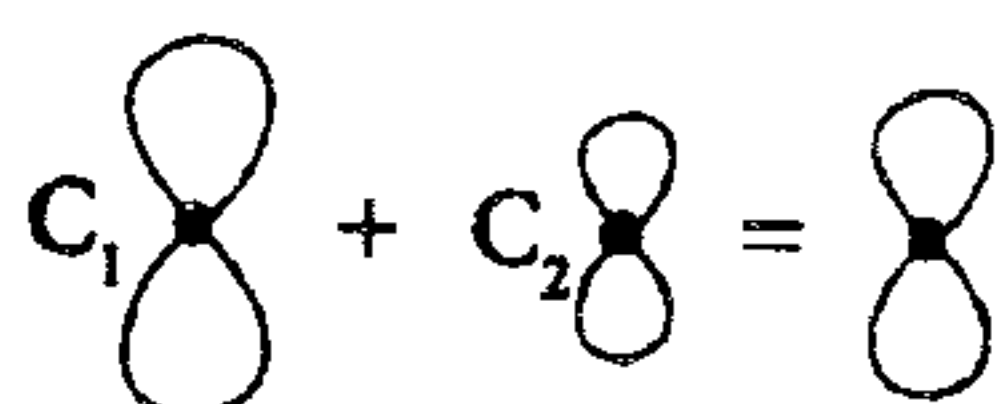
H: 1s

C: 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>

Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set is a minimal basis set (although it is not the smallest possible basis set). It uses three gaussian primitives per basis function, which accounts for the “3G” in its name. “STO” stands for “Slater-type orbitals,” and the STO-3G basis set approximates Slater orbitals with gaussian functions.<sup>†</sup>

<sup>†</sup> Slater orbitals have been demonstrated to be more accurate than a similar number of gaussian functions for molecular orbital computations, but they are not as mathematically convenient to use. This is why it is preferable to gaussian functions even if larger numbers of functions are required.

## Split Valence Basis Sets



The first way that a basis set can be made larger is to increase the number of basis functions per atom. *Split valence basis sets*, such as 3-21G and 6-31G,<sup>†</sup> have two (or more) sizes of basis function for each valence orbital. For example, hydrogen and carbon are represented as:

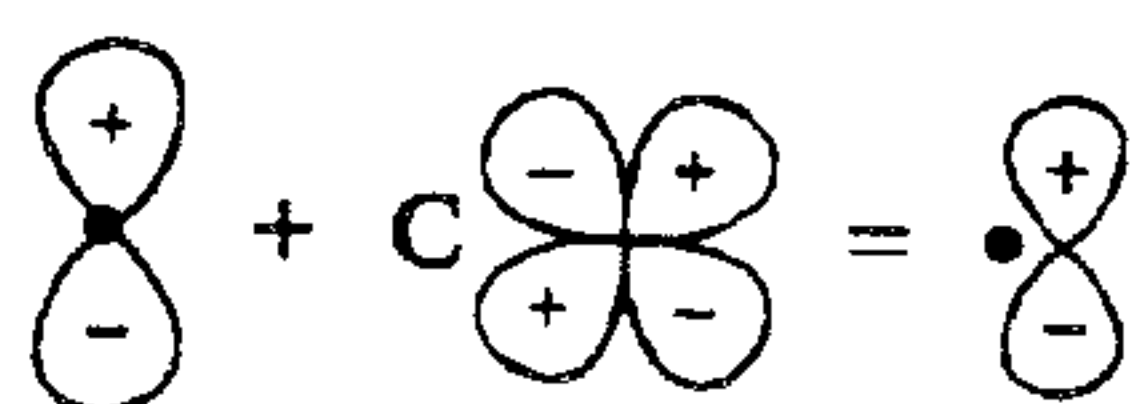
H: 1s, 1s'

C: 1s, 2s, 2s', 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>, 2p<sub>x</sub>', 2p<sub>y</sub>', 2p<sub>z</sub>'

where the primed and unprimed orbitals differ in size.

The *double zeta* basis sets, such as the Dunning-Huzinaga basis set (D95), form all molecular orbitals from linear combinations of two sizes of functions for each atomic orbital. Similarly, *triple split valence* basis sets, like 6-311G, use three sizes of contracted functions for each orbital-type.

## Polarized Basis Sets



Split valence basis sets allow orbitals to change size, but not to change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example, polarized basis sets add d functions to carbon atoms and f functions to transition metals, and some of them add p functions to hydrogen atoms.

So far, the only polarized basis set we've used is 6-31G(d). Its name indicates that it is the 6-31G basis set with d functions added to heavy atoms. This basis set is becoming very common for calculations involving up to medium-sized systems. This basis set is also known as 6-31G\*. Another popular polarized basis set is 6-31G(d,p), also known as 6-31G\*\*, which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms.

<sup>†</sup> For details on basis set nomenclature, consult the *Gaussian 94 User's Reference*.

## To The Teacher: Basis Set Details

The concept of polarization is often a difficult one to introduce. Students will typically ask, "Why do you need to include d function on a first row atom like carbon?" A good analogy for explaining this is the hybridization of orbitals discussed in Valence Bond Theory. For example,  $sp^3$  orbitals are formed on carbon by mixing filled 2s orbitals and partially-filled 2p orbitals. A natural extension to this is allowing some small contribution from unfilled 3d orbitals as well. Similarly, diffuse functions (discussed in the next section of this chapter) can be thought of as the mixing in of 3s orbitals.

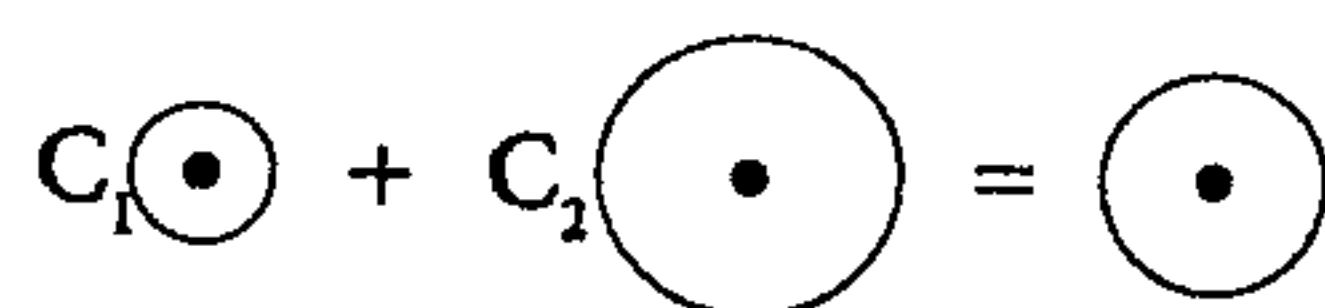
d polarization functions can consist of the 6 Cartesian types, which have added s character to the 5 pure types, or they can be the actual 5 pure types themselves:

*Cartesian:*  $d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$

*Pure:*  $d_{z^2-r^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$

Each polarized basis set includes which type is used as part of its definition (this is illustrated in Advanced Exercise 5.5). You may want to discuss the differences between the two. You can specify the use of one or the other type explicitly by including the **5D** or **6D** keyword in the route section (the keywords **7F** and **10F** similarly apply to all higher angular momentum basis functions).

## Diffuse Functions



Diffuse functions are large-size versions of s- and p-type functions (as opposed to the standard valence-size functions). They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, descriptions of absolute acidities, and so on.

The 6-31+G(d) basis set is the 6-31G(d) basis set with diffuse functions added to heavy atoms. The double plus version, 6-31++G(d), adds diffuse functions to the hydrogen atoms as well. Diffuse functions on hydrogen atoms seldom make a significant difference in accuracy.

**Example 5.1: Methanol vs. Methoxide Anion Optimizations**

file: e5\_01

We ran geometry optimizations of methanol (gauche form) and methoxide anion using both the 6-31G(d) and 6-31+G(d) basis sets in order to determine the effects of diffuse functions on the predicted structures. Here are the results:

Methanol	6-31G(d)	6-31+G(d)	Experiment
CO bond	1.3966	1.4019	1.427±0.007
CH bond	1.0873	1.0865	1.096±0.01
OH bond	0.9463	0.9464	0.956±0.015
COH angle	109.406	110.346	108.9±2.0
HCH angle	108.4127	108.6555	109.3±0.75
OCH angle	112.008	111.691	

Methoxide anion	6-31G(d)	6-31+G(d)	6-311++G(3df,2pd)
CO bond	1.3107	1.3304	1.3223
CH bond	1.1332	1.121	1.1209
HCH angle	101.5713	103.4298	103.2904
OCH angle	116.537	114.9919	115.1097

Diffuse functions have very little effect on the optimized structure of methanol but do significantly affect the bond angles in negatively charged methoxide anion. We can conclude that they are required to produce an accurate structure for the anion by comparing the two calculated geometries to that predicted by Hartree-Fock theory at a very large basis set (which should eliminate basis set effects).

## High Angular Momentum Basis Sets

Even larger basis sets are now practical for many systems. Such basis sets add multiple polarization functions per atom to the triple zeta basis set. For example, the 6-31G(2d) basis set adds two d functions per heavy atom instead of just one, while the 6-311++G(3df,3pd) basis set contains three sets of valence region functions, diffuse functions on both heavy atoms and hydrogens, and multiple polarization functions: 3 d functions and 1 f function on heavy atoms and 3 p functions and 1 d function on hydrogen atoms. Such basis sets are useful for describing the interactions between

electrons in electron correlation methods; they are not generally needed for Hartree-Fock calculations.

Some large basis sets specify different sets of polarization functions for heavy atoms depending upon the row of the periodic table in which they are located. For example, the 6-311+(3df,2df,p) basis set places 3 d functions and 1 f function on heavy atoms in the second and higher rows of the periodic table, and it places 2 d functions and 1 f function on first row heavy atoms and 1 p function on hydrogen atoms. Note that quantum chemists ignore H and He when numbering the rows of the periodic table.

**Example 5.2: PO Bond Distance**  
file: e5\_02

The optimized bond length in PO will serve to illustrate the effect of larger basis sets. Here are the predicted values for several medium and large basis sets (all optimizations were run at the B3LYP level of theory):

Basis Set	Bond Length (Å)
6-31G(d)	1.4986
6-311G(d)	1.4914
6-311G(2d)	1.4818
6-311G(2df)	1.4796
6-311G(3df)	1.4758

The experimental bond length is 1.476. Both the triple zeta basis set and multiple polarization functions are needed to produce a very accurate structure for this molecule.

## Basis Sets for Post-Third-Row Atoms

Basis sets for atoms beyond the third row of the periodic table are handled somewhat differently. For these very large nuclei, electrons near the nucleus are treated in an approximate way, via effective core potentials (ECPs). This treatment includes some relativistic effects, which are important in these atoms. The LANL2DZ basis set is the best known of these.



## Exercises

### Exercise 5.1: HF Bond Length

file: 5\_01

The experimental bond length for the hydrogen fluoride molecule is 0.917Å. Determine the basis set required to predict this structure accurately. Perform your optimizations at the MP4 level of theory (electron correlation is known to be important for this system).

**Solution** Here are the predicted values for several medium and large basis sets:

Basis Set	Bond Length (Å)
6-31G(d)	0.93497
6-31G(d,p)	0.92099
6-31+G(d,p)	0.94208
6-31++G(d,p)	0.92643
6-311G(d,p)	0.91312
6-311++G(d,p)	0.91720
6-311G(3df,3pd)	0.91369
6-311++G(3df,3pd)	0.91739

Exp = 0.917

The values in red are within 0.01Å of the experimental value. Using the 6-31G basis set, including diffuse functions on the hydrogen atom, improves the result over that obtained with diffuse functions only on the fluorine atom, although the best result with this basis set is obtained with no diffuse functions at all.

All of the geometries predicted with the 6-311G basis set are quite accurate. Adding two sets of diffuse functions yields a more accurate structure. However, adding additional polarization functions does not significantly affect the results. 6-311++G(d,p) thus appears to achieve the basis set limit for this model chemistry. ■

TABLE 6.2. Effect of Electron Correlation on 6-31G\* Equilibrium Geometries of AH<sub>n</sub> Molecules

Molecule	Point Group	Geometrical Parameter	HF <sup>a</sup>	MP2 <sup>b</sup>	MP3 <sup>c</sup>	MP4SDQ <sup>d</sup>	MP4 <sup>d</sup>	CID <sup>c</sup>	Expt.
H <sub>2</sub>	D <sub>∞h</sub>	r(HH)	0.730	0.738	0.742	0.744	0.744	0.746	0.742
LiH	C <sub>∞v</sub>	r(LiH)	1.636	1.640	1.643	1.648	1.648	1.649	1.596
CH <sub>4</sub>	T <sub>d</sub>	r(CH)	1.084	1.090	1.091	1.093	1.094	1.091	1.092
NH <sub>3</sub>	C <sub>3v</sub>	r(NH)	1.002	1.017	1.017	1.019	1.021	1.016	1.012
		<(HNH)	107.2	106.3	106.2	106.0	105.8	106.3	106.7
H <sub>2</sub> O	C <sub>2v</sub>	r(OH)	0.947	0.969	0.967	0.969	0.970	0.966	0.958
		<(HOH)	105.5	104.0	104.3	104.0	103.9	104.3	104.5
HF	C <sub>∞v</sub>	r(FH)	0.911	0.934	0.932	0.934	0.935	0.931	0.917
NaH	C <sub>∞v</sub>	r(NaH)	1.914						1.887
SiH <sub>4</sub>	T <sub>d</sub>	r(SiH)	1.475	1.484					1.481
PH <sub>3</sub>	C <sub>3v</sub>	r(PH)	1.403	1.415					1.420
		<(HPH)	95.4	94.6					93.3
H <sub>2</sub> S	C <sub>2v</sub>	r(SH)	1.326	1.340					1.336
		<(HSH)	94.4	93.3					92.1
HCl	C <sub>∞v</sub>	r(ClH)	1.266	1.280					1.275

<sup>a</sup>HP (1974); DLPBHP (1979); FPHBGDP (1982).

<sup>b</sup>DLPBHP (1979); W. J. Hehre and D. J. DeFrees, unpublished calculations.

<sup>c</sup>DKSP (1982).

<sup>d</sup>J. A. Pople, unpublished calculations.

3 pages

"Ab Initio Molecular Orbital Theory"

by W.J. Hehre, L. Radom, P.v.R. Schleyer & J.A. Pople

(Wiley, NY, 1985)

Molecule	Point Group	Geometrical Parameter	STO-3G <sup>a</sup>	3-21G <sup>b</sup>	3-21G(*) <sup>c</sup>	6-31G* <sup>d</sup>	6-31G** <sup>e</sup>	6-311G** <sup>f</sup>	Expt.
H <sub>2</sub>	D <sub>∞h</sub>	r(HH)	0.712	0.735	0.735	0.730	0.732	0.735	0.742
LiH	C <sub>∞v</sub>	r(LiH)	1.510	1.640	1.640	1.636	1.623	1.607	1.596
CH <sub>4</sub>	T <sub>d</sub>	r(CH)	1.083	1.083	1.083	1.084	1.084	1.084	1.092
NH <sub>3</sub>	C <sub>3v</sub>	r(NH)	1.033	1.003	1.003	1.002	1.001	1.001	1.012
		<(HNH)	104.2	112.4	112.4	107.2	107.6	107.4	106.7
H <sub>2</sub> O	C <sub>2v</sub>	r(OH)	0.990	0.967	0.967	0.947	0.943	0.941	0.958
		<(HOH)	100.0	107.6	107.6	105.5	105.9	105.4	104.5
HF	C <sub>∞v</sub>	r(FH)	0.956	0.937	0.937	0.911	0.901	0.896	0.917
NaH	C <sub>∞v</sub>	r(NaH)	1.654	1.926	1.930	1.914	1.912		1.887
SiH <sub>4</sub>	T <sub>d</sub>	r(SiH)	1.422	1.487	1.475	1.475	1.476		1.481
PH <sub>3</sub>	C <sub>3v</sub>	r(PH)	1.378	1.423	1.402	1.403	1.405		1.420
		<(HPH)	95.0	96.1	95.2	95.4	95.6		93.3
H <sub>2</sub> S	C <sub>2v</sub>	r(SH)	1.329	1.350	1.327	1.326	1.327		1.336
		<(HSH)	92.5	95.8	94.4	94.4	94.4		92.1
HCl	C <sub>∞v</sub>	r(ClH)	1.313	1.293	1.267	1.267	1.266		1.275

Amone  
0.961  
103.5

KH	C <sub>∞v</sub>	r(KH)	2.081						2.243
GeH <sub>4</sub>	T <sub>d</sub>	r(GeH)	1.431						1.525
AsH <sub>3</sub>	C <sub>3v</sub>	r(AsH)	1.457						1.511
		<(HAsH)	94.0						92.1
SeH <sub>2</sub>	C <sub>2v</sub>	r(SeH)	1.440						1.460
		<(HSeH)	92.5						90.6
HBr	C <sub>∞v</sub>	r(BrH)	1.412						1.414
RbH	C <sub>∞v</sub>	r(RbH)	2.211						2.367
SnH <sub>4</sub>	T <sub>d</sub>	r(SnH)	1.630						1.711
SbH <sub>3</sub>	C <sub>3v</sub>	r(SbH)	1.644						1.704
		<(HSbH)	94.4						91.6
TeH <sub>2</sub>	C <sub>2v</sub>	r(TeH)	1.624						1.658
		<(HTeH)	92.4						90.3
HI	C <sub>∞v</sub>	r(IH)	1.599						1.609

<sup>a</sup>LHCP (1971); BPH (1980); PLHS (1980); PBHHDS (1981); GBPPH (1982).

<sup>b</sup>BPH (1980); GBPPH (1982).

<sup>c</sup>PFHDPB (1982).

<sup>d</sup>HP (1974); FPHBGDP (1982).

<sup>e</sup>FPHBGDP (1982).

A2.10

TABLE 6.6. Hartree-Fock and Experimental Equilibrium Structures for  $AH_mBH_n$  Molecules. First- and Second-Row Elements

Molecule	Point Group	Geometrical Parameter <sup>a</sup>	STO-3G <sup>b</sup>	3-21G <sup>c</sup>	3-21G(*) <sup>d</sup>	6-31G* <sup>e</sup>	6-31G** <sup>f</sup>	6-311G*** <sup>g</sup>	Expt.
Li <sub>2</sub>	$D_{\infty h}$	$r(\text{LiLi})$	2.698	2.816	2.816	2.812	2.812	2.785	2.673
LiOH	$C_{\infty v}$	$r(\text{LiO})$	1.432	1.537	1.537	1.592			1.582
		$r(\text{OH})$	0.971	0.955	0.955	0.938			
LiF	$C_{\infty v}$	$r(\text{LiF})$	1.407	1.520	1.520	1.555	1.555	1.557	1.564
LiCl	$C_{\infty v}$	$r(\text{LiCl})$	1.933	2.112	2.091	2.072			2.021
B <sub>2</sub> H <sub>6</sub>	$D_{2h}$	$r(\text{BB})$	1.805	1.786	1.786	1.778	1.778	1.783	1.763
		$r(\text{BH}_a)$	1.154	1.182	1.182	1.185	1.185	1.185	1.201
		$r(\text{BH}_b)^h$	1.327	1.315	1.315	1.316	1.317	1.322	1.320
		$\angle(\text{H}_a\text{BH}_a)$	122.6	122.4	122.4	122.1	122.0	122.0	121.0
C <sub>2</sub> H <sub>2</sub>	$D_{\infty h}$	$r(\text{CC})$	1.168	1.188	1.188	1.185	1.186	1.182	1.203
		$r(\text{CH})$	1.065	1.051	1.051	1.057	1.057	1.056	1.061
C <sub>2</sub> H <sub>4</sub>	$D_{2h}$	$r(\text{CC})$	1.306	1.315	1.315	1.317	1.316	1.316	1.339
		$r(\text{CH})$	1.082	1.074	1.074	1.076	1.076	1.077	1.085
		$\angle(\text{HCH})$	115.6	116.2	116.2	116.4	116.5	116.6	117.8
C <sub>2</sub> H <sub>6</sub>	$D_{3d}$	$r(\text{CC})$	1.538	1.542	1.542	1.527			1.531
		$r(\text{CH})$	1.086	1.084	1.084	1.086			1.096
		$\angle(\text{HCH})$	108.2	108.1	108.1	107.7			107.8
HCN	$C_{\infty v}$	$r(\text{CN})$	1.153	1.137	1.137	1.133	1.133	1.127	1.153
		$r(\text{CH})$	1.070	1.050	1.050	1.059	1.059	1.058	1.065
HNC	$C_{\infty v}$	$r(\text{NC})$	1.170	1.160	1.160	1.154	1.155	1.149	1.169
		$r(\text{NH})$	1.011	0.983	0.983	0.985	0.984	0.984	0.994
CH <sub>2</sub> NH	$C_s$	$r(\text{CN})$	1.273	1.256	1.256	1.250	1.250	1.248	1.273
		$r(\text{CH}_{\text{syn}})$	1.091	1.081	1.081	1.084	1.085	1.086	1.103
		$r(\text{CH}_{\text{anti}})$	1.089	1.075	1.075	1.080	1.081	1.082	1.081
		$r(\text{NH})$	1.048	1.015	1.015	1.006	1.006	1.006	1.023
		$\angle(\text{H}_{\text{syn}}\text{CN})$	125.4	125.3	125.3	124.7	124.7	124.5	123.4

1.326  
1.098  
122.7  
(121.2)  
↑  
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TABLE 6.7. Effect of Electron Correlation on 6-31G\* Equilibrium Geometries of Two-Heavy-Atom Molecules Containing First- and Second-Row Elements

Molecule	Point Group	Geometrical Parameter <sup>a</sup>	HF/6-31G* <sup>b</sup>	MP2/6-31G* <sup>b</sup>	MP3/6-31G* <sup>c</sup>	CID/6-31G* <sup>c</sup>	Expt.
Li <sub>2</sub>	<i>D</i> <sub>∞h</sub>	<i>r</i> (LiLi)	2.812	2.782	2.760	2.724	2.673
LiOH	<i>C</i> <sub>∞v</sub>	<i>r</i> (LiO)	1.592	1.594			1.582
		<i>r</i> (OH)	0.938	0.960			
LiF	<i>C</i> <sub>∞v</sub>	<i>r</i> (LiF)	1.555	1.570	1.565	1.562	1.564
LiCl	<i>C</i> <sub>∞v</sub>	<i>r</i> (LiCl)	2.072	2.069			2.021
B <sub>2</sub> H <sub>6</sub>	<i>D</i> <sub>2h</sub>	<i>r</i> (BB)	1.778	1.754	1.753	1.750	1.763
		<i>r</i> (BH <sub>a</sub> )	1.185	1.190	1.192	1.190	1.201
		<i>r</i> (BH <sub>b</sub> ) <sup>d</sup>	1.316	1.311	1.312	1.310	1.320
		<(H <sub>a</sub> BH <sub>a</sub> )	122.1	121.7	121.6	121.5	121.0
C <sub>2</sub> H <sub>2</sub>	<i>D</i> <sub>∞h</sub>	<i>r</i> (CC)	1.185	1.218	1.206	1.202	1.203
		<i>r</i> (CH)	1.057	1.066	1.066	1.065	1.061
C <sub>2</sub> H <sub>4</sub>	<i>D</i> <sub>2h</sub>	<i>r</i> (CC)	1.317	1.336	1.334	1.328	1.339
		<i>r</i> (CH)	1.076	1.085	1.086	1.084	1.085
		<(HCH)	116.4	116.6	116.4	116.3	117.8
C <sub>2</sub> H <sub>6</sub>	<i>D</i> <sub>3d</sub>	<i>r</i> (CC)	1.527	1.527			1.531
		<i>r</i> (CH)	1.086	1.094			1.096
		<(HCH)	107.7	107.7			107.8
HCN	<i>C</i> <sub>∞v</sub>	<i>r</i> (CN)	1.133	1.177	1.158	1.154	1.153
		<i>r</i> (CH)	1.059	1.070	1.067	1.067	1.065
HNC	<i>C</i> <sub>∞v</sub>	<i>r</i> (CN)	1.154	1.187	1.174	1.171	1.169
		<i>r</i> (NH)	0.985	1.002	1.000	0.997	0.994
CH <sub>2</sub> NH	<i>C</i> <sub>s</sub>	<i>r</i> (CN)	1.250	1.282	1.275	1.268	1.273
		<i>r</i> (CH <sub>syn</sub> )	1.084	1.096	1.095	1.092	1.103
		<i>r</i> (CH <sub>anti</sub> )	1.080	1.090	1.090	1.087	1.081
		<i>r</i> (NH)	1.006	1.027	1.025	1.021	1.023
		<(H <sub>syn</sub> CN)	124.7	125.4	125.2	125.1	123.4
		<(H <sub>anti</sub> CN)	119.2	116.1	116.1	116.1	119.7
		<(HNC)	111.6	109.7	110.1	110.1	
CH <sub>3</sub> NH <sub>2</sub>	<i>C</i> <sub>s</sub>	<i>r</i> (CN)	1.450				

6.7

							EXP.	
		<(H <sub>syn</sub> CN)	124.7		125.4		125.1	123.4
		<(H <sub>anti</sub> CN)	119.2		116.1		116.1	119.7
		<(HNC)	111.6		109.7		110.1	110.5
CH <sub>3</sub> NH <sub>2</sub>	C <sub>s</sub>	r(CN)	1.453		1.465		1.466	1.471
		r(CH <sub>tr</sub> )	1.091		1.100		1.101	1.099
		r(CH <sub>g</sub> )	1.084		1.092		1.093	1.099
		r(NH <sub>a</sub> )	1.001		1.018		1.018	1.010
		<(NCH <sub>tr</sub> )	114.8		115.4		115.2	113.9
		<(NCH <sub>g,g'</sub> )	123.9		123.7		123.2	124.4
		<(H <sub>g</sub> CH <sub>g'</sub> )	107.5		107.5		107.5	108.0
		<(CNH <sub>a,a'</sub> )	126.3		123.6		123.6	125.7
		<(HNH)	106.9		105.9		105.9	107.1
CO	C <sub>∞v</sub>	r(CO)	1.114		1.151		1.135	1.128
H <sub>2</sub> CO	C <sub>2v</sub>	r(CO)	1.184		1.221		1.210	1.208
		r(CH)	1.092		1.104		1.104	1.116
		<(HCH)	115.7		115.6		116.0	116.5
CH <sub>3</sub> OH	C <sub>s</sub>	r(CO)	1.400		1.424		1.421	1.421
		r(CH <sub>tr</sub> )	1.081		1.090		1.091	1.094
		r(CH <sub>g</sub> )	1.087		1.097		1.098	1.094
		r(OH)	0.946		0.970		0.967	0.963
		<(OCH <sub>tr</sub> )	107.2		106.4		106.4	107.2
		<(OCH <sub>g,g'</sub> )	130.1		130.7		130.5	129.9
		<(H <sub>g</sub> CH <sub>g'</sub> )	108.7		108.7		108.8	108.5
		<(HOC)	109.4		107.4		107.7	108.0
CH <sub>3</sub> F	C <sub>3v</sub>	r(CF)	1.365		1.392		1.388	1.383
		r(CH)	1.082		1.092		1.093	1.100
		<(HCH)	109.8		109.8		109.9	110.6
CH <sub>3</sub> SiH <sub>3</sub>	C <sub>3v</sub>	r(CSi)	1.888				109.8	1.867
		r(CH)	1.086					1.093
		r(SiH)	1.478					1.485
		<(HCH)	108.3					107.7
		<(HSiH)	107.8					108.3

TABLE 6.61. Calculated and Experimental A—B Bond Dissociation Energies,  $D_e^a$ 

Bond Dissociation Reaction	6-31G**//6-31G*	MP2	MP3	MP4SDQ	MP4	Expt. <sup>b</sup>	Correlation Error
		/6-31G**//6-31G*					
$\text{CH}_3\text{—CH}_3 \rightarrow \text{CH}_3\cdot + \text{CH}_3\cdot$	69	99	96	95	97	97	28
$\text{CH}_3\text{—NH}_2 \rightarrow \text{CH}_3\cdot + \text{NH}_2\cdot$	58	93	87	86	88	93	35
$\text{CH}_3\text{—OH} \rightarrow \text{CH}_3\cdot + \text{OH}\cdot$	58	98	91	91	92	98	40
$\text{CH}_3\text{—F} \rightarrow \text{CH}_3\cdot + \text{F}\cdot$	69	113	105	106	108	114	45
$\text{NH}_2\text{—NH}_2 \rightarrow \text{NH}_2\cdot + \text{NH}_2\cdot$	34	73	65	65	67	73	39
$\text{HO—OH} \rightarrow \text{OH}\cdot + \text{OH}\cdot$	0	53	43	44	47	55	55
$\text{HO—F} \rightarrow \text{OH}\cdot + \text{F}\cdot$	-11	48	38	40	43	54	65
$\text{F—F} \rightarrow \text{F}\cdot + \text{F}\cdot$	-33	35	24	27	30	38	71

<sup>a</sup>Theoretical data from: J. A. Pople, unpublished calculations. See also: J. S. Binkley and M. J. Frisch, *Int. J. Quantum Chem., Symp.*, 17, 331 (1983).

<sup>b</sup>Experimental data from: D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, Selected Values for Inorganic and C<sub>1</sub> and C<sub>2</sub> Organic Substances in SI Units, *J. Phys. Chem. Ref. Data*, Suppl. no. 2 to vol. 11, 1982.

## THERMOCHEMICAL STABILITY

Even the simplest of the MP2/6-31G\*\* bond dissociation energies, the largest deviation from the experimental level of agreement between the 6-31G\*\* model with the 6-31G\*\* model is (in part) fortuitous, and the 6-31G\*\* model is a Plesset model with the 6-31G\*\* model. Plesset energies for this set of AH bond dissociation energies and MP3 reaction energies for bond breaking in F<sub>2</sub>. The results are much closer to the experimental values, only 3 kcal mol<sup>-1</sup>, and only 3 kcal mol<sup>-1</sup>. Thus, it is again likely that any residual errors are of that basis set.

## 6.5.3. Energies of Hydrogenation

How effective is Hartree-Fock in describing only closed-shell species for homolytic bond-breaking reactions is typical: H<sub>2</sub> in a given molecule to the same such reactions relate to the same to bonds involving hydrogen to give methane and ethane.

Full reduction of the energy requires an additional model.

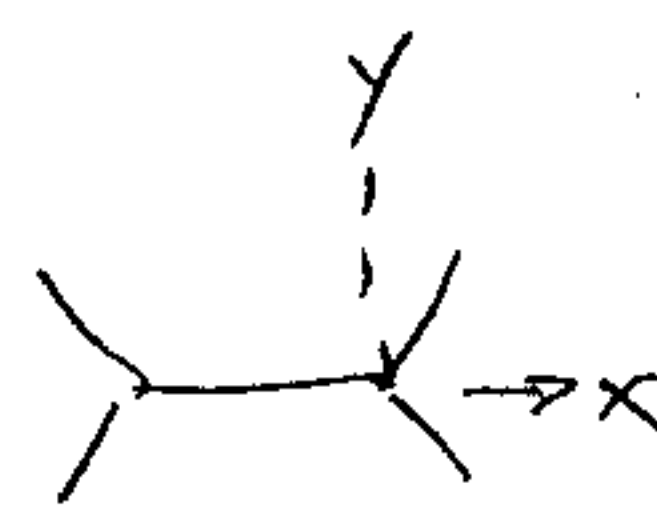
Multiple hydrogenation process consists of two steps.

the second of which is to add up the total hydrogenation data for a subset of one or two second-row atoms. These



TABLE 6.41. (Continued)

Molecule	Symmetry of Vibration	Description of Mode	Theoretical Frequency			Experimental Frequency <sup>d</sup>			
			HF/3-21G <sup>a</sup>	HF/6-31G <sup>*b</sup>	MP2/6-31G <sup>*c</sup>				
HBO	$\sigma^+$	BH stretch	3094	3042	2982	2849 <sup>g</sup>			
		BO stretch	1938	2022	1821	1817			
		bend	856	878	799	754			
C <sub>2</sub> H <sub>2</sub>	$\sigma_g^+$	CH stretch	3719	3719	3593	3374	(3497) <sup>h</sup>		
		CC stretch	2234	2247	2006	1974	(2011)		
		CH stretch	3596	3607	3516	3289	(3415)		
		CH bend	918	794	444	612	(624)		
		CH bend	902	883	783	730	(747)		
C <sub>2</sub> H <sub>4</sub>	$\pi_g$ $\pi_u$ $a_g$	CH <sub>2</sub> s-stretch	3238	3344	3231	3026	3210 (3153) <sup>i</sup>		
		CC stretch	1842	1856	1724	1623	1826 (1655)		
		CH <sub>2</sub> scis.	1522	1499	1425	1342	1388 (1370)		
		CH <sub>2</sub> twist	1165	1155	1083	1023	874 (1044)		
		CH <sub>2</sub> a-stretch	3371	3394	3297	3103	(3232)		
		CH <sub>2</sub> rock	1387	1353	1265	1236	1167 (1245)		
		CH <sub>2</sub> wag	1115	1095	980	949	1068 (969) — z		
		CH <sub>2</sub> wag	1157	1099	931	943	1056 (959)		
		CH <sub>2</sub> a-stretch	3403	3420	3323	3106	(3234) <sup>i</sup>		
		CH <sub>2</sub> rock	944	897	873	826	834 (843)		
		CH <sub>2</sub> s-stretch	3305	3321	3222	2989	(3147) —		
		CH <sub>2</sub> scis.	1640	1610	1523	1444	1412 (1473)		
		C <sub>2</sub> H <sub>6</sub>	$a_{1g}$	CH <sub>3</sub> s-stretch	3200	3201	3086	2954	(3043) <sup>j</sup>
				CH <sub>3</sub> s-deform	1571	1584	1493	1388	(1449)
CC stretch	1004			1063	1040	995	(1016)		
torsion	314			331	452	289	(303)		
	$a_{2u}$	CH <sub>3</sub> s-stretch	3196	3194	3104	2986	(3061)		



xy  
z  
xz  
y  
x

3210  
1826

AD