

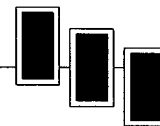
Exploring Chemistry with Electronic Structure Methods

Second Edition
(1995)

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Part 2: Model Chemistries

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F_3^- and $M^+F_3^-$	D. J. Tozer and C. P. Sosa, "The alkali metal trifluorides $M^+F_3^-$: How well can theory predict experiment?", <i>J. Chem. Phys.</i> , submitted (1996).
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Introduction

Real research studies with *Gaussian* involve not only larger molecules than the ones we've generally looked at so far, but also multiple calculations to thoroughly investigate systems of interest. Here is an example procedure that might be used to predict the total energy of a system:

A General
Procedure for
Predicting
Total Energies

- ◆ Perform a low-level geometry optimization with a medium-sized basis set, for example, a Hartree-Fock or B3LYP Density Functional Theory calculation with the 6-31G(d) basis set. (For very large systems, a smaller basis set might be necessary.)
- ◆ Predict the zero point or thermal energy by running a frequency job at the optimized geometry, using the same method and basis set. (Note that these two steps may be run via a single *Gaussian* job via the **Opt Freq** keyword.)
- ◆ If it is computationally feasible, improve on the structure by using it as the starting point for a more accurate optimization (using a larger basis set and/or run at a higher level of theory).
- ◆ Run a very high level single point energy calculation—for example, MP4 or QCISD(T)—at the newly optimized structure, using a large basis set. Final energies should be computed at the most accurate model chemistry that is practical for the system in question. You may also choose to compute the energy using a high-accuracy compound method (discussed in Chapter 7).

Once these steps are complete, the energy can then be computed as the sum of the final single point energy and the zero point or thermal energy, as appropriate.

This hypothetical sequence of jobs should give you a sense of how a real study might proceed. We'll begin this part of the book by looking at each of the components of a model chemistry in more detail.

Model Chemistries

In the first chapter, we described a model chemistry as an unbiased, uniquely defined, and uniformly applicable theoretical model for predicting the properties of chemical systems. A model chemistry generally consists of the combination of a theoretical method with a basis set. Each such unique pairing of method with basis set represents

a different approximation to the Schrödinger equation. Results for different systems generally may only be compared when they have been predicted via the same model chemistry. Different model chemistries may be compared and tested by comparing their results on the same systems to one another and to the results of experiments.

The chart below lists various model chemistries definable via traditional *ab initio* methods and standard basis sets:

		Electron Correlation →					Full CI
		HF	MP2	MP3	MP4	QCISD(T)	
B a s i s S e t	Minimal STO-3G						
	Split valence 3-21G						
	Polarized 6-31G(d)						
	6-311G(d,p)						
	Diffuse 6-311+G(d,p)						
	High ang. momentum 6-311+G(2d,p)						
	6-311++G(3df,3pd)						
	...						
	∞	HF Limit					
							Schrödinger Equation

Each cell in the chart defines a model chemistry. The columns correspond to different theoretical methods and the rows to different basis sets. The level of correlation increases as you move to the right across any row, with the Hartree-Fock method at the extreme left (including no correlation), and the Full Configuration Interaction method at the right (which fully accounts for electron correlation). In general, computational cost and accuracy increase as you move to the right as well. The relative costs of different model chemistries for various job types is discussed in

Chapter 6 (page 122); the relative accuracies of various model chemistries is discussed in Chapter 7 (page 146). See Appendix A for a discussion of the approximation techniques used by the various methods.

The rows of the chart correspond to increasingly larger basis sets. The specific basis sets cited there serve as examples, illustrating the additional types of functions added as you move down any column. The bottom row of the chart represents a completely flexible basis set, and the cells in it correspond to the *basis set limit* for each specified theoretical method.

The cell in the lower right corner of the chart represents the exact solution of the Schrödinger equation, the limit toward which all approximate methods strive. Full CI using an infinitely flexible basis set is the exact solution.[†]

The first cell in the last row of the table represents the *Hartree-Fock limit*: the best approximation that can be achieved without taking electron correlation into account. Its location on the chart is rather far from the exact solution. Although in some cases, quite good results can be achieved with Hartree-Fock theory alone, in many others, its performance ranges from only fair to quite poor. We'll look at some these cases in Chapters 5 and 6.

Choosing a model chemistry almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer. We'll provide some specific examples of these effects throughout the chapters in this part of the book.

Terminology

We will designate model chemistries using this naming convention (which we have already used in earlier chapters without comment):

energy_method/energy_basis_set // geometry_method/geometry_basis_set

where the model to the left of the double slash is the one at which the energy is computed, and the model to the right of the double slash is the one at which the molecular geometry was optimized. For example, *RHF/6-31+G(d,p)//RHF/6-31G(d)* means that the energy calculation was performed using Hartree-Fock theory and the 6-31+G(d,p) basis set on a structure previously optimized with Hartree-Fock theory and the 6-31G(d) basis set. Similarly, *MP4/6-311+G(2d,p)//MP2/6-31G(d)* specifies an MP4 single point energy calculation using the 6-311+G(2d,p) basis set computed at the MP2/6-31G(d) geometry.

[†] Non-relativistic, Born-Oppenheimer.

Recommendations for Selecting Research Models

The following table summarizes some recommended research-level model chemistries for predicting total energies for molecular systems of various sizes (the details of the reasons behind these choices will unfold along with the chapters in this part of the book), arranged in order of increasing computational cost:

Model Chemistry	MAD [†] /Max. Error on G2 Molecule Set	Range of Applicability [# heavy atoms]	Relative Cost
AM1 // AM1	19.7/176.3	many hundreds	1
B3LYP/6-31G(d) // AM1	11.7/54.2	hundreds	2.5
B3LYP/6-31G(d) // HF/6-21G(d)	8.0/54.2	100	10
B3LYP/6-311+G(3df,2df,2p) // HF/6-31G(d) [‡]	~3.2/~21.2	50-75	40-50
B3LYP/6-311+G(3df,2df,2p) // B3LYP/6-31G(d)	2.7/12.5	50	50-100
CBS-4	2.0/7.0	25	80-100
CBS-Q	1.0/3.8	10	400-800
CBS-APNO	0.5/1.5	5	>5000

[†] Mean absolute deviation.

[‡] Larger, floppy molecules might need to be optimized with a smaller basis set.

The general strategy embodied by this table is to select the most accurate calculation that is computationally practical for a given size system. Note that for the lower-cost methods, you will also need to add diffuse functions and/or additional polarization functions on the hydrogen atoms as appropriate for the systems you are studying.

All models include zero-point corrections via frequency calculations at the optimized geometry and using the same method. The ranges of applicability are approximate and represent what is “practical” as of this writing: we are assuming that the combined calculations must take less than a week of CPU time on a high-end workstation such as an IBM RS/6000 or DEC AlphaStation 600. Users with significantly greater or fewer CPU resources will need to adjust the applicability ranges and/or model chemistries accordingly.

The relative accuracies of various model chemistries are discussed in more detail in Chapter 7 (page 146). Resource requirements for various models and calculation types are discussed in Chapter 6 (page 122). Recommended models for NMR calculations were discussed earlier in this work (pages 21 and 53).

Zero-point and thermal energy corrections are usually computed with the same model chemistry as the geometry optimization. However, you may also choose to follow the common practice of always using the HF/6-31G(d) model chemistry for predicting zero-point and thermal energies (see page 149). Of course, such frequency calculations must follow a HF/6-31G(d) geometry optimization.

Selecting Methods for Zero-Point
and Thermal Energies

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:

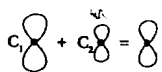
H: 1s

C: 1s, 2s, 2p_x, 2p_y, 2p_z

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.[†]

[†] 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,[†] have two (or more) sizes of basis function for each valence orbital. For example, hydrogen and carbon are represented as:

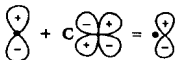
H: 1s, 1s'

C: 1s, 2s, 2s', 2p_x, 2p_y, 2p_z, 2p_x', 2p_y', 2p_z'

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.

[†] 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.

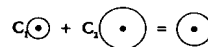
d polarization functions can consist of the 6 Cartesian types, which have added s character to the 5 pure types, or they can be the actual 5 pure types themselves:

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

Pure: $d_{3z^2-r^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$

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.

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

SC

Some Recommended Standard Basis Sets

Basis Set [Applicable Atoms]	Description	# Basis Functions 1st row atoms	hydrogen atoms	Default Function Types [†]
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

[†] 6D denotes Cartesian, 6-component d functions, 5D and 7F denote "pure," 5-component d functions and 7-component f functions, respectively.

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

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. ■

Solution

The two basis sets differ in the value of the exponent on the d functions for these elements:

Basis Set	Exponent			
	C	N	O	F
6-31G(d)	0.8	0.8	0.8	0.8
6-31G†	0.626	0.913	1.292	1.75

6-31G(d) arbitrarily assigns an exponent of 0.8 to all four elements. The dagger basis set uses the exponents from the d functions in the 6-311G basis set (you can run an additional job to verify this), which have been individually optimized for each element.

The larger exponent on nitrogen, oxygen and fluorine has the effect of making the resulting valence function tighter in extent (it falls off more quickly as you move away from the nucleus). The arbitrary 0.8 value results in an orbital that is too diffuse for these elements, falling outside of the valence region at times. As the value indicates, this is especially true for fluorine. In fact, the 6-31G(d) basis set (and its variations) is known to have difficulties with some fluorine-containing compounds. You should keep this in mind when modeling such molecular systems. ■

References**Basis Set Concepts and Definitions**

A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (New York: Macmillan, 1982), §3.6, pp. 180-190.

N,N-Dimethylformamide

G. Schultz and I. Hargittai, *J. Chem. Phys.*, **97**, 4966 (1993).

NMR Calculations

J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, "A Comparison of Models for Calculating Nuclear Magnetic Resonance Shielding Tensors," *J. Chem. Phys.*, **104**, 5497 (1996).

6-31G† and 6-31G†† Basis Sets

G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.*, **89**, 2193 (1988).

G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, **94**, 6081 (1991).

Selecting an Appropriate Theoretical Method*In This Chapter:***Semi-Empirical Models****The Limits of HF Theory****Electron Correlation and Post-SCF Methods****DFT Methods**

In this chapter, we will consider the other half of a model chemistry definition: the theoretical method used to model the molecular system. This chapter will serve as an introductory survey of the major classes of electronic structure calculations. The examples and exercises will compare the strengths and weaknesses of various specific methods in more detail. The final section of the chapter considers the CPU, memory and disk resource requirements of the various methods.

We will complete our consideration of model chemistries in Chapter 7, which describes compound methods for computing very accurate energies. It also includes a section discussing the relative accuracies of various model chemistries, as measured by their performance on the G2 set of test computations (see page 146).

Using Semi-Empirical Methods

Semi-empirical methods are characterized by their use of parameters derived from experimental data in order to simplify the approximation to the Schrödinger equation. As such, they are relatively inexpensive and can be practically applied to very, very large molecules. There are a variety of semi-empirical methods. Among the best known are AM1, PM3 and MNDO. *Gaussian* includes a variety of semi-empirical models, and they are also the central focus or present in many other programs including AMPAC, MOPAC, HyperChem and Spartan.

Semi-empirical methods are appropriate for a variety of modeling tasks, including the following:

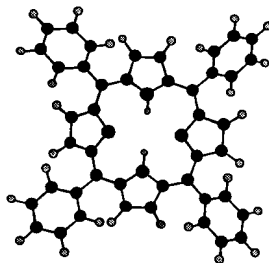
- ◆ For very large systems for which they are the only computationally practical quantum mechanical methods.
- ◆ As a first step for large systems. For example, you might run a semi-empirical optimization on a large system to obtain a starting structure for a subsequent Hartree-Fock or Density Functional Theory optimization. We used this approach in Exercise 3.6.
- ◆ For ground state molecular systems for which the semi-empirical method is well-parametrized and well-calibrated. In general, semi-empirical methods have been developed to focus on simple organic molecules.

- ◆ To obtain qualitative information about a molecule, such as its molecular orbitals, atomic charges or vibrational normal modes. In some cases, semi-empirical methods may also be successfully used to predict energy trends arising from alternate conformations or substituent effects in a qualitative or semi-quantitative way (but care must be taken in this area).

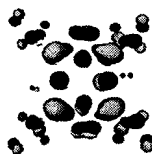
Example 6.1: TPP Molecular Orbitals file: e6_01

We will perform an AM1 calculation on tetraphenylporphyrin (TPP), pictured at right, in order to examine the four important molecular orbitals for this molecule: the second-highest and highest occupied MO's and the lowest and second-lowest unoccupied MO's (which we denote HOMO-1, HOMO, LUMO and LUMO+1, respectively).

The orbitals we are interested in are the ones numbered 112 through 115, which are plotted below:



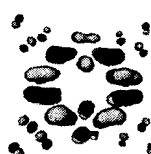
HOMO-1



HOMO



LUMO

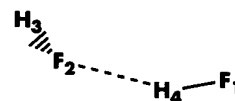


LUMO+1

We can make the following comments about these orbitals

- ◆ The HOMO-1 is localized on the central rings and has no contribution from the phenyl rings. There are nodal planes running perpendicular to the viewing plane every 45 degrees. There is another nodal plane that is the molecular plane.
- ◆ The HOMO is quite delocalized and has contributions from the phenyl rings. Nitrogen p orbitals figure prominently at the center of this orbital, and these are all in phase with one another (the positive lobes all line up).
- ◆ The LUMO is similar to the HOMO, but the lobes do not align. This appears more like an anti-bonding orbital.
- ◆ The LUMO+1 is very similar to the LUMO rotated by 90 degrees.

Example 6.2: HF Dimer file: e6_02



While orbitals may be useful for qualitative understanding of some molecules, it is important to remember that they are merely mathematical functions that represent solutions to the Hartree-Fock equations for a given molecule. Other orbitals exist which will produce the same energy and properties and which may look quite different. *There is ultimately no physical reality which can be associated with these images.* In short, individual orbitals are mathematical not physical constructs.

Limitations of Semi-Empirical Methods

Semi-empirical methods may only be used for systems where parameters have been developed for all of their component atoms. In addition to this, semi-empirical models have a number of well-known limitations. Types of problems on which they do not perform well include hydrogen bonding, transition structures, molecules containing atoms for which they are poorly parametrized, and so on. We consider one such case in the following example, and the exercises will discuss others.

Here, we optimize the structure of the $\text{HF}\cdots\text{HF}$ complex. The following table lists the results for our AM1, PM3[†] and HF/6-31+G(d) optimizations as well as an MP2/6-311++G(2d,2p) tight-convergence optimization taken from the Gaussian Quantum Chemistry Archive:

Parameter	AM1	PM3	HF	MP2
R(H-F)	0.83	0.94	0.92	0.92
R(H ₄ -F ₂)	2.09	1.74	1.88	1.84
R(F-F)	2.87	2.65	2.79	2.76
A(F-H ₄ -F)	159.3	159.8	168.3	170.6
A(H ₃ -F-F)	143.8	143.1	117.7	111.8

Both semi-empirical structures are quite far from the high-level results, especially with respect to the bond angles, although the AM1 bond lengths are also distorted. In contrast, the Hartree-Fock geometry is in reasonable agreement with the MP2 structure. Note that the Hartree-Fock optimization starting from the PM3 structure took 20 steps to converge (illustrating that semi-empirical structures are not always a good starting point for Hartree-Fock optimizations).

[†] Basis set keywords are not used for semi-empirical methods as they are inherent in the method's definition.

Electron Correlation and Post-SCF Methods

As we have seen throughout this book, the Hartree-Fock method provides a reasonable model for a wide range of problems and molecular systems. However, Hartree-Fock theory also has limitations. They arise principally from the fact that Hartree-Fock theory does not include a full treatment of the effects of *electron correlation*: the energy contributions arising from electrons interacting with one another. For systems and situations where such effects are important, Hartree-Fock results may not be satisfactory. The theory and methodology underlying electron correlation is discussed in Appendix A.

A variety of theoretical methods have been developed which include some effects of electron correlation. Traditionally, such methods are referred to as *post-SCF methods* because they add correlation corrections to the basic Hartree-Fock model. As of this writing, there are many correlation methods available in *Gaussian*, including the following:[†]

- ◆ Møller-Plesset perturbation theory: energies through fifth-order (accessed via the keywords **MP2**, **MP3**, **MP4**, and **MP5**), optimizations via analytic gradients[‡] for second-order (**MP2**), third-order (**MP3**) and fourth-order (without triples: **MP4SDQ**), and analytic frequencies for second-order (**MP2**).
- ◆ Quadratic CI energies, optionally including triples and quadruples terms (**QCISD**, **QCISD(T)**, and **QCISD(TQ)**) and optimizations via analytic gradients for **QCISD**.
- ◆ Coupled Cluster methods, including doubles (energies and optimizations) or singles and doubles (energies only), and optional triples terms (**CCD**, **CCSD**, **CCSD(T)**).
- ◆ Brueckner Doubles energies, optionally including triples and quadruples (**BD**, **BD(T)**, **BD(TQ)**).

All of these methods provide some improvement in the accurate description of molecules, but they vary quite a bit in terms of computational cost.

Methods based on Density Functional Theory also include some electron correlation effects (we'll consider them a bit later in this chapter). Of the traditional post-SCF methods, we'll be primarily using **MP2**, **MP4**, **QCISD** and **QCISD(T)** in this work.

[†] Consult the current *Gaussian User's Reference* for up-to-date information on method availability.

[‡] Numerical optimizations are available for methods lacking analytic gradients (first derivatives of the energy), but they are much, much slower. Similarly, frequencies may be computed numerically for methods without analytic second derivatives.

The Limits of Hartree-Fock Theory

Hartree-Fock theory is very useful for providing initial, first-level predictions for many systems. It is also reasonably good at computing the structures and vibrational frequencies of stable molecules and some transition states. As such, it is a good base-level theory. However, its neglect of electron correlation makes it unsuitable for some purposes. For example, it is insufficient for accurate modeling of the energetics of reactions and bond dissociation.

Example 6.3: HF Bond Energy

file: e6_03

There are many systems where electron correlation is essential for accurate predictions. One of the simplest is hydrogen fluoride, whose bond length we examined earlier. We calculate the bond energy by computing the energies of hydrogen and fluorine and then subtracting their sum from the energy of HF; this difference in energy must be accounted for by the H-F bond, which is present in the product but not in the reactants.

The following table lists the predicted bond energy of hydrogen fluoride computed with various methods using the 6-311++G(3df,3pd) basis set. We chose this basis set because it is near the basis set limit for this problem[†]; errors that remain can be assumed to arise from the method itself and not from the basis set.

Method	Computed Energy			ΔE^{bond} kcal/mol
	H atom	F atom	HF	
HF/STO-3G	-0.46658	-97.98651	-98.57082	73.9
HF	-0.49979	-99.40181	-100.05761	97.9
MP2		-99.60212	-100.33282	144.9
MP3		-99.61313	-100.33184	137.9
MP4(SDTQ)		-99.61731	-100.34306	141.8
QCISD		-99.61388	-100.33488	138.8
QCISD(T)		-99.61780	-100.34166	140.6
Experiment				141.2

We can compute all of the results except those in the first row by running just three jobs: **QCISD(T,E4T)** calculations on HF and fluorine and a Hartree-Fock calculation on hydrogen (with only one electron, the electron correlation energy is zero). Note that the **E4T** option to the **QCISD(T)** keyword requests that the triples computation be included in the component MP4 calculation as well as in the QCISD calculation (they are not needed or computed by default).

[†] We do not recommend using this basis set as a matter of course unless you have opulent CPU resources.

The experimental value for the H-F bond energy is 141.2 kcal·mol⁻¹. The Hartree-Fock value is in error by over 40 kcal·mol⁻¹ (we've also included the HF/STO-3G values to indicate just how bad very low level calculations can be). However, both the MP4 and QCISD(T) values are in excellent agreement with experiment.

The computed MP2 bond energy is too large, with higher levels of correlation lowering it. MP2 often overcorrects the Hartree-Fock results, while higher levels of correlation return to the proper range. For this particular system, both a high level of theory and a large basis set are needed for accurate predictions.

The MP_n Methods

Prior to the widespread usage of methods based on Density Functional Theory, the MP2 method was one of the least expensive ways to improve on Hartree-Fock and it was thus often the first correlation method to be applied to new problems. It can successfully model a wide variety of systems, and MP2 geometries are usually quite accurate. Thus, MP2 remains a very useful tool in a computational chemist's toolbox. We'll see several examples of its utility in the exercises.

There are problems for which MP2 theory fails as well, however. In general, the more unusual the electronic structure a system has, the higher level of theory that will be needed to model it accurately.

Higher-level MP orders are available for cases where the second-order solution of MP2 is inadequate. In practice, however, only MP4 sees wide use: MP3 is usually not sufficient to handle cases where MP2 does poorly, and it seldom offers improvements over MP2 which are commensurate with its additional computational cost. In contrast, although significantly more expensive than MP2, MP4 does successfully address many problems which MP2 cannot handle. We will examine some examples in the exercises.

For reasons similar to those for MP3, as well as its substantial computational cost, MP5 is also a rarely-used method.

Example: Convergence of the Møller-Plesset Orders

Nobes, Pople, Radom, Handy and Knowles have studied the convergence of the Møller-Plesset orders in some detail. They computed the energies of hydrogen cyanide, cyanide anion and cyano radical through order 24 as well as at the full Configuration Interaction level. Here are some of their results:

Method	HCN	CN ⁻	CN
MP2	-91.82033	-91.07143	-91.11411
MP3	-91.82242	-91.06862	-91.12203
MP4	-91.82846	-91.07603	-91.13538
MP5	-91.83129	-91.07539	-91.14221
MP6	-91.83233	-91.07694	-91.14855
MP7	-91.83264	-91.07678	-91.15276
MP8	-91.83289	-91.07699	-91.15666
Full CI	-91.83317	-91.07706	-91.17006
ΔE < 0.001 at	MP6	MP6	MP19
Full CI - MP4 (kcal·mol ⁻¹)	-2.96	-0.65	-21.76

These computations were performed using the STO-3G basis set for practicality reasons. While the absolute energies may be poor due to using such a small basis set, the trends across methods remain valid. For both HCN and CN⁻, the MP series converges fairly rapidly; we have noted the points at which the energy is within 0.001 Hartrees of the full CI value. However, for the CN radical, the same level of convergence is not achieved until MP19. This is a consequence of severe spin contamination in the Hartree-Fock reference determinant. We see the same effect in the difference between the full CI and MP4 results (the highest order which is practical for most systems). It is about 3 kcal·mol⁻¹ for HCN and less than 1 kcal·mol⁻¹ for the anion, but is over 21 kcal·mol⁻¹ for CN.

Coupled Cluster and Quadratic Configuration Interaction Methods

The Coupled Cluster and QCI methods represent a higher-level treatment of electron correlation beyond MP4, usually providing even greater accuracy. Moreover, there are systems for which the Møller-Plesset orders converge rather slowly that these methods can successfully model. Coupled Cluster and QCI methods are very similar to one another. Both iteratively include the effects of single and double substitutions, effectively adding higher order terms than MP4, and can optionally include triples and quadruples. As of this writing, *Gaussian* includes its implementations of these

methods via the **CCSD**, **CCSD(T)**, **QCISD**, **QCISD(T)** and **QCISD(TQ)** keywords. We will be using the QCISD and QCISD(T) methods in this chapter.

Including triply excited configurations is often needed in order to obtain very accurate results with MP4, QCISD or CCSD (see Appendix A for some of the computational details). The following example illustrates this effect.

Example 6.4: Optimization of Ozone file: e6_04

The structure of ozone is a well-known “pathological case” for electronic structure theory. Prior to the QCI and coupled cluster methods, it proved very difficult to model accurately. The following table summarized the results of geometry optimizations of ozone, performed at the MP2, QCISD and QCISD(T) levels using the 6-31G(d) basis set:

Parameter	MP2	QCISD	QCISD(T)	Experiment
R(O-O)	1.307	1.311	1.298	1.272
A(O-O-O)	113.2	114.6	116.7	116.8

When we speak of “accurate” geometries, we generally refer to bond lengths that are within about 0.01-0.02Å of experiment and bond and dihedral angles that are within about 1-2° of the experimentally-measured value (with the lower end of both ranges being more desirable). Only the QCISD(T) geometry can be termed accurate in the case of ozone (and its bond length is still a bit too long).

Density Functional Theory Methods

In the last few years, methods based on Density Functional Theory have gained steadily in popularity. The best DFT methods achieve significantly greater accuracy than Hartree-Fock theory at only a modest increase in cost (far less than MP2 for medium-size and larger molecular systems). They do so by including some of the effects of electron correlation much less expensively than traditional correlated methods.

DFT methods compute electron correlation via general *functionals*[†] of the electron density (see Appendix A for details). DFT functionals partition the electronic energy into several components which are computed separately: the kinetic energy, the electron-nuclear interaction, the Coulomb repulsion, and an exchange-correlation term accounting for the remainder of the electron-electron interaction (which is itself

[†] A *functional* is defined in mathematics as a function of a function. In Density Functional Theory, functionals are functions of the electron density (itself a function of coordinates in real space).

Traditional Functionals

divided into separate exchange and correlation components in most actual DFT formulations).

A variety of functionals have been defined, generally distinguished by the way that they treat the exchange and correlation components:

- ♦ *Local* exchange and correlation functionals involve only the values of the electron spin densities. Slater and $X\alpha$ are well-known local exchange functionals, and the local spin density treatment of Vosko, Wilk and Nusair (VWN) is a widely-used local correlation functional.
- ♦ *Gradient-corrected* functionals involve both the values of the electron spin densities and their gradients. Such functionals are also sometimes referred to as *non-local* in the literature. A popular gradient-corrected exchange functional is one proposed by Becke in 1988; a widely-used gradient-corrected correlation functional is the LYP functional of Lee, Yang and Parr. The combination of the two forms the B-LYP method (available via the **BLYP** keyword in *Gaussian*). Perdew has also proposed some important gradient-corrected correlation functionals, known as Perdew 86 and Perdew-Wang 91.

Hybrid Functionals

There are also several *hybrid functionals*, which define the exchange functional as a linear combination of Hartree-Fock, local, and gradient-corrected exchange terms; this exchange functional is then combined with a local and/or gradient-corrected correlation functional. The best known of these hybrid functionals is Becke's three-parameter formulation; hybrid functionals based on it are available in *Gaussian* via the **B3LYP** and **B3PW91** keywords. Becke-style hybrid functionals have proven to be superior to the traditional functionals defined so far, as the next example illustrates.

Example 6.5: CO₂ Structure and Atomization Energy

files: e6_05a (HF)
e6_05b (SVWN)
e6_05c (SVWN5)
e6_05d (BLYP)
e6_05e (B3LYP)
e6_05f (B3PW91)
e6_05g (MP2)

Atomization energies are often difficult to model accurately, and Hartree-Fock theory is seldom adequate. We will calculate the total atomization energy for carbon dioxide using a variety of DFT functionals by optimizing the structure of CO₂, performing a frequency calculation at the optimized structure in order to compute the zero-point energy, and then performing single point energy calculations for the carbon and oxygen atoms using tight SCF convergence (specified via **SCF=Tight**). The total atomization energy is then given by the formula: $D_0 = (E^C + 2E^O) - (E^{CO_2} + ZPE)$.

All jobs were run using the 6-31G(d) basis set. Our results are summarized in the following table, which also presents HF and MP2 values for comparison:

Method	Carbon Dioxide			Carbon E	Oxygen E	D ₀	Δ(Exp) (kcal·mol ⁻¹)
	R(C-O)	E	ZPE				
HF	1.143	-187.63418	0.0114	-37.68086	-74.78393	234.7	147.2
SVWN	1.171	-187.61677	0.0116	-37.56616	-74.64334	472.1	-90.2
SVWN5	1.172	-187.18193	0.0116	-37.45370	-74.48842	464.2	-82.3
BLYP	1.183	-188.56306	0.0112	-37.83202	-75.04696	392.8	-10.9
B3LYP	1.169	-188.58094	0.0114	-37.84628	-75.06062	377.8	4.1
B3PW91	1.168	-188.50695	0.0115	-37.82569	-75.03133	381.0	0.9
MP2	1.180	-188.10775	0.0111	-37.73297	-74.88004	378.8	3.1
Exp.	1.162					381.9	

The carbon dioxide zero-point energies in the table are scaled, using the scaling factors listed on page 64.[†]

All of the predicted structures are at least reasonably good. The two hybrid functionals produce the best structures, in excellent agreement with the experimental geometry. The SVWN and SVWN5[‡] functionals both produce good structures, while the BLYP geometry is the least accurate.

When we consider the predicted atomization energy, however, we see vast differences among the functionals. Like Hartree-Fock theory, the SVWN and SVWN5 functionals are completely inadequate for predicting this system's atomization energy (which is not an atypical result). The BLYP value is also quite poor.

Only the values computed by the hybrid functionals and MP2 are at all reasonable, and the B3PW91 value is in excellent agreement with experimental observations. The MP2 and B3LYP values are only modestly outside of the desired accuracy of 2 kcal·mol⁻¹. In Chapter 7, we will consider methods which were developed to consistently produce such very accurate thermochemical results.

[†] We've somewhat arbitrarily used the SVWN scale factor for SVWN5 and the B3LYP scale factor for B3PW91, since no one has computed scale factors for those functionals as of this writing.

[‡] These two functionals differ in the form of the VWN correlation functional that they use. References in the literature to the LSDA functional usually refer to SVWN5, but some earlier references meant SVWN by LSDA. Gaussian's LSDA keyword is a synonym for SVWN. However, other DFT programs refer to what Gaussian calls SVWN5 as LSDA. Check program documentation carefully when making comparisons of various "LSDA" functionals. For these reasons, we do not use the term LSDA at all.

Example 6.6: F₃⁻ Structure and Frequencies

file: e6_06



As a second example, we'll consider the structure and frequencies of the F₃⁻ anion. Tozer and Sosa studied this molecule at a variety of levels of theory, using the LANL2DZ basis set augmented with polarization and diffuse functions. We ran Opt Freq jobs using the SVWN5, BLYP and B3LYP functionals using the D95V+*(d)* basis set for all jobs (which is essentially the same basis set as that used by the original researchers). The following table summarizes the results of these calculations, as well as Tozer and Sosa's HF and MP2 results:

Method	R	Frequencies		
		ω ₁ Symm. Str.	ω ₂ Bend	ω ₃ Asymm. Str.
HF	1.646	501	315	522i
SVWN5	1.706	448	278	524
BLYP	1.777	390	255	477
B3LYP	1.728	425	268	441
MP2	1.733	392	251	699
Experiment		440 ± 10	260 ± 10	535 ± 20

All frequencies are scaled using the scaling factors listed in Chapter 4 (page 64).

The DFT and MP2 calculations produce very similar structures, although the BLYP bond length is again longer than those of the other functionals. Hartree-Fock theory predicts a bond length which is significantly shorter than the methods including electron correlation.

Hartree-Fock theory is quite poor at predicting the two lower frequencies; note also that it predicts an imaginary frequency for this structure (F₃⁻ is not a stable minimum at the Hartree-Fock level). MP2 does well only for the frequency corresponding to the bending mode. The SVWN5 frequencies are all in excellent agreement with the (rather approximate) experimental values, as are the B3LYP results for the lower two frequencies (B3LYP's prediction for the frequency corresponding to the symmetric stretching mode is somewhat low). The lower two BLYP frequencies follow the MP2 pattern and its highest frequency is also somewhat low, resulting in an overall vibrational spectrum which is only fair.

These SVWN5 results are somewhat fortuitous. Be careful not to overgeneralize from their agreement to experiment. We will see a different result in Exercise 6.7. Several other exercises will also include comparisons of DFT methods to Hartree-Fock theory, MP2 and other electron correlation methods.

Resource Usage

We've alluded to the fact that more accurate calculations come only at the expense of greater computational cost. In this section, we'd like to make that statement more concrete. We'll also look at memory requirements for jobs involving f and higher basis functions.

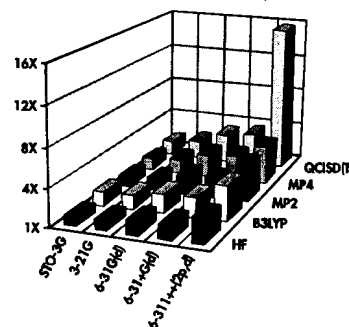
The table on the next page indicates the relationship between problem size and resource requirements for various theoretical methods. Problem size is measured primarily as the total number of basis functions (N) involved in a calculation, which itself depends on both the system size and the basis set chosen; some items depend also on the number of occupied and virtual (unoccupied) orbitals (O and V respectively), which again depend on both the molecular system and the basis set. The table lists both the formal, algorithmic dependence and the actual dependence as implemented in *Gaussian* (as of this writing), which may be somewhat better due to various computational techniques.

The table indicates how resource usage varies by problem size. For example, it indicates that for direct MP2 energy calculations, CPU requirements scale roughly as the fourth power of the number of basis functions if the number of electrons stays the same. Using the table with timings from previous jobs (using the same method and executed on the same computer system) should enable you to estimate how long a potential job will run.

Resource Usage by Method and Job Type

Method	Formal			Actual	
	CPU	Memory	Disk	CPU	Disk
Conventional SCF	N^4	N^2	N^4	$N^{3.5}$	$N^{3.5}$
Direct SCF	N^4	N^2	—	$N^{2.7}$	N^2
MP2 Energies					
Conventional	ON^4	N^2	N^4	ON^4	N^4
Direct	ON^4	OVN	—	O^2N^3	N^2
Semi-Direct	ON^4	N^2	VN^2	O^2N^3	VN^2
MP2 Gradients					
Conventional	ON^4	N^2	N^4	ON^4	N^4
Direct	ON^4	N^3	—	O^2N^3	N^2
Semi-Direct	ON^4	N^2	N^3	O^2N^3	N^3
MP4, QCISD(T)	O^3V^4	N^2	N^4	O^3V^4	N^4
Full CI (CPU)	$((O+V)/O!V!)^2$				

The following tables present timing information for single point energy calculations on CH_4 and C_5H_{12} , run at various levels of theory using a range of basis sets. All times are relative to the time used for the smallest job for each system (All jobs were run with *Gaussian 94*, using the default of 4 MW of memory for methane, 8 MW for pentane in general, with the two largest jobs requiring 16 MW). Timing ratios may vary depending on the computer architecture, but these sample values should give you a sense of the relative cost of various types of calculations.



Here are the results for CH_4 from an IBM RS/6000 Model 550:

Method	Basis Set [# basis functions]				
	STO-3G [9]	3-21G [17]	6-31G(d) [23]	6-31+G(d) [27]	6-311++G(2d,p) [55]
HF	1.0 [§]	1.1	1.5	1.5	2.6
B3LYP	1.4	1.5	2.0	2.1	3.8
MP2	1.1	1.3	1.9	2.0	3.9
MP4	1.3	1.5	2.4	2.6	4.0
QCISD(T)	1.5	1.9	3.0	3.4	15.6

[§] Job time: 11 seconds.

It may be somewhat surprising that there is so little variation in CPU time among the various jobs. However, most of these jobs are dominated by computational overhead since they are so small. Only the largest basis set jobs even approach typical research-sized problems. This table should serve as a caution against drawing performance conclusions from such small, "toy" jobs.

The performance data for C_5H_{12} is more representative of real-world problems (although this system is still on the small side). These jobs were all run on a Cray T-94 computer system[†]:

Method	Basis Set [# basis functions]			
	3-21G [69]	6-31G(d) [99]	6-31+G(d) [119]	6-311++G(2d,p) [219]
HF	1.0 [§]	3.8	5.0	23.1
B3LYP	2.5	5.0	7.0	31.0
MP2	1.4	7.6	10.2	60.8
MP4	29.9	131.5	296.7	4066.2
QCISD(T)	63.3	220.9	558.3	8900.3

[§] Job time: 6.4 seconds.

[†] The authors gratefully acknowledge Cray Research for providing the computer time to complete this study and thank John Carpenter and Carlos Sosa for their assistance.