Chapter

1

Computational Models & Model Chemistries

In This Chapter:

All chemists use models.[†] Beginning chemistry students use plastic models to help them understand and visualize the structures of molecules. Recently, both students and experienced researchers have begun to use chemical drawing programs for the same purpose.

Not all models are physical or pictorial objects. For example, the S_N2 mechanism is a simple model for a particular class of reactions that successfully explains a lot of chemistry. What all of these things have in common is that they use a set of pre-defined objects and rules to approximate real chemical entities and processes.

In a similar way, *computational chemistry* simulates chemical structures and reactions numerically, based in full or in part on the fundamental laws of physics. It allows chemists to study chemical phenomena by running calculations on computers rather than by examining reactions and compounds experimentally. Some methods can be used to model not only stable molecules, but also short-lived, unstable intermediates and even transition states. In this way, they can provide information about molecules and reactions which is impossible to obtain through observation. Computational chemistry is therefore both an independent research area and a vital adjunct to experimental studies.

An Overview of Computational Chemistry

There are two broad areas within computational chemistry devoted to the structure of molecules and their reactivity: *molecular mechanics* and *electronic structure theory.* They both perform the same basic types of calculations:

- Computing the energy of a particular molecular structure (spatial arrangement of atoms or nuclei and electrons). Properties related to the energy may also be predicted by some methods.

[†] In fact, certain philosophers of science argue that chemistry itself—indeed all science—functions as a model of certain aspects of the physical universe.

- Performing geometry optimizations, which locate the lowest energy molecular structure in close proximity to the specified starting structure.[†] Geometry optimizations depend primarily on the gradient of the energy—the first derivative of the energy with respect to atomic positions.
- Computing the vibrational frequencies of molecules resulting from interatomic motion within the molecule. Frequencies depend on the second derivative of the energy with respect to atomic structure, and frequency calculations may also predict other properties which depend on second derivatives. Frequency calculations are not possible or practical for all computational chemistry methods.

Molecular Mechanics

Molecular mechanics simulations use the laws of classical physics to predict the structures and properties of molecules. Molecular mechanics methods are available in many computer programs, including MM3, HyperChem, Quanta, Sybyl, and Alchemy. There are many different molecular mechanics methods. Each one is characterized by its particular *force field*. A force field has these components:

- A set of equations defining how the potential energy of a molecule varies with the locations of its component atoms.
- A series of *atom types*, defining the characteristics of an element within a specific chemical context. Atom types prescribe different characteristics and behavior for an element depending upon its environment. For example, a carbon atom in a carbonyl is treated differently than one bonded to three hydrogens. The atom type depends on hybridization, charge and the types of the other atoms to which it is bonded.
- One or more *parameter sets* that fit the equations and atom types to experimental data. Parameter sets define *force constants*, which are values used in the equations to relate atomic characteristics to energy components, and structural data such as bond lengths and angles.

Molecular mechanics calculations don't explicitly treat the electrons in a molecular system. Instead, they perform computations based upon the interactions among the nuclei. Electronic effects are implicitly included in force fields through parametrization.

This approximation makes molecular mechanics computations quite inexpensive computationally, and allows them to be used for very large systems containing many

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[†] Strictly speaking, optimizations do not always find minimum energy structures. This point will be discussed at length in Chapter 4.

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thousands of atoms. However, it also carries several limitations as well. Among the most important are these:

- Each force field achieves good results only for a limited class of molecules, related to those for which it was parametrized. No force field can be generally used for all molecular systems of interest.
- Neglect of electrons means that molecular mechanics methods cannot treat chemical problems where electronic effects predominate. For example, they cannot describe processes which involve bond formation or bond breaking. Molecular properties which depend on subtle electronic details are also not reproducible by molecular mechanics methods.

Electronic Structure Methods

Electronic structure methods use the laws of quantum mechanics rather than classical physics as the basis for their computations. Quantum mechanics states that the energy and other related properties of a molecule may be obtained by solving the Schrödinger equation:

$$\mathbf{H}\Psi = \mathbf{E}\Psi$$

For any but the smallest systems, however, exact solutions to the Schrödinger equation are not computationally practical. Electronic structure methods are characterized by their various mathematical approximations to its solution. There are two major classes of electronic structure methods:

- *Semi-empirical methods*, such as AM1, MINDO/3 and PM3, implemented in programs like MOPAC, AMPAC, HyperChem, and *Gaussian*, use parameters derived from experimental data to simplify the computation. They solve an approximate form of the Schrödinger equation that depends on having appropriate parameters available for the type of chemical system under investigation. Different semi-emipirical methods are largely characterized by their differing parameter sets.
- *Ab initio methods*, unlike either molecular mechanics or semi-empirical methods, use no experimental parameters in their computations. Instead, their computations are based solely on the laws of quantum mechanics—the first principles referred to in the name *ab initio*—and on the values of a small number of physical constants:
    - The speed of light
    - The masses and charges of electrons and nuclei
    - Planck's constant

Gaussian offers the entire range of electronic structure methods. This work provides guidance and examples in using all of the most important of them.

Ab initio methods compute solutions to the Schrödinger equation using a series of rigorous mathematical approximations. These procedures are discussed in detail in Appendix A, *The Theoretical Background.*

Semi-empirical and ab initio methods differ in the trade-off made between computational cost and accuracy of result. Semi-empirical calculations are relatively inexpensive and provide reasonable qualitative descriptions of molecular systems and fairly accurate quantitative predictions of energies and structures for systems where good parameter sets exist.

In contrast, ab initio computations provide high quality quantitative predictions for a broad range of systems. They are not limited to any specific class of system. Early ab initio programs were quite limited in the size of system they could handle. However, this is not true for modern ab initio programs. On a typical workstation, *Gaussian 94* can compute the energies and related properties for systems containing a dozen heavy atoms in just a few minutes. It can handle jobs of up to a few hundred atoms, and it can predict the structures of molecules having as many as one hundred atoms on the same size computer system.[†] Corresponding larger systems can be handled on supercomputer systems, based upon their specific CPU performance characteristics.

The ab initio methods in *Gaussian* are also capable of handling any type of atom, including metals. *Gaussian* computes a variety of molecular properties in addition to the energies and structures. *Gaussian* can investigate molecules in their excited states and in solution.

Density Functional Methods

Recently, a third class of electronic structure methods have come into wide use: *density functional methods.*[‡] These DFT methods are similar to ab initio methods in many ways. DFT calculations require about the same amount of computation resources as Hartree-Fock theory, the least expensive ab initio method.

DFT methods are attractive because they include the effects of *electron correlation*—the fact that electrons in a molecular system react to one another's motion and attempt to keep out of one another's way—in their model. Hartree-Fock calculations consider this effect only in an average sense—each electron sees and

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[†] Such large calculations will take on the order of one to a few days, depending on the exact molecular system and computer system. However, even larger calculations are possible, provided you are willing to allocate the necessary CPU resources to them. What constitutes a "practical" calculation is ultimately a matter of individual judgement. We'll look at how resource requirements vary with molecule size and calculation type at appropriate points in the course of this work.

[‡] Whether density functional methods are ab initio methods or not is a controversial question which we will not attempt to address.

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reacts to an averaged electron density—while methods including electron correlation account for the instantaneous interactions of pairs of electrons with opposite spin.[†] This approximation causes Hartree-Fock results to be less accurate for some types of systems. Thus, DFT methods can provide the benefits of some more expensive ab initio methods at essentially Hartree-Fock cost. See Appendix A for more details about these methods.

Model Chemistries

The theoretical philosophy underlying *Gaussian* is characterized by the following principle:

> A theoretical model should be *uniformly applicable* to molecular systems of any size and type, up to a maximum size determined only by the practical availability of computer resources.

This is in contrast to an alternate view which holds that the highest—most accurate—level of theory which is practical ought to be used for any given molecular system. The Schrödinger equation can be approximated much more closely for small systems than for large ones (and can even be solved exactly for the smallest possible system: the hydrogen atom). However, using different levels of theory for different size molecules makes comparing results among systems unreliable.

This principle has a number of implications:

- A theoretical model should be *uniquely defined* for any given configuration of nuclei and electrons. This means that specifying a molecular structure is all that is required to produce an approximate solution to the Schrödinger equation; no other parameters are needed to specify the problem or its solution.
- A theoretical model ought to be *unbiased*. It should rely on no presuppositions about molecular structure or chemical processes which would make it inapplicable to classes of systems or phenomena where these assumptions did not apply. It should not in general invoke special procedures for specific types of molecules.

The implementation of such a theoretical model is termed a theoretical-model chemistry, or simply a *model chemistry*.

[†] This is a bit of an oversimplification (see Appendix A).

Once a theoretical model has been defined and implemented, it should be systematically tested on a variety of chemical systems, and its results should be compared to known experimental values. Once a model demonstrates that it can reproduce experimental results, it can be used to predict properties of systems for which no data exist.

Other desirable features of a model chemistry include:

- *Size consistency*: the results given for a system of molecules infinitely separated from one another ought to equal the sum of the results obtained for each individual molecule calculated separately. Another way of describing this requirement is that the error in the predictions of any method should scale roughly in proportion to the size of the molecule. When size consistency does not hold, comparing the properties of molecules of different sizes will not result in quantitatively meaningful differences.

- Reproducing the *exact solution for the relevant n-electron problem*: a method ought to yield the same results as the exact solution to the Schrödinger equation to the greatest extent possible. What this means specifically depends on the theory underlying the method. Thus, Hartree-Fock theory should be (and is) able to reproduce the exact solution to the one electron problem, meaning it should be able to treat cases like H_2^+ and HeH^+ essentially exactly.

  Higher order methods similarly ought to reproduce the exact solution to their corresponding problem. Methods including double excitations (see Appendix A) ought to reproduce the exact solution to the 2-electron problem, methods including triple excitations, like QCISD(T), ought to reproduce the exact solution to the three-electron problem, and so on.

- *Variational*: the energies predicted by a method ought to be an upper bound to the real energy resulting from the exact solution of the Schrödinger equation.

- *Efficient*: calculations with a method ought to be practical with existing computer technology.

- *Accurate*: ideally, a method ought to produce highly accurate quantitative results. Minimally, a method should predict qualitative trends in molecular properties for groups of molecular systems.

Not every model can completely achieve all of these ideals. We'll look at the characteristics of the various methods in *Gaussian* in Appendix A.

Defining Model Chemistries

Gaussian includes many different model chemistries. The theoretical model chemistries in *Gaussian* have been subjected to the testing procedure described previously and so may be recommended for general use with any system for which they are computationally feasible.

Model chemistries are characterized by the combination of theoretical procedure and basis set. Every calculation performed with *Gaussian* must specify the desired theoretical model chemistry in addition to specifying the molecular system to consider and which results to compute for it.

Method

The *Gaussian* program contains a hierarchy of procedures corresponding to different approximation methods (commonly referred to as different *levels of theory*). Theoretical descriptions for each of them may be found in Appendix A. The ones we'll be concerned with most often in this work are listed in the following table:

Keyword	Method	Availability
HF	Hartree-Fock Self-Consistent Field	Through 2nd derivatives
B3LYP	Becke-style 3-Parameter Density Functional Theory (using the Lee-Yang-Parr correlation functional)	Through 2nd derivatives
MP2	2nd Order Møller-Plesset Perturbation Theory	Through 2nd derivatives
MP4	4th Order Møller-Plesset Perturbation Theory (including Singles, Doubles, Triples and Quadruples by default)	Energies only
QCISD(T)	Quadratic CI (Single, Doubles & Triples)	Energies only

More accurate methods become correspondingly more expensive computationally. Recommended uses of each level of theory will be discussed throughout the work, and a consideration of the entire range of electronic structure methods is the subject of Chapter 6.

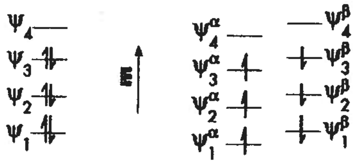
Basis Set

A *basis set* is a mathematical representation of the molecular orbitals within a molecule. The basis set can be interpreted as restricting each electron to a particular region of space. Larger basis sets impose fewer constraints on electrons and more accurately approximate exact molecular orbitals. They require correspondingly more computational resources. Available basis sets and their characteristics are discussed in Chapter 5.

Open vs. Closed Shell

Although not strictly part of a model chemistry, there is a third component to every *Gaussian* calculation involving how electron spin is handled: whether it is performed using an *open shell* model or a *closed shell* model; the two options are also referred to as *unrestricted* and *restricted* calculations, respectively. For closed shell molecules, having an even number of electrons divided into pairs of opposite spin, a spin restricted model is the default. In other words, closed shell calculations use doubly occupied orbitals, each containing two electrons of opposite spin.

Open shell systems—for example, those with unequal numbers of spin up and spin down electrons—are usually modeled by a spin unrestricted model (which is the default for these systems in *Gaussian*).[†] Restricted, closed shell calculations force each electron pair into a single spatial orbital, while open shell calculations use separate spatial orbitals for the spin up and spin down electrons (α and β respectively):



Unrestricted calculations are needed for systems with unpaired electrons, including:

- Molecules with odd numbers of electrons (e.g. some ions).
- Excited states.
- Other systems with unusual electronic structure (for example, 2 or more unpaired outer electrons).
- Processes such as bond dissociation which require the separation of an electron pair and for which restricted calculations thus lead to incorrect products (even though there is an even number of electrons).

In *Gaussian*, open shell calculations are requested by prepending the method keyword with a **U** (for unrestricted); similarly, closed shell calculations use an initial **R** (for example, **RHF** versus **UHF**, **RMP2** versus **UMP2** and so on).[‡]

Compound Models

Traditional electronic structure energy calculations consist of a single job. However, a calculation at a very accurate level of theory can take a very long time to complete. In an effort to achieve high accuracy results at less computational cost, several new model chemistries have been defined as a series of calculations to be run and a

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[†] It is also possible to define spin restricted open shell models (keyword prefix **RO**). See the *Gaussian User's Reference* for more information.

[‡] For some cases, additional measures must be taken to force an unrestricted wavefunction to be used (for example, **Guess=Mix** or **Guess=Alter**).

procedure for combining their results to predict an energy value for the molecule under investigation. Even though multiple calculations are run, their total computational cost is still significantly less than that of the single, high-accuracy model which they are designed to approximate.

We will consider several of these multi-job models in Chapter 7, including Gaussian-1 and Gaussian-2 theory and their variants and several Complete Basis Set (CBS) methods.

References

J. B. Foresman, "Ab Initio Techniques in Chemistry: Interpretation and Visualization," Chapter 14 in *What Every Chemist Should Know About Computing*, Ed. M. L Swift and T. J. Zielinski (ACS Books, Washington, D.C., 1996).

A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1982).

W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).

M. J. Frisch, Æ. Frisch and J. B. Foresman, *Gaussian 94 User's Reference* (Gaussian, Inc., Pittsburgh, 1995).

Chapter 2

Single Point Energy Calculations

In This Chapter:

Computing Energies of Molecular Systems

Examining Molecular Orbitals

Predicting Multipole Moments and Atomic Charges

In this chapter, we'll elaborate further on the type of calculation we performed in the *Quick Start*. A single point energy calculation is a prediction of the energy[†] and related properties for a molecule with a specified geometric structure. The phrase *single point* is key, since this calculation is performed at a single, fixed point on the potential energy surface[‡] for the molecule. The validity of results of these calculations depends on having reasonable structures for the molecules as input.

Single point energy calculations are performed for many purposes, including the following:

- To obtain basic information about a molecule.
- As a consistency check on a molecular geometry to be used as the starting point for an optimization.
- To compute very accurate values for the energy and other properties for a geometry optimized at a lower level of theory.
- When it is the only affordable calculation for a system of interest.

Single point energy calculations can be performed at any level of theory and with small or large basis sets. The ones we'll do in this chapter will be at the Hartree-Fock level with medium-sized basis sets, but keep in mind that high accuracy energy computations are set up and interpreted in very much the same way.

Setting Up Energy Calculations

Setting up an input file for a *Gaussian* single point energy calculation follows the steps we used in the *Quick Start*. To request this type of calculation, you must supply the following information:

- The type of job and level of theory for the calculation.
- A title for the job.

[†] That is, the sum of the electronic energy and nuclear repulsion energy of the molecule at the specified nuclear configuration. This quantity is commonly referred to as the *total energy*. However, more complete and accurate energy predictions require a thermal or zero-point energy correction (see Chapter 4, p. 68).

[‡] This term is defined in detail in Chapter 3.

- The structure of the molecule: its charge and spin multiplicity and the locations of the nuclei in space.

These items form the route section, the title section, and the molecule specification section of the input file, respectively. We'll look at each of them again briefly as we set up an input file for an energy calculation on formaldehyde.

The Route Section

The route section of a *Gaussian* input file specifies the kind of job you want to run as well as the specific theoretical method and basis set which should be used. All of these items are specified via keywords. Recall that the first line of the route section begins with a **#** sign (or **#T** to request terse output).

A single point energy is the default calculation type in *Gaussian*, so no special keyword is needed in the route section to request one (although you can include the **SP** keyword if you want to); simply specifying a procedure and basis set in the route section requests a single point energy calculation. We'll be running our formaldehyde calculation at the Hartree-Fock level, using the 6-31G(d) basis set.

Here are some other useful keywords for single point energy calculations (and other types of jobs as well):

Keyword	Effect
Test	Prevents *Gaussian* from entering this job's results into the site archive.
Pop=Reg	Displays highest five occupied and lowest five virtual molecular orbitals and other information not included in the output by default. Use **Pop=Full** to display all orbitals.
Units	Specifies that alternate units have been used in the molecule specification (discussed later in this section).
SCF=Tight	Requests that the wavefunction convergence criteria be made more rigorous. The default criteria for single point energy calculations are chosen as the best tradeoff between accuracy and computation speed, and they are generally accurate enough for comparing the energies of similar molecules and for predicting properties such as molecular orbitals and the dipole moment. **SCF=Tight** can be used to compute the energy using even tighter SCF convergence criteria. See Exercise 2.6 for more details about this topic.

We'll be including **Pop=Full** in our job in order to include information about all of the molecular orbitals in the output.

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The Title Section

This section of the input file consists of one or more lines describing the calculation in any way that the user desires. It often consists of just one line, and the section ends with a blank line.

The Molecule Specification Section

All molecule specifications require that the *charge* and *spin multiplicity* be specified (as two integers) on the first line of this section. The structure of the molecule follows, in either Cartesian coordinates, internal coordinates (a Z-matrix), or a combination of the two.

Charge on the Molecule

The charge is a positive or negative integer specifying the total charge on the molecule. Thus, 1 or +1 would be used for a singly-charged cation, -1 designates a singly-charged anion, and 0 represents a neutral molecule.

Spin Multiplicity

The *spin multiplicity* for a molecule is given by the equation $2S + 1$, where S is the total spin for the molecule. Paired electrons contribute nothing to this quantity. They have a net spin of zero since an alpha electron has a spin of +½ and a beta electron has a spin of -½. Each unpaired electron contributes +½ to S. Thus, a singlet—a system with no unpaired electrons—has a spin multiplicity of 1, a doublet (one unpaired electron) has a spin multiplicity of 2, a triplet (two unpaired electrons of like spin) has a spin multiplicity of 3, and so on.

Molecular Structure

The structure of the molecular system to be investigated follows the initial charge and spin multiplicity line in the molecule specification section. The structure may be obtained in a variety of ways: from the coordinates generated by or converted from a drawing program (as demonstrated in the *Quick Start*), by constructing a Z-matrix by hand (see Appendix B), from the experimental literature, from the results of a previous calculation, and so on.

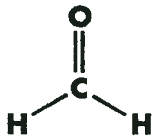
Multi-Step Jobs

Multiple *Gaussian* calculations can be performed from a single input file. See Appendix B (page 294) for details on multi-step jobs.

Locating Results in *Gaussian* Output

Example 2.1: Formaldehyde Single Point Energy

***file:* e2_01**



In this section, we'll identify the major results predicted by a single point energy calculation by looking at the output of a calculation on formaldehyde. Here is the complete input file:

```
#T RHF/6-31G(d) Pop=Full Test

Formaldehyde Single Point

0 1
C  0.0   0.0  0.0
O  0.0   1.22 0.0
H  0.94 -0.54 0.0
H -0.94 -0.54 0.0
```

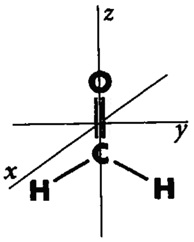
Here we give the molecule specification in Cartesian coordinates. The route section specifies a single point energy calculation at the Hartree-Fock level, using the 6-31G(d) basis set. We've specified a restricted Hartree-Fock calculation (via the **R** prepended to the **HF** procedure keyword) because this is a closed shell system. We've also requested that information about the molecular orbitals be included in the output with **Pop=Reg**.

We'll look at each of the major items separately, in the order in which they appear in the output.

Standard Orientation Geometry

This section displays positioning of the atoms in the molecule used by the program internally, in Cartesian coordinates. This orientation is chosen for maximum calculation efficiency, and corresponds to placing the center of nuclear charge for the molecule at the origin. Most molecular properties are reported with respect to the standard orientation. Note that this orientation usually does not correspond to the one used in the input molecule specification; the latter is printed earlier in the output as the "Z-matrix orientation."

Here is the standard orientation generated for formaldehyde:



```
                  Standard orientation:
 ---------------------------------------------------------
 Center  Atomic        Coordinates (Angstroms)
 Number  Number       X            Y            Z
 ---------------------------------------------------------
 1          6     0.000000     0.000000    -0.542500
 2          8     0.000000     0.000000     0.677500
 3          1     0.000000     0.940000    -1.082500
 4          1     0.000000    -0.940000    -1.082500
 ---------------------------------------------------------
```

The molecule is positioned in the YZ-plane, with the C=O bond coinciding with the Z-axis.

Energy

The total energy of the system, computed at the Hartree-Fock level, is given by this line of the output:

```
SCF Done:  E(RHF) =  -113.863697598       A.U. after  6 cycles
```

One hartree is 627.51 kcal-mol^{-1}

The value is in hartrees. The number of cycles it took the SCF calculation to converge is also given on this line (refer to Appendix A for a discussion of the iterative nature of the SCF method). When we discuss energies in this work, we will generally use hartrees (atomic units); when we discuss energy differences, kcal-mol^{-1} will often be a more convenient unit (especially when comparing calculation predictions to experimental results).

In a higher level energy calculation, values for the energy computed using the more accurate procedure appear shortly after the Hartree-Fock energy. Here is the output from a formaldehyde calculation done at the MP2 level (**RMP2** replaces **RHF** in the route section:

```
E2 =    -0.3029540001D+00     EUMP2 =    -0.11416665769315D+03
```

The number following EUMP2 is the predicted energy at the MP2 level, approximately -114.16666 hartrees.

Here is part of the energy output from an MP4 calculation:

```
SCF DONE: E(RHF) = -113.863697598 A.U. AFTER 6 CYCLES
...
E2 =    -0.3029540001D+00    EUMP2 =  -0.11416665769315D+03
...
E3= -0.25563412D-02 EUMP3= -0.1141669850323D+03
E4(DQ)= -0.13383605D-02 UMP4(DQ)= -0.1141669872345D+03
E4(SDQ)= -0.31707330D-02 UMP4(SDQ)= -0.1141678953224D+03
E4(SDTQ)= -0.10020409D-01 UMP4(SDTQ)= -0.114168745328D+03
```

Notice that the energies for all of the lower-level methods—HF, MP2, MP3, MP4(DQ) and MP4(SDQ)—are also given in a full MP4(SDTQ) calculation.

Molecular Orbitals and Orbital Energies

The **Pop=Reg** keyword in the route section requested data about the molecular orbitals be included in the output. They appear at the beginning of the population analysis section (output is shortened):

```
Molecular Orbital Coefficients
                          1          2         3          4          5
                      (A1)--O    (A1)--O   (A1)--O    (A1)--O    (B2)--O
 EIGENVALUES — -20.58275 -11.33951 -1.39270 -0.87260 -0.69717
 1   1 C    1S      0.00000    0.99566 -0.11059 -0.16263   0.00000
 2          2S     -0.00047    0.02675  0.20980  0.33995   0.00000
 3          2PX     0.00000    0.00000  0.00000  0.00000   0.00000
 4          2PY     0.00000    0.00000  0.00000  0.00000   0.42014
 5          2PZ    -0.00007    0.00066  0.17258 -0.18448   0.00000
 16 2 O     1S      0.99472    0.00038 -0.19672  0.08890   0.00000
 17         2S      0.02094   -0.00025  0.44186 -0.20352   0.00000
 18         2PX     0.00000    0.00000  0.00000  0.00000   0.00000
 19         2PY     0.00000    0.00000  0.00000  0.00000   0.32128
 20         2PZ    -0.00153    0.00029 -0.13538 -0.14221   0.00000
 31 3 H     1S      0.00002   -0.00210  0.03017  0.17902   0.19080
 33 4 H     1S      0.00002   -0.00210  0.03017  0.17902  -0.19080
```

The atomic orbital contributions for each atom in the molecule are given for each molecular orbital, numbered in order of increasing energy (the MO's energy is given in the row labeled `EIGENVALUES` preceding the orbital coefficients). The symmetry of the orbital and whether it is an occupied orbital or a virtual (unoccupied) orbital appears immediately under the orbital number.

When looking at the orbital coefficients, what is most important is their relative magnitudes with respect to one another within that orbital (regardless of sign). For example, for the first—lowest energy—molecular orbital, the carbon 2s and $2p_z$, the oxygen 1s, 2s, and $2p_z$ and the 1s orbitals on both hydrogens all have non-zero coefficients. However, the magnitude of the 1s coefficient on the oxygen is much, much larger than all the others, and so this molecular orbital essentially corresponds to the oxygen 1s orbital. Similarly, the important component for the second molecular orbital is the 1s orbital from the carbon atom.

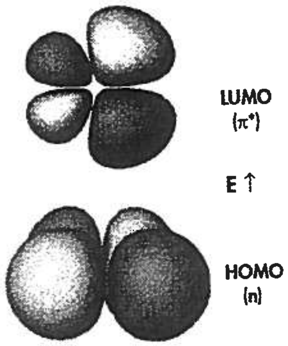
The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) may be identified by finding the point where the occupied/virtual code letter in the symmetry designation changes from O to V.

Here are the energies and symmetry designations for the next set of molecular orbitals for formaldehyde:

```
                      6         7        8         9        10
                   (A1)--O   (B1)--O  (B2)--O   (B1)--V   (A1)--V
 EIGENVALUES --  -0.63955  -0.52296 -0.44079   0.13572   0.24842
```

For formaldehyde, molecular orbital number 8 is the HOMO, and molecular orbital number 9 is the LUMO. In this case, the energy also changes sign at the point separating the occupied from the unoccupied orbitals.

Molecule lies in a plane perpendicular to the page



To The Teacher: Molecular Orbitals

When discussing molecular orbitals, three-dimensional models or visualization software may be very instructive.

However, it is also important to emphasize that orbitals are actually mathematical conveniences and not physical quantities (despite how real models may make them seem). While the energy, electron density, and optimized geometry are physical observables, the orbitals are not. In fact, several different sets of orbitals can lead to the same energy. Nevertheless, orbitals are very useful in qualitative descriptions of bonding and reactivity.

Charge Distribution

By default, *Gaussian* jobs perform a Mulliken population analysis, which partitions the total charge among the atoms in the molecule. Here is the key part of output for formaldehyde:

```
Total atomic charges:
1 C  0.128551
2 O -0.439946
3 H  0.155697
4 H  0.155697
Sum of Mulliken charges= 0.00000
```

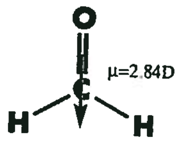
This analysis places a slight negative charge on the oxygen atom and divides the balancing positive charge between the remaining three atoms.

Mulliken population analysis is an arbitrary scheme for assigning charges. Indeed, all such schemes are ultimately arbitrary. Atomic charges—unlike the electron density—are not a quantum mechanical observable, and are not unambiguously predictable from first principles. Other methods for assigning charges to atoms are explored in Exercises 8.4 and 8.5 (beginning on page 194).

Dipole and Higher Multipole Moments

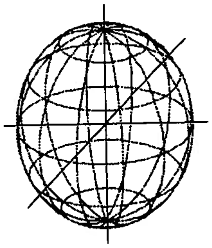
Gaussian also predicts dipole moments and higher multipole moments (through hexadecapole). The dipole moment is the first derivative of the energy with respect to an applied electric field. It is a measure of the asymmetry in the molecular charge distribution, and is given as a vector in three dimensions. For Hartree-Fock calculations, this is equivalent to the expectation value of X, Y, and Z, which are the quantities reported in the output.

Here are the predicted dipole and quadrupole moments for formaldehyde:



```
Dipole moment (Debye):
X=     0.0000    Y=    0.0000    Z=   -2.8427    Tot= 2.8427
Quadrupole moment (Debye-Ang):
XX= -11.5395   YY= -11.3085   ZZ= -11.8963
XY=   0.0000   XZ=    0.0000   YZ=    0.0000
```

The dipole moment is broken down into X, Y, and Z components. In this case, the dipole moment is entirely along the Z-axis. By referring to the standard orientation for the molecule, we realize that this is pointing away from the oxygen atom, which is the negatively charged part of the molecule. Dipole moments are always given in units of debye.[†]



Quadrupole moments[‡] provide a second-order approximation of the total electron distribution, providing at least a crude idea of its shape. For example, equal XX, YY, and ZZ components indicate a spherical distribution. This is approximately the case for formaldehyde. One of these components being significantly larger than the others would represent an elongation of the sphere along that axis. If present, the off-axis components represent trans-axial distortion (stretching or compressing) of the ellipsoid. Quadrupole (and higher) moments are generally of significance only when the dipole moment is 0.

Another way of obtaining information about the distribution of electrons is by computing the polarizability. This property depends on the second derivative of the energy with respect to an electric field. We'll examine the polarizability of formaldehyde in Chapter 4.

CPU Time and Other Resource Usage

Gaussian jobs report the CPU time used and the sizes of their scratch files upon completion. Here is the data for our formaldehyde job:

```
Job cpu time: 0 days 0 hours 0 minutes 9.1 seconds.
File lengths (MBytes): RWF= 5 Int= 0 D2E= 0 Chk= 1 Scr= 1
```

Predicting NMR Properties

Example 2.2: Methane NMR Shielding Constants
***file:* e2_02**

NMR shielding tensors are another property that can be computed in the context of a single point energy calculation. Such a calculation is requested by including the **NMR** keyword in the route section for the job. For example:

```
#T RHF/6-31G(d) NMR Test
```

We will run this job on methane at the Hartree-Fock level using the 6-31G(d) basis; our molecule specification is the result of a geometry optimization using the B3LYP Density Functional Theory method with the same basis set. This combination is cited

---

[†] Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation.

[‡] You must use # rather than #T in order for quadrupole and higher moments to be included in the output.

- ✦ Describe the general nature of the predicted charge distribution.

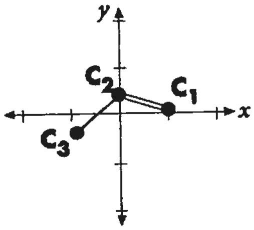
Use the 6-31G(d) basis set for your calculation. Obtain the structure for propene from one of the sources we have discussed, or see Appendix B for detailed information on setting up a Z-matrix for propene.

Solution Here is the route section for this job:

```
#T RHF/6-31G(d) Test
```

Here is the standard orientation from the output:

```
                Standard orientation:
 ---------------------------------------------------------
 Center  Atomic      Coordinates (Angstroms)
 Number  Number         X           Y           Z
 ---------------------------------------------------------
   1       6       1.273694    0.103415    0.000000
   2       6       0.000000    0.519712    0.000000
   3       6      -1.131346   -0.495403    0.000000
   4       1       1.496403   -0.953373    0.000000
   5       1       2.077545    0.824680    0.000000
   6       1      -0.222709    1.576500    0.000000
   7       1      -2.088089    0.026845    0.000000
   8       1      -1.058621   -1.120498    0.889981
   9       1      -1.058621   -1.120498   -0.889981
 ---------------------------------------------------------
```



The plane of the molecule corresponds to the XY-plane (since most of the Z values are 0), with the two other hydrogens slightly in front of and behind it. The three carbons are oriented as in the diagram.

The Hartree-Fock/6-31G(d) energy is -117.06570 hartrees:

```
SCF Done:  E(RHF) =  -117.065698056     A.U. after 6 cycles
```

by Cheeseman and coworkers as the minimum recommended model chemistry for predicting NMR properties.

Here is the predicted shielding value for the carbon atom in methane:

```
GIAO Magnetic shielding tensor (ppm):
 1  C    Isotropic =    199.0522   Anisotropy =      0.0000
  XX=   199.0522   YX=      0.0000   ZX=      0.0000
  XY=     0.0000   YY=    199.0522   ZY=      0.0000
  XZ=     0.0000   YZ=      0.0000   ZZ=    199.0522
  Eigenvalues:   199.0522   199.0522   199.0522
```

The output gives the predicted value for each atom in the molecule in turn. Here we see that the predicted value for the carbon atom is about 199.1 parts-per-million.

Shielding constants reported in experimental studies are usually shifts relative to a standard compound, often tetramethylsilane (TMS). In order to compare predicted values to experimental results, we also need to compute the absolute shielding value for TMS, using exactly the same model chemistry. Here is the relevant output for TMS:

```
GIAO Magnetic shielding tensor (ppm):
 1  C    Isotropic =    195.1196   Anisotropy =     17.5214
```

To obtain the predicted shift for the carbon atom in methane, we subtract its absolute value from that of the reference molecule, resulting in a predicted shift of -3.9 ppm, which is in reasonable agreement with the experimental value of -7.0. Note the sign convention for shifts: a negative number indicates that there is more shielding in the specified molecule than in the reference molecule, and a positive number indicates that there is less shielding than in the reference molecule.

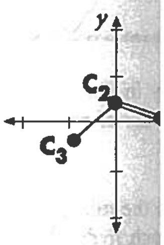
Exercises

Exercise 2.1: Propene Single Point Energy

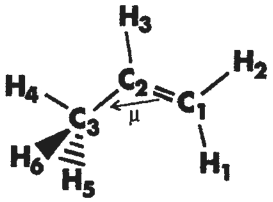
***file:* 2_01**

Run a single point energy calculation on propene and determine the following information from the output:

- What is the standard orientation of the molecule? In what plane do most of the atoms lie?
- What is the predicted Hartree-Fock energy?
- What is the magnitude and direction of the dipole moment for propene?



Here is the output giving the dipole moment and atomic charges:



```
Total atomic charges:
          1
1  C  -0.388420
2  C  -0.156442
3  C  -0.507090
4  H   0.170180
5  H   0.173519
6  H   0.183866
7  H   0.165399
8  H   0.179494
9  H   0.179495
Sum of Mulliken charges= 0.00000
...
Dipole moment (Debye):
X= -0.2982  Y= -0.0310  Z= 0.0000  Tot= 0.2998
```

The dipole moment has a magnitude of about 0.3 debye, mostly in the negative X direction. This is a weak dipole moment, indicating that the centers of positive and negative charge are relatively close together in this molecule.

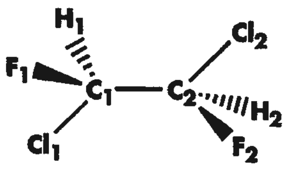
The negative charges are confined to the carbons, with the one on the middle carbon being appreciably smaller than that on the other two carbons. Each hydrogen has a small positive charge. ■

Exercise 2.2: 1,2-Dichloro-1,2-Difluoroethane Conformer Energies

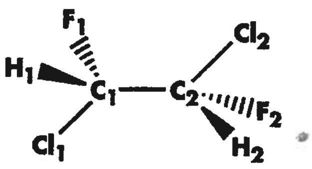
***files:* 2_02a (RR)**
2_02b (SS)
2_02c (meso)

Make a table of the energies and dipole moments for the three stereoisomers of 1,2-dichloro-1,2-difluoroethane (stoichiometry: CHFCl–CHFCl). You'll need to set up and run a HF/6-31G(d) single point energy calculation for each form.

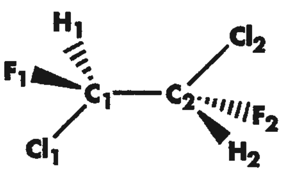
Here are the three forms:



RR



SS



meso

All three molecules are positioned so that the carbons and chlorines all lie in the plane of the paper, with other atoms above or below it as indicated. (Appendix B contains detailed instructions for setting up Z-matrices for these molecules.)

Solution Running all three jobs yields the following results:

Form	Energy	μ
RR	-1194.7153	$-2.8\hat{z}$
SS	-1194.7153	$-2.8\hat{z}$
meso	-1194.7178	0.0

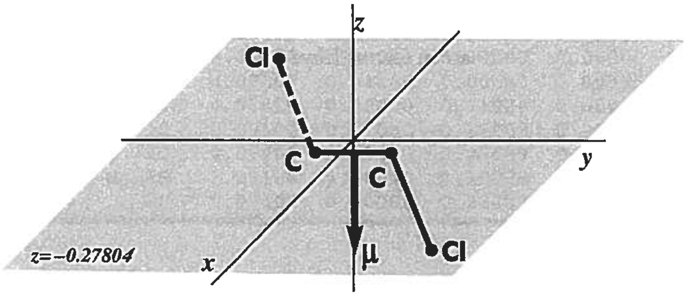
1 hartree = 627.51 kcal mol^{-1}

The RR and SS forms have exactly the same values for the energy and the dipole moment. The energy difference between them and the meso form is about 2.5 millihartrees, which corresponds to about 1.5 kcal mol^{-1}. This is a small but significant difference in energy.

The RR and SS forms both have a dipole moment of 2.8 debye along the negative Z-axis. To locate this within the molecule, we need to examine the standard orientation. Here is the output for the RR form:

```
                  Standard orientation:
 ---------------------------------------------------------
 Center   Atomic        Coordinates (Angstroms)
 Number   Number      X            Y             Z
 ---------------------------------------------------------
   1        6      0.000000    0.765000   -0.278044
   2        6      0.000000   -0.765000   -0.278044
   3       17     -1.660072    1.349604   -0.278044
   4       17      1.660072   -1.349604   -0.278044
   5        9      0.645709    1.222315    0.840358
   6        1      0.511868    1.130642   -1.168210
   7        9     -0.645709   -1.222315    0.840358
   8        1     -0.511868   -1.130642   -1.168210
 ---------------------------------------------------------
```

Here is a graph showing the positions of the carbon and chlorine atoms in the XY-plane, ignoring their common Z-coordinate:



If we define the positive Z direction as up, the hydrogen atoms lie below this plane, and the fluorine atoms lie above it. The dipole moment points down, toward the hydrogen atoms, which is where we expect the positive charge to be. The same is true for the SS form.

The meso form has no dipole moment. If we look again at the structure, this makes sense, since the molecule has a center of inversion. ■

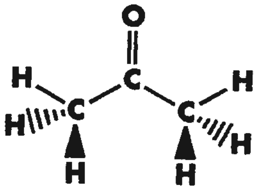
Exercise 2.3: Acetone Compared to Formaldehyde

***file:* 2_03**

Acetone has a structure similar to formaldehyde, with methyl groups replacing the hydrogens on the carbon atom. What is the effect of making this substitution? What properties change, and which ones do not? (Use the same model chemistry as for the previous exercise.)

Solution

Here is a table of the major results for the two jobs:



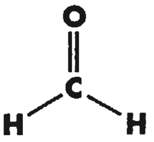
Molecule	Energy	Dipole Moment
Formaldehyde	-113.86370	$-2.84\hat{z}$
Acetone	-191.95961	$-3.26\hat{z}$

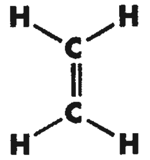
Although the energies are very different, comparing them directly is of little value. Energies for two systems can be compared only when the number and type of nuclei are the same. Thus, we could compare the energies of the alternate forms of 1,2-dichloro-1,2-difluoroethane, and we can compare the energies for the reactants and products of reactions when the total number of nuclei of each type are the same. But we cannot make any meaningful statement about formaldehyde versus acetone based upon comparing their energies.

We can compare their dipole moments, however. In this case, we note that the methyl groups in acetone have the effect of increasing the magnitude of the dipole moment, which points away from the oxygen along the double bond in both cases. This means that the centers of positive and negative charge are farther apart in acetone than they are in formaldehyde. ■

Exercise 2.4: Ethylene and Formaldehyde Molecular Orbitals

***file:* 2_04**





Ethylene is another molecule that is similar to formaldehyde. The two compounds are isoelectronic. In the case of ethylene, the oxygen in formaldehyde is replaced by a carbon with two additional hydrogens attached to it.

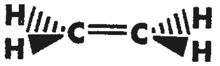
Compare the dipole moment of ethylene and formaldehyde. Then compare the HOMO and LUMO in both molecules. Use the data from the formaldehyde example earlier in this chapter.

Here is the output for the relevant orbitals for formaldehyde for reference:

```
                          6         7         8         9        10
                       (A1)--O   (B1)--O   (B2)--O   (B1)--V   (A1)--V
EIGENVALUES --      -0.63955  -0.52296  -0.44079   0.13572   0.24842
   1 1    C   1S     0.01941   0.00000   0.00000   0.00000  -0.12212
   2          2S    -0.06072   0.00000   0.00000   0.00000   0.14897
   3          2PX    0.00000   0.32522   0.00000   0.40259   0.00000
   4          2PY    0.00000   0.00000  -0.19817   0.00000   0.00000
   5          2PZ   -0.37596   0.00000   0.00000   0.00000  -0.21086
   6          3S     0.03976   0.00000   0.00000   0.00000   1.98096
   7          3PX    0.00000   0.21235   0.00000   0.71120   0.00000
   8          3PY    0.00000   0.00000  -0.04485   0.00000   0.00000
   9          3PZ   -0.08854   0.00000   0.00000   0.00000  -0.74976
  10          4XX    0.00549   0.00000   0.00000   0.00000  -0.00273
  11          4YY    0.02734   0.00000   0.00000   0.00000  -0.01266
  12          4ZZ   -0.01933   0.00000   0.00000   0.00000  -0.00459
  13          4XY    0.00000   0.00000   0.00000   0.00000   0.00000
  14          4XZ    0.00000   0.03558   0.00000  -0.03289   0.00000
  15          4YZ    0.00000   0.00000   0.06034   0.00000   0.00000
  16 2    O   1S    -0.06967   0.00000   0.00000   0.00000  -0.00099
  17          2S     0.15358   0.00000   0.00000   0.00000  -0.01034
  18          2PX    0.00000   0.49029   0.00000  -0.38148   0.00000
  19          2PY    0.00000   0.00000   0.56588   0.00000   0.00000
  20          2PZ    0.50940   0.00000   0.00000   0.00000   0.05334
  21          3S     0.32365   0.00000   0.00000   0.00000   0.10031
  22          3PX    0.00000   0.35352   0.00000  -0.52798   0.00000
  23          3PY    0.00000   0.00000   0.44338   0.00000   0.00000
  24          3PZ    0.28718   0.00000   0.00000   0.00000   0.05069
  25          4XX    0.00485   0.00000   0.00000   0.00000   0.00130
  26          4YY    0.00745   0.00000   0.00000   0.00000  -0.01009
  27          4ZZ   -0.03495   0.00000   0.00000   0.00000  -0.00048
  28          4XY    0.00000   0.00000   0.00000   0.00000   0.00000
  29          4XZ    0.00000  -0.04166   0.00000   0.00355   0.00000
  30          4YZ    0.00000   0.00000  -0.01928   0.00000   0.00000
  31 3    H   1S     0.09100   0.00000  -0.18068   0.00000  -0.04749
  32          2S     0.07400   0.00000  -0.22489   0.00000  -1.47348
  33 4    H   1S     0.09100   0.00000   0.18068   0.00000  -0.04749
  34          2S     0.07400   0.00000   0.22489   0.00000  -1.47348
```

Solution

Molecules lie in a plane perpendicular to the page



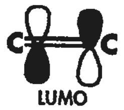
Here are the dipole moments for the two molecules:

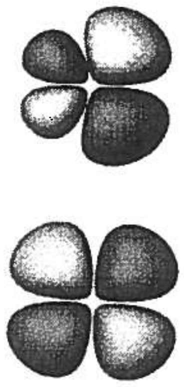
Formaldehyde	$-2.84\hat{z}$ (*away from the oxygen atom*)
Ethylene	0.0

While the oxygen atom induces a dipole moment in formaldehyde, the center of inversion in ethylene results in no dipole moment.

Here are the HOMO and LUMO for ethylene (some non-significant lines have been removed from the output):

```
                                   8           9
                              (B3U)--O    (B3U)--V
      EIGENVALUES --         -0.37467     0.18399
   1 1    C  1S               0.00000     0.00000
   3         2PX              0.37552     0.33994
   7         3PX              0.30346     0.74838
  14         4XZ             -0.02553     0.02420
  16 2    C  1S               0.00000     0.00000
  18         2PX              0.37552    -0.33994
  22         3PX              0.30346    -0.74838
  29         4XZ             -0.02553     0.02420
  31 3    H  1S               0.00000     0.00000
  33 4    H  1S               0.00000     0.00000
  35 5    H  1S               0.00000     0.00000
  37 6    H  1S               0.00000     0.00000
```

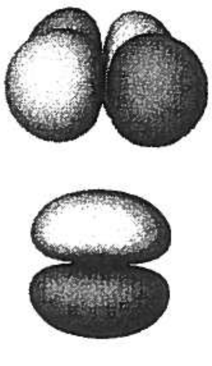




Lowest unoccupied molecular orbital for formaldehyde (top) and ethylene

Since both molecules have the same number of electrons, the orbital numbered 8 is the HOMO, and the one numbered 9 is the LUMO in both cases. However, they are not the same type orbitals. Let's consider ethylene first.

In ethylene, both the HOMO and LUMO are formed primarily from p_x orbitals from the two carbons. The carbons lie in the YZ-plane, and so the p_x orbitals lie above and below the C-C bond. In the HOMO, the orbitals have like signs, and so they combine to form a bonding π molecular orbital. In contrast, in the LUMO, they have opposite signs, indicating that they combine to form an antibonding π^* molecular orbital.



Highest occupied molecular orbital for formaldehyde (top) and ethylene

Orbitals 7 and 9 (the latter is the LUMO) of formaldehyde exhibit this same character. Orbital 7 is a bonding π orbital, and orbital 9 is a π^*. However, the π orbital formed of the p_x orbitals from the carbon and the oxygen (which also lie in the YZ plane) is not the HOMO. Instead, an orbital formed from p_y orbitals from the carbon and the oxygen and from the s orbitals on the hydrogens is the highest occupied orbital. The contributions from the carbon and oxygen are situated along the double bond while the HOMO in ethylene was perpendicular to this bond.

This difference is due to the two lone pairs on the oxygen. Of the six valence electrons on the oxygen atom, two are involved in the double bond with the carbon, and the other four exist as two lone pairs. In Chapter 4, we'll examine the IR spectra for these two molecules. The orbitals suggest that we'll find very different frequencies for the two systems. In Chapter 9, we'll look at the transition to the first excited state in formaldehyde. ■

Exercise 2.5: NMR Properties of Alkanes, Alkenes and Alkynes

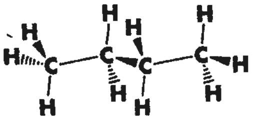
***files*: 2_05a**
2_05b
2_05c

The NMR magnetic shielding for atoms like carbon is affected greatly by what it is bonded to and the type of bond to its neighbor. Use the inner carbon atoms of normal butane as the reference atom and calculate the shift in ^{13}C isotropic shielding for 2-butene and 2-butyne. Can you explain these shifts as a function of the changing molecular environments?

Run your NMR calculations at the HF/6-31G(d) level; here are the structures of the three molecules calculated at the B3LYP/6-31G(d) level:

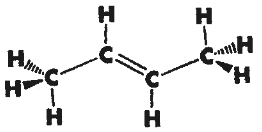
butane

```
C  0.000000   0.767105   0.000000
C  0.000000  -0.767105   0.000000
C  1.407571   1.372311   0.000000
C -1.407571  -1.372311   0.000000
H  1.372874   2.467846   0.000000
H -1.372874  -2.467846   0.000000
H  1.974414   1.056859   0.884767
H  1.974414   1.056859  -0.884767
H -1.974414  -1.056859   0.884767
H -1.974414  -1.056859  -0.884767
H -0.554359   1.127932  -0.878287
H -0.554359   1.127932   0.878287
H  0.554359  -1.127932  -0.878287
H  0.554359  -1.127932   0.878287
```



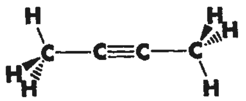
trans 2-butene

```
C  0.000000   0.667614   0.000000
C  0.000000  -0.667614   0.000000
C  1.226946  -1.535762   0.000000
C -1.226946   1.535762   0.000000
H -0.957948  -1.192291   0.000000
H  0.957948   1.192291   0.000000
H  2.143559  -0.935724   0.000000
H -2.143559   0.935724   0.000000
H  1.251318  -2.192033   0.880777
H  1.251318  -2.192033  -0.880777
H -1.251318   2.192033   0.880777
H -1.251318   2.192033  -0.880777
```



2-butyne

```
C  0.000052   0.000000  -0.604592
C -0.000052   0.000000   0.604592
C  0.000016   0.000000  -2.066136
C -0.000016   0.000000   2.066136
H -1.021490   0.000000  -2.466263
H  0.510752  -0.884627  -2.466360
H  0.510752   0.884627  -2.466360
H  1.021490   0.000000   2.466263
H -0.510752  -0.884627   2.466360
H -0.510752   0.884627   2.466360
```



Note that the inner carbon atoms are the first two atoms listed for each compound. The predicted NMR shielding values will appear in the output in the same order as the atoms are listed in the molecule specification section.

Solution The predicted absolute shielding value for the central carbons in butane is 176.3 ppm, which is what we will use as the reference value, subtracting the computed shielding values for the outer carbons in butane and for each type of carbon in the other two compounds from it.

Here are the predicted shifts with respect to the C2 carbon in butane (all values are given in ppm):

	C1 (outer)		C2 (inner)	
Compound	calc.	exp.	calc.	exp.
butane	-7.8	-11.8	0.0	0.0
2-butene	-5.3	-7.6	101.0	100.8
2-butyne	-19.1		48.5	48.4

The agreement with experiment is very good for these cases even with this inexpensive model.

For the C2 carbons, the shielding decreases greatly as we move from the alkane to the alkene. This is due to that fact that the sp3 orbitals have a greater ability to oppose the applied magnetic field. The shift is much smaller when moving to the alkyne, which has been explained by the fact that the π bonding present in an sp environment creates a cylinder of electric charge acting to oppose the applied magnetic field. ■

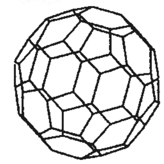
To The Teacher: Magnetic Properties

For another dramatic illustration of chemical shifts, have students calculate the magnetic shielding of nitrogen in pyridine and compare it to its saturated cyclohexane analogue.

Advanced Exercise 2.6: C_{60} Single Point Energy

***file:* 2_06**

Fullerene compounds have receieved a lot of attention in recent years. In this exercise we predict the energy of C_{60} and look at its highest occupied molecular orbital, predicted at the Hartree-Fock level with the 3-21G basis set[†]. Include **SCF=Tight** in the route section of the job.



Solution

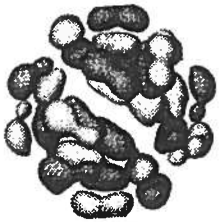
Here is the route section for the job:

```
#T HF/3-21G SCF=Tight Pop=Reg Test
```

The predicted energy is -2259.04767 hartrees. The HOMO is plotted at the left.

If you forget to include **SCF=Tight** in your job, it will probably have failed, giving error messages something like the following:

```
>>>>>>>>>> Convergence criterion not met.
SCF Done:  E(RHF) = ...
...
Convergence failure -- run terminated.
```



HOMO

These messages indicate that the SCF calculation, which is an iterative process, failed to converge. The predicted energy should accordingly be ignored. ■

Advanced Exercise 2.7: CPU Resource Usage by Calculation Size

***file:* 2_07**

This exercise is concerned with resource usage as a function of system size and introduces the use of the direct SCF method in *Gaussian* jobs (it is the default). Compare the total CPU time required to compute the Hartree-Fock energies of the series of hydrocarbons described below, using the 6-31G(d) basis set for the conventional SCF algorithm (**SCF=Conven**) and the direct SCF method (the default algorithm). Use **SCF=Tight** to request stricter convergence criteria for the SCF wavefunction for the direct jobs (tight convergence is the default for the conventional SCF algorithm). Also, include the keyword **IOP(5/19=1)** in the direct SCF calculations, which prevents them from being run entirely in memory (*in-core*).[‡]

[†] We select a smaller basis set than usual in order to keep the calculation manageable.

[‡] By default, *Gaussian* will substitute the in-core method for direct SCF when there is enough memory because it is faster. When we ran these computations, we explicitly prevented *Gaussian* from using the in-core method. When you run your jobs, however, the in-core method will undoubtedly be used for some jobs, and so your values may differ. An in-core job is identified by the following line in the output: `Two-electron integrals will be kept in memory.`

Plot the CPU time used for each method as a function of the number of carbon atoms (N). Theoretically, CPU time required should scale as the fourth power of the number of carbon atoms (N^4). How do the actual times depend on N?

The systems we'll use in this exercise are hydrocarbons of the form C_nH_{2n+2}, where *n* runs from 1 to some upper limit ≤ 10. The place to stop depends on the CPU capacity of your system. Users of *Gaussian 94W* will probably want to go no higher than 7 or 8. We used the 6-31G(d) basis set, but you could substitute a smaller one to save time (3-21G or STO-3G).

Basis Function Data in *Gaussian* Output

Gaussian output indicates the number of basis functions for a molecule in its output, just below the standard orientation:

```
Isotopes: H-1,C-12,H-1,H-1,H-1
   23 basis functions       44 primitive gaussians
    5 alpha electrons        5 beta electrons
      nuclear repulsion energy        13.4353902217 Hartrees.
```

This output is for CH_4, which uses 23 basis functions with the 6-31G(d) basis set.

Solution

The basic strategy behind the direct SCF method is recomputing certain intermediate quantities within the calculation—specifically the two-electron integrals—as needed, rather than storing them on disk. This has the advantage of making it possible to study systems which would require more disk space than is available on the system.

Direct SCF also has a significant performance advantage over the conventional algorithm for large systems. There is always a crossover point in terms of molecule size beyond which direct SCF will be faster than the conventional algorithm. The exact location of this crossover varies according to the characteristics of the computer system running the program.

Here are the results we obtained by running these hydrocarbon single point energy calculations on a DEC AlphaStation $600^{5/266}$ computer (in CPU seconds). In the table, *N* is the number of carbons in the system:

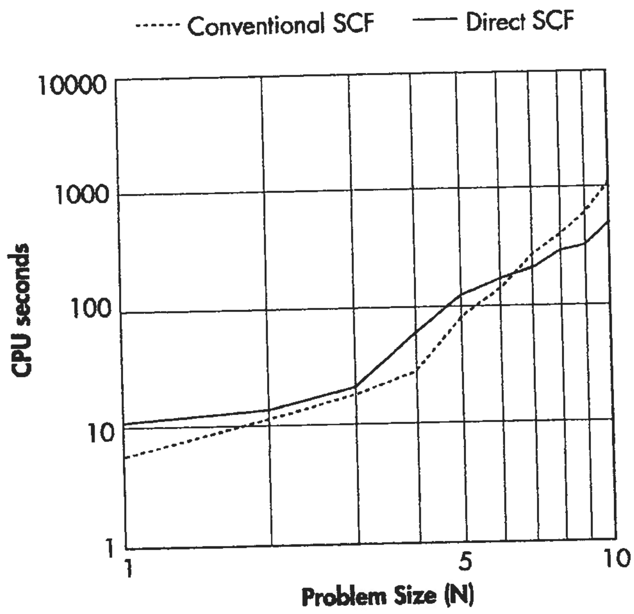
SCF CPU and Disk Requirements by Problem Size for Linear C_NH_{2N+2}

		Conventional SCF		Direct SCF
N	# Basis Functions	*MB for INT file*	*CPU seconds*	*CPU seconds*
1	23	2	8.6	12.8
2	42	4	11.9	19.8
3	61	16	23.2	38.8

SCF CPU and Disk Requirements by Problem Size for Linear C_NH_{2N+2}

		Conventional SCF		Direct SCF
N	# Basis Functions	*MB for INT file*	*CPU seconds*	*CPU seconds*
4	80	42	48.7	72.1
5	99	92	95.4	122.5
6	118	174	163.4	186.8
7	137	290	354.5	268.0
8	156	437	526.5	375.0
9	175	620	740.2	488.0
10	194	832	1028.4	622.1

Here is our plot. It is a log-log plot, so we can estimate the exponent for *N* by computing the slope of each line. The actual scaling for the direct algorithm is more like $N^{2.5}$ than N^4:



For this computer system, the crossover point where direct SCF beats the conventional algorithm happens at around 120 basis functions (~N=7). This level may be lower for some vector processors. ■

Advanced Exercise 2.8: SCF Stability Calculations

***files:* 2_08a (O$_2$)**
2_08b (O$_3$)

In this exercise, we introduce SCF stability calculations. A stability calculation determines whether the wavefunction computed for the molecular system is stable or not: in other words, whether there is a lower energy wavefunction corresponding to a different solution of the SCF equations. If the wavefunction is unstable, then whatever calculation you are performing is not being done on the expected/desired state of the molecule. For example, if a stability calculation indicates an unstable wavefunction for a system for which you were attempting to model its ground state, then the calculation does *not* in fact correspond to the ground state, and any energy comparisons for or other conclusions about the ground state based on it will be invalid.

When Wavefunction Stability Should Be Tested

The stability of SCF solutions for unknown systems should *always* be tested. Stability considerations apply to and may be tested for in calculations using Density Functional Theory methods as well.

The following *Gaussian* keywords will be of use:

Keyword	Effect
Stable	Tests the stability of the SCF solution computed for the molecule. This involves determining whether any lower energy wavefunction exists for the system, obtained by relaxing constraints placed on it by default (e.g., allowing the wavefunction to become open shell or reducing the symmetry of the orbitals).
Stable=Opt	Test the stability of the SCF solution and reoptimize the wavefunction to the lower energy solution if any instability is found. When we speak of optimizing the wavefunction, we are *not* referring to a geometry optimization, which locates the lowest energy conformation near a specified starting molecular structure. Predicting an SCF energy involves finding the lowest energy solution to the SCF equations. Stability calculations ensure that this optimized electronic wavefunction is a minimum in wavefunction space—and not a saddle point—which is an entirely separate process from locating minima or saddle points on a nuclear potential energy surface. See Appendix A for more details on the internals of SCF calculations.

In order to illustrate how stability calculations work, we'll run the following RHF calculation on molecular oxygen:

```
#T RHF/6-31G(d) Stable Test

Oxygen stability: RHF on singlet (!!)

0 1
O
O 1 1.22
```

We can be sure that the RHF wavefunction for molecular oxygen is unstable, since we know the ground state of the molecule is a triplet. The output from the stability calculation confirms this:

```
The wavefunction has an RHF -> UHF instability.
```

This indicates that there is a UHF wavefunction which is lower in energy than the RHF wavefunction, which is what we expect in this case. Note that instabilities can be of many different types. The most common kinds are:

- The lowest energy wavefunction is a singlet, but not a closed shell singlet (e.g., biradicals). This is an RHF-to-UHF instability.
- There is a lower-lying triplet state than the singlet (the current case). This is an RHF-to-UHF instability.
- There is more than one solution to the SCF equations for the system, and the calculation procedure converges to a solution which is not the minimum (often a saddle point in wavefunction space). This indicates an RHF-to-RHF or UHF-to-UHF instability, depending on the wavefunction type.

Run a stability calculation on the true (triplet) ground state of molecular oxygen. What is the energy difference between the ground state and the singlet state?

Once you have completed this first calculation, devise and run calculations which will determine the lowest energy electronic state for ozone. Use the experimental geometry: O–O bond lengths=1.272 Å, O–O–O bond angle=116.8°.

Solution

Running a **Stable** calculation indicates that the computed UHF wavefunction for triplet molecular oxygen is stable:

```
The wavefunction is stable under the perturbations considered.
```

The predicted energy, which appears in the SCF summary section preceding the stability analysis output, is -149.61266 hartrees, which is about 53.5 kcal/mol lower than that corresponding to the RHF wavefunction (-149.52735).

Since we knew molecular oxygen is a triplet, we should have performed this calculation as an open shell calculation.

Ozone is a singlet, but it has an unusual electronic structure and is thus often difficult to model. An **RHF Stable=Opt** calculation finds an RHF→UHF instability, and the reoptimization of the wavefunction leads to a UHF solution with an energy of -224.34143 hartrees.

At this point, we might expect that a UHF calculation would be sufficient. However, when we perform a **UHF Stable=Opt** calculation, the predicted wavefunction is again found to be unstable:

```
The wavefunction has an internal instability.
```

Reoptimization of the wavefunction again leads to the same lower-energy electronic state as was found by the RHF calculation. Even for a UHF calculation, it is necessary to modify the default electronic configuration in order to specify the proper ground state of ozone. This is not surprising given the known significantly biradical character of ozone resulting from the coupling of the singly-occupied π orbitals on the terminal oxygen atoms.

In order to specify the proper electronic state, ozone calculations should be performed as unrestricted calculations, and the keyword **Guess=Mix** should always be included. This keyword tells the program to mix the HOMO and LUMO within the wavefunction in an effort to destroy α-β and spatial symmetries, and it is often useful in producing a UHF wavefunction for a singlet system. Running a **UHF Guess=Mix Stable** calculation confirms that the resulting wavefunction is stable, and it predicts the same energy (-224.34143 hartrees) as the previous **Stable=Opt** calculations.

Specific electronic states may also be specified using the **Guess=Alter** keyword, which allows you to explicitly designate orbital occupancies. See the *Gaussian User's Reference* for details.

As a final note, be aware that Hartree-Fock calculations performed with small basis sets are many times more prone to finding unstable SCF solutions than are larger calculations. Sometimes this is a result of spin contamination; in other cases, the neglect of electron correlation is at the root. The same molecular system may or may not lead to an instability when it is modeled with a larger basis set or a more accurate method such as Density Functional Theory. Nevertheless, wavefunctions should still be checked for stability with the **SCF=Stable** option. ■

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Appendix

A

The Theoretical Background

Ab initio molecular orbital theory is concerned with predicting the properties of atomic and molecular systems. It is based upon the fundamental laws of quantum mechanics and uses a variety of mathematical transformation and approximation techniques to solve the fundamental equations. This appendix provides an introductory overview of the theory underlying ab initio electronic structure methods. The final section provides a similar overview of the theory underlying Density Functional Theory methods.

The Schrödinger Equation

Quantum mechanics explains how entities like electrons have both particle-like and wave-like characteristics. The Schrödinger equation describes the wavefunction of a particle:

$$\left\{\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right\}\Psi(\vec{r}, t) = \frac{ih}{2\pi}\frac{\partial\Psi(\vec{r}, t)}{\partial t} \qquad [1]$$

In this equation, Ψ is the wavefunction, m is the mass of the particle, h is Planck's constant, and V is the potential field in which the particle is moving.[†] The product of Ψ with its complex conjugate ($\Psi^*\Psi$, often written as $|\Psi|^2$) is interpreted as the probability distribution of the particle.

The Schrödinger equation for a collection of particles like a molecule is very similar. In this case, Ψ would be a function of the coordinates of all the particles in the system as well as t.

The energy and many other properties of the particle can be obtained by solving the Schrödinger equation for Ψ, subject to the appropriate boundary conditions. Many different wavefunctions are solutions to it, corresponding to different stationary states of the system.

[†] The differential operator on the left side of the equation is known as "del-squared." The operator del is equivalent to partial differentiation with respect to x, y, and z components:

$$\nabla = \frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}$$

If V is not a function of time, the Schrödinger equation can be simplified using the mathematical technique known as separation of variables. If we write the wavefunction as the product of a spatial function and a time function:

$$\Psi(\vec{r}, t) = \psi(\vec{r})\tau(t) \qquad [2]$$

and then substitute these new functions into Equation 1, we will obtain two equations, one of which depends on the position of the particle independent of time and the other of which is a function of time alone. For the problems in which we are interested, this separation is valid, and we focus entirely on the familiar time-independent Schrödinger equation:

$$\mathbf{H}\psi(\vec{r}) = E\psi(\vec{r}) \qquad [3]$$

where E is the energy of the particle, and **H** is the *Hamiltonian operator*, equal to:

$$\mathbf{H} = \frac{-h^2}{8\pi^2 m}\nabla^2 + V \qquad [4]$$

The various solutions to Equation 3 correspond to different stationary states of the particle (molecule). The one with the lowest energy is called the *ground state*. Equation 3 is a non-relativistic description of the system which is not valid when the velocities of particles approach the speed of light. Thus, Equation 3 does not give an accurate description of the core electrons in large nuclei.

Note also that Equation 3 is an *eigenvalue equation*: an equation in which an operator acting on a function produces a multiple of the function itself as its result, having the general form:

$$\mathbf{Op}\,f = c\,f \qquad [5]$$

where **Op** is an operator, *f* is a function, and *c* is a constant. The set of functions for which the equation holds are its *eigenfunctions*, each of which has an associated value for *c*, known as its *eigenvalue*. In the case of the Schrödinger equation, the eigenvalues are the energies corresponding to the different stationary states of the molecular system.

The Molecular Hamiltonian

For a molecular system, Ψ is a function of the positions of the electrons and the nuclei within the molecule, which we will designate as $\mathbf{r}$ and $\mathbf{R}$, respectively. These symbols are a shorthand for the set of component vectors describing the position of each particle. We'll use subscripted versions of them to denote the vector corresponding to a particular electron or nucleus: $\mathbf{r}_i$ and $\mathbf{R}_I$. Note that electrons are treated individually, while each nucleus is treated as an aggregate; the component nucleons are not treated individually.

The Hamiltonian is made up of kinetic and potential energy terms:

$$\mathbf{H} = \mathbf{T} + \mathbf{V} \tag{6}$$

The kinetic energy is a summation of ∇^2 over all the particles in the molecule:

$$\mathbf{T} = -\frac{h^2}{8\pi^2}\sum_k \frac{1}{m_k}\left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2}\right) \tag{7}$$

The potential energy component is the Coulomb repulsion between each pair of charged entities (treating each atomic nucleus as a single charged mass):

$$\mathbf{V} = \frac{1}{4\pi\varepsilon_0}\sum_j \sum_{k<j} \frac{e_j e_k}{\Delta r_{jk}} \tag{8}$$

where Δr_{jk} is the distance between the two particles, and e_j and e_k are the charges on particles *j* and *k*. For an electron, the charge is *-e*, while for a nucleus, the charge is *Ze*, where *Z* is the atomic number for that atom. Thus,

$$\mathbf{V} = \frac{1}{4\pi\varepsilon_0}\left(-\sum_i^{\textit{electrons}} \sum_I^{\textit{nuclei}} \left(\frac{Z_I e^2}{\Delta r_{iI}}\right) + \sum_i^{\textit{electrons}} \sum_{j<i} \left(\frac{e^2}{\Delta r_{ij}}\right) + \sum_I^{\textit{nuclei}} \sum_{J<I} \left(\frac{Z_I Z_J e^2}{\Delta R_{IJ}}\right)\right) \tag{9}$$

The first term corresponds to electron-nuclear attraction, the second to electron-electron repulsion, and the third to nuclear-nuclear repulsion.

Atomic Units

The fundamental equations of quantum chemistry are usually expressed in units designed to simplify their form by eliminating fundamental constants. The atomic unit of length is the *Bohr radius*:

$$a_0 = \frac{h^2}{4\pi^2 m_e e^2} = 0.52917725\text{Å} \tag{10}$$

Coordinates can be transformed to bohrs by dividing them by a_0. Energies are measured in *hartrees*, defined as the Coulomb repulsion between two electrons separated by 1 bohr:

$$1\,\textit{hartree} = \frac{e^2}{a_0} \tag{11}$$

Masses are also specified in terms of electron mass units (i.e. define m_e=1).

We will use these units in all future equations.

The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is the first of several approximations used to simplify the solution of the Schrödinger equation. It simplifies the general molecular problem by separating nuclear and electronic motions. This approximation is reasonable since the mass of a typical nucleus is thousands of times greater than that of an electron. The nuclei move very slowly with respect to the electrons, and the electrons react essentially instantaneously to changes in nuclear position. Thus, the electron distribution within a molecular system depends on the positions of the nuclei, and not on their velocities. Put another way, the nuclei look fixed to the electrons, and electronic motion can be described as occurring in a field of fixed nuclei.

The full Hamiltonian for the molecular system can then be written as:

$$\mathbf{H} = \mathbf{T}^{elec}(\vec{\mathbf{r}}) + \mathbf{T}^{nucl}(\vec{\mathbf{R}}) + \mathbf{V}^{nucl\text{-}elec}(\vec{\mathbf{R}}, \vec{\mathbf{r}}) + \mathbf{V}^{elec}(\vec{\mathbf{r}}) + \mathbf{V}^{nucl}(\vec{\mathbf{R}}) \tag{12}$$

The Born-Oppenheimer approximation allows the two parts of the problem to be solved independently, so we can construct an electronic Hamiltonian which neglects the kinetic energy term for the nuclei:

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$V^{nucl}(\vec{R})$ [12]

the problem to be
nian which neglects

$$\mathbf{H}^{elec} = -\frac{1}{2}\sum_{i}^{electrons}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)-\sum_{i}^{electrons}\sum_{I}^{nuclei}\left(\frac{Z_I}{|\vec{\mathbf{R}}_I-\vec{\mathbf{r}}_i|}\right)$$
$$+\sum_{i}^{electrons}\sum_{j<i}\left(\frac{1}{|\vec{\mathbf{r}}_i-\vec{\mathbf{r}}_j|}\right)+\sum_{I}^{nuclei}\sum_{J<I}\left(\frac{Z_I Z_J}{|\vec{\mathbf{R}}_I-\vec{\mathbf{R}}_J|}\right) \quad [13]$$

Note that the fundamental physical constants drop out with the use of atomic units.

This Hamiltonian is then used in the Schrödinger equation describing the motion of electrons in the field of fixed nuclei:

$$\mathbf{H}^{elec}\psi^{elec}(\vec{\mathbf{r}},\vec{\mathbf{R}}) = \mathbf{E}^{eff}(\vec{\mathbf{R}})\,\psi^{elec}(\vec{\mathbf{r}},\vec{\mathbf{R}}) \quad [14]$$

Solving this equation for the electronic wavefunction will produce the effective nuclear potential function $\mathbf{E}^{eff}$.[†] It depends on the nuclear coordinates and describes the potential energy surface for the system.

Accordingly, $\mathbf{E}^{eff}$ is also used as the effective potential for the nuclear Hamiltonian:

$$\mathbf{H}^{nucl} = \mathbf{T}^{nucl}(\vec{\mathbf{R}}) + \mathbf{E}^{eff}(\vec{\mathbf{R}}) \quad [15]$$

This Hamiltonian is used in the Schrödinger equation for nuclear motion, describing the vibrational, rotational, and translational states of the nuclei. Solving the nuclear Schrödinger equation (at least approximately) is necessary for predicting the vibrational spectra of molecules.

From this point on, we will focus entirely on the electronic problem. We will omit the superscripts on all operators and functions.

Restrictions on the Wavefunction

We've noted that ψ^2 is interpreted as the probability density for the particle(s) it describes. Therefore, we require that ψ be *normalized*; if we integrate over all space,

---

[†] For a given set of nuclear coordinates, this corresponds to the total energy predicted by a single point energy calculation, although such calculations, of course, do not solve this equation exactly. The approximation methods used to solve it will be discussed in subsequent sections of this appendix.

the probability should be the number of particles (the particles *are* somewhere). Accordingly, we multiply ψ by a constant such that:

$$\int_{-\infty}^{+\infty} |c\psi|^2 \, dv = n_{particles}{}^{\dagger} \qquad [16]$$

We can do this because the Schrödinger equation is an eigenvalue equation, and in general, if f is a solution to an eigenvalue equation, then cf is also, for any value of c. For the Schrödinger equation, it is easy to show that $H(c\psi) = cH(\psi)$ and that $E(c\psi) = c(E\psi)$; thus, if ψ is a solution to the Schrödinger equation, then $c\psi$ is as well.

Secondly, ψ must also be *antisymmetric*, meaning that it must change sign when two identical particles are interchanged. For a simple function, antisymmetry means that the following relation holds:

$$f(i,j) = -f(j,i) \qquad [17]$$

For an electronic wavefunction, antisymmetry is a physical requirement following from the fact that electrons are fermions.[‡] It is essentially a requirement that ψ agree with the results of experimental physics. More specifically, this requirement means that any valid wavefunction must satisfy the following condition:

$$\psi(\vec{\mathbf{r}}_1, \ldots, \vec{\mathbf{r}}_i, \ldots, \vec{\mathbf{r}}_j, \ldots, \vec{\mathbf{r}}_n) = -\psi(\vec{\mathbf{r}}_1, \ldots, \vec{\mathbf{r}}_j, \ldots, \vec{\mathbf{r}}_i, \ldots, \vec{\mathbf{r}}_n) \qquad [18]$$

Hartree-Fock Theory

> *The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*
>
> — P. A. M. Dirac, 1929

[†] If ψ is complex, the integral becomes: $c^*c\iiint_{-\infty}^{+\infty} \psi^*\psi \, dx\, dy\, dz = n$

[‡] Fermions are particles that have the properties of antisymmetry and a half-integral spin quantum number, among others.

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An exact solution to the Schrödinger equation is not possible for any but the most trivial molecular systems. However, a number of simplifying assumptions and procedures do make an approximate solution possible for a large range of molecules.

Molecular Orbitals

The first approximation we'll consider comes from the interpretation of $|\psi|^2$ as a probability density for the electrons within the system. Molecular orbital theory decomposes ψ into a combination of molecular orbitals: ϕ_1, ϕ_2, ... To fulfill some of the conditions on ψ we discussed previously, we choose a normalized, orthogonal set of molecular orbitals:

$$\iiint \phi_i^* \phi_i \, dx\, dy\, dz = 1$$
$$\iiint \phi_i^* \phi_j \, dx\, dy\, dz = 0; \qquad i \neq j \tag{19}$$

The simplest possible way of making ψ as a combination of these molecular orbitals is by forming their *Hartree product*:

$$\psi(\vec{r}) = \phi_1(\vec{r}_1)\ \phi_2(\vec{r}_2) \ldots \phi_n(\vec{r}_n) \tag{20}$$

However, such a function is not antisymmetric, since interchanging two of the $\vec{r}_i$'s—equivalent to swapping the orbitals of two electrons—does not result in a sign change. Hence, this Hartree product is an inadequate wavefunction.

Electron Spin

The simplest antisymmetric function that is a combination of molecular orbitals is a determinant. Before forming it, however, we need to account for a factor we've neglected so far: electron spin. Electrons can have spin up (+½) or down (–½). Equation 20 assumes that each molecular orbital holds only one electron. However, most calculations are closed shell calculations, using doubly occupied orbitals, holding two electrons of opposite spin. For the moment, we will limit our discussion to this case.

We define two spin functions, α and β, as follows:

$$\alpha(\uparrow)=1 \qquad \alpha(\downarrow)=0$$
$$\beta(\uparrow)=0 \qquad \beta(\downarrow)=1 \tag{21}$$

The α function is 1 for a spin up electron, and the β function is 1 when the electron is spin down. The notation $\alpha(i)$ and $\beta(i)$ will designate the values of α and β for electron *i*; thus, $\alpha(1)$ is the value of α for electron 1.

Multiplying a molecular orbital function by α or β will include electron spin as part of the overall electronic wavefunction ψ. The product of the molecular orbital and a spin function is defined as a *spin orbital*, a function of both the electron's location and its spin.[†] Note that these spin orbitals are also orthonormal when the component molecular orbitals are.

We can now build a closed shell wavefunction by defining $n/2$ molecular orbitals for a system with n electrons, and then assigning electrons to these orbitals in pairs of opposite spin:

$$\psi(\vec{r}) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}_1)\alpha(1) & \phi_1(\vec{r}_1)\beta(1) & \phi_2(\vec{r}_1)\alpha(1) & \phi_2(\vec{r}_1)\beta(1) & \cdots & \phi_{\frac{n}{2}}(\vec{r}_1)\alpha(1) & \phi_{\frac{n}{2}}(\vec{r}_1)\beta(1) \\ \phi_1(\vec{r}_2)\alpha(2) & \phi_1(\vec{r}_2)\beta(2) & \phi_2(\vec{r}_2)\alpha(2) & \phi_2(\vec{r}_2)\beta(2) & \cdots & \phi_{\frac{n}{2}}(\vec{r}_2)\alpha(2) & \phi_{\frac{n}{2}}(\vec{r}_2)\beta(2) \\ \vdots & & & & & & \vdots \\ \phi_1(\vec{r}_i)\alpha(i) & \phi_1(\vec{r}_i)\beta(i) & \phi_2(\vec{r}_i)\alpha(i) & \phi_2(\vec{r}_i)\beta(i) & \cdots & \phi_{\frac{n}{2}}(\vec{r}_i)\alpha(i) & \phi_{\frac{n}{2}}(\vec{r}_i)\beta(i) \\ \phi_1(\vec{r}_j)\alpha(j) & \phi_1(\vec{r}_j)\beta(j) & \phi_2(\vec{r}_j)\alpha(j) & \phi_2(\vec{r}_j)\beta(j) & \cdots & \phi_{\frac{n}{2}}(\vec{r}_j)\alpha(j) & \phi_{\frac{n}{2}}(\vec{r}_j)\beta(j) \\ \vdots & & & & & & \vdots \\ \phi_1(\vec{r}_n)\alpha(n) & \phi_1(\vec{r}_n)\beta(n) & \phi_2(\vec{r}_n)\alpha(n) & \phi_2(\vec{r}_n)\beta(n) & \cdots & \phi_{\frac{n}{2}}(\vec{r}_n)\alpha(n) & \phi_{\frac{n}{2}}(\vec{r}_n)\beta(n) \end{vmatrix} \qquad [22]$$

Each row is formed by representing all possible assignments of electron *i* to all orbital-spin combinations. The initial factor is necessary for normalization. Swapping two electrons corresponds to interchanging two rows of the determinant, which will have the effect of changing its sign.

This formulation is not just a mathematical trick to form an antisymmetric wavefunction. Quantum mechanics specifies that an electron's location is not deterministic but rather consists of a probability density; in this sense, it can be anywhere. This determinant mixes all of the possible orbitals of all of the electrons in the molecular system to form the wavefunction.

[†] Some texts use a separate notation for spin orbitals. We will not do so here.

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Basis Sets

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:

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

where the coefficients $c_{\mu i}$ are known as the *molecular orbital expansion coefficients.* The basis functions $\chi_1 \cdots \chi_N$ 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, χ_μ refers to an arbitrary basis function in the same way that ϕ_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:

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

where $\vec{r}$ is of course composed of x, y and z. α 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:

$$\int_{\mathit{all\ space}} g^2 = 1 \qquad [25]$$

Thus, c depends on α, l, m and n.

Here are three representative gaussian functions (s, p_y and d_{xy} types, respectively):

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

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:

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

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:

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

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 Ξ, then the expectation value for the energy corresponding to Ξ will always be greater than the energy for the exact wavefunction:

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

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.

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The Roothaan-Hall Equations

The variational principle leads to the following equations describing the molecular orbital expansion coefficients, $c_{\nu i}$, derived by Roothaan and by Hall[†]:

$$\sum_{\nu=1}^{N} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu})\, c_{\nu i} = 0 \qquad \mu = 1, 2, \ldots, N \tag{30}$$

Equation 30 can be rewritten in matrix form:

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{31}$$

where each element is a matrix. ε is a diagonal matrix of orbital energies, each of its elements ε_i is the one-electron orbital energy of molecular orbital χ_i.

F is called the *Fock matrix*, and it represents the average effects of the field of all the electrons on each orbital. For a closed shell system, its elements are:

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} P_{\lambda\sigma}\Big[(\mu\nu|\lambda\sigma) - \tfrac{1}{2}(\mu\lambda|\nu\sigma)\Big] \tag{32}$$

where $H_{\mu\nu}^{core}$ is another matrix representing the energy of a single electron in the field of the bare nuclei, and P is the *density matrix*, defined as:

$$P_{\lambda\sigma} = 2\sum_{i=1}^{occupied} c_{\lambda i}^{*} c_{\sigma i} \tag{33}$$

The coefficients are summed over the occupied orbitals only, and the factor of two comes from the fact that each orbital holds two electrons.

Finally, the matrix S from Equation 31 is the *overlap matrix*, indicating the overlap between orbitals.

Both the Fock matrix—through the density matrix—and the orbitals depend on the molecular orbital expansion coefficients. Thus, Equation 31 is not linear and must be solved iteratively. The procedure which does so is called the *Self-Consistent Field*

[†] We alter the subscripts slightly here from what has preceded in order to follow common usage.

(SCF) method. At convergence, the energy is at a minimum, and the orbitals generate a field which produces the same orbitals, accounting for the method's name. The solution produces a set of orbitals, both *occupied* ($\phi_{i,j...}$) and *virtual* (unoccupied, conventionally denoted $\phi_{a,b...}$). The total number of orbitals is equal to the number of basis functions used.

The term $(\mu\nu|\lambda\sigma)$ in Equation 32 signifies the *two-electron repulsion integrals.* Under the Hartree-Fock treatment, each electron sees all of the other electrons as an average distribution; there is no instantaneous electron-electron interaction included. Higher level methods attempt to remedy this neglect of electron correlation in various ways, as we shall see.

The general strategy used by the SCF method (after initial setup steps) is as follows:

- Evaluate the integrals. In a conventional algorithm, they are stored on disk and read in for each iteration. In a direct algorithm, integrals are computed a few at a time as the Fock matrix is formed.
- Form an initial guess for the molecular orbital coefficients, and construct the density matrix.
- Form the Fock matrix.
- Solve for the density matrix.
- Test for convergence. If it fails, begin the next iteration. If it succeeds, go on to perform other parts of the calculation (such as population analysis).

Open Shell Methods

So far, we have considered only the restricted Hartree-Fock method. For open shell systems, an unrestricted method, capable of treating unpaired electrons, is needed.[†] For this case, the alpha and beta electrons are in different orbitals, resulting in two sets of molecular orbital expansion coefficients:

$$\begin{aligned} \phi_i^{\alpha} &= \sum_{\mu} c_{\mu i}^{\alpha} \chi_{\mu} \\ \phi_i^{\beta} &= \sum_{\mu} c_{\mu i}^{\beta} \chi_{\mu} \end{aligned} \qquad [34]$$

[†] Refer also to the discussion of open shell calculations in Chapter 1 (page 10).

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The two sets of coefficients result in two sets of Fock matrices (and their associated density matrices), and ultimately to a solution producing two sets of orbitals. These separate orbitals produce proper dissociation to separate atoms, correct delocalized orbitals for resonant systems, and other attributes characteristic of open shell systems. However, the eigenfunctions are not pure spin states, but contain some amount of *spin contamination* from higher states (for example, doublets are contaminated to some degree by functions corresponding to quartets and higher states).

Electron Correlation Methods

As we've noted several times, Hartree-Fock theory provides an inadequate treatment of the correlation between the motions of the electrons within a molecular system, especially that arising between electrons of opposite spin.

When Hartree-Fock theory fulfills the requirement that $|\Psi^2|$ be invarient with respect to the exchange of any two electrons by antisymmetrizing the wavefunction, it automatically includes the major correlation effects arising from pairs of electrons with the same spin. This correlation is termed *exchange correlation.* The motion of electrons of opposite spin remains uncorrelated under Hartree-Fock theory, however.

Any method which goes beyond SCF in attempting to treat this phenomenon properly is known as an *electron correlation* method (despite the fact that Hartree-Fock theory does include some correlation effects) or a *post-SCF* method. We will look briefly at two different approaches to the electron correlation problem in this section.

Configuration Interaction

Configuration Interaction (CI) methods begin by noting that the exact wavefunction Ψ cannot be expressed as a single determinant, as Hartree-Fock theory assumes. CI proceeds by constructing other determinants by replacing one or more occupied orbitals within the Hartree-Fock determinant with a virtual orbital.

In a *single substitution*, a virtual orbital, say ϕ_a, replaces an occupied orbital ϕ_i within the determinant. This is equivalent to exciting an electron to a higher energy orbital.

Similarly, in a *double substitution*, two occupied orbitals are replaced by virtual orbitals: $\phi_a \leftarrow \phi_i$ and $\phi_b \leftarrow \phi_j$, for example, $\Psi_{ia} = | \phi_1, \ldots \phi_i, \phi_{a+1}, \ldots \phi_{i-1}, \phi_a, \ldots \phi_n|$. *Triple substitutions* would exchange three orbitals, and so on.

Full CI

The full CI method forms the wavefunction ψ as a linear combination of the Hartree-Fock determinant and all possible substituted determinants:

$$\psi = b_0\psi_0 + \sum_{s>0} b_s\psi_s$$ [35]

where the 0-indexed term is the Hartree-Fock level, and s runs over all possible substitutions. The b's are the set of coefficients to be solved for, again by minimizing the energy of the resultant wavefunction.

At a physical level, Equation 35 represents a mixing of all of the possible electronic states of the molecule, all of which have some probability of being attained according to the laws of quantum mechanics. Full CI is the most complete non-relativistic treatment of the molecular system possible, within the limitations imposed by the chosen basis set. It represents the possible quantum states of the system while modelling the electron density in accordance with the definition (and constraints) of the basis set in use. For this reason, it appears in the rightmost column of the following methods chart:

			Electron Correlation →				
Basis Set Type	HF	MP2	MP3	MP4	QCISD(T)	...	Full CI
Minimal						...	
Split-valence						...	
Polarized						...	
Diffuse						...	
High ang. momentum						...	
...	...	...	...	...	...		...
∞	*HF Limit*					...	**Schrödinger Equation**

As the basis set becomes infinitely flexible, full CI approaches the exact solution of the time-independent, non-relativistic Schrödinger equation.

$$\begin{aligned}\psi &= \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \lambda^3\psi^{(3)} + \ldots \\ E &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots\end{aligned} \qquad [37]$$

The perturbed wavefunction and energy are substituted back into the Schrödinger equation:

$$(\mathbf{H}_0 + \lambda\mathbf{V})\,(\psi^{(0)} + \lambda\psi^{(1)} + \ldots) = (E^{(0)} + \lambda E^{(1)} + \ldots)\,(\psi^{(0)} + \lambda\psi^{(1)} + \ldots) \qquad [38]$$

After expanding the products, we can equate the coefficients on each side of the equation for each power of λ, leading to a series of relations representing successively higher orders of perturbation. Here are the first three such equations (after some rearranging), corresponding to powers of 0, 1, and 2 of λ:

$$\begin{aligned}(\mathbf{H}_0 - E^{(0)})\,\psi^{(0)} &= 0 \\ (\mathbf{H}_0 - E^{(0)})\,\psi^{(1)} &= (E^{(1)} - \mathbf{V})\,\psi^{(0)} \\ (\mathbf{H}_0 - E^{(0)})\,\psi^{(2)} &= (E^{(1)} - \mathbf{V})\,\psi^{(1)} + E^{(2)}\psi^{(0)}\end{aligned} \qquad [39]$$

So far, we've presented only general perturbation theory results. We'll now turn to the particular case of Møller-Plesset perturbation theory. Here, H_0 is defined as the sum of the one-electron Fock operators:[†]

$$\mathbf{H}_0 = \sum_i F^i \qquad [40]$$

The Hartree-Fock determinant and all of the substituted determinants are eigenfunctions of H_0; these are the solutions to the part of the divided Hamiltonian for which we have a solution. Thus:

$$\mathbf{H}_0\psi_s = E_s\psi_s \qquad [41]$$

for all substituted determinant wavefunctions.

[†] F^i is the Fock operator acting on the i^{th} electron.

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We'll consider each of the relations in Equation 39 in turn. In the first case, by forming the inner product of each side with $<\psi^{(0)}$, we obtain the following expression for $E^{(0)}$:

$$\begin{gathered}\langle\psi^{(0)}|\mathbf{H}_0 - E^{(0)}|\psi^{(0)}\rangle = \mathbf{0} \quad \Rightarrow \\ \langle\psi^{(0)}|\mathbf{H}_0|\psi^{(0)}\rangle = E^{(0)}\langle\psi^{(0)}|\psi^{(0)}\rangle = E^{(0)}\end{gathered} \qquad [42]$$

Since the ψ's are orthonormal, the inner product of any with itself is one, and the inner product of any distinct two of them is 0.

Since H_0 is the sum of Fock operators, then $E^{(0)}$ is the sum of the orbital energies:

$$E^{(0)} = \langle\psi^{(0)}|\mathbf{H}_0|\psi^{(0)}\rangle = \sum_i \varepsilon_i \qquad [43]$$

The expression for $E^{(1)}$ also follows easily from simple linear algebra. We begin by again forming the inner product of both sides of the second relation from Equation 39 with $<\psi^{(0)}$:

$$\begin{gathered}\langle\psi^{(0)}|(\mathbf{H}_0 - E^{(0)})|\psi^{(1)}\rangle = \langle\psi^{(0)}|(E^{(1)} - \mathbf{V})|\psi^{(0)}\rangle \quad \Rightarrow \\ \langle\psi^{(0)}|\mathbf{H}_0|\psi^{(1)}\rangle - E^{(0)}\langle\psi^{(0)}|\psi^{(1)}\rangle = E^{(1)}\langle\psi^{(0)}|\psi^{(0)}\rangle - \langle\psi^{(0)}|\mathbf{V}|\psi^{(0)}\rangle\end{gathered} \qquad [44]$$

Now, since $H_0\psi^{(0)}=E^{(0)}\psi^{(0)}$ and H_0 is an Hermitian operator ($H_0\psi^{(0)}=\psi^{(0)}H_0$), the left hand side of the final Equation 44 goes to 0, leaving this expression for $E^{(1)}$:

$$E^{(1)} = \langle\psi^{(0)}|\mathbf{V}|\psi^{(0)}\rangle \qquad [45]$$

Adding $E^{(0)}$ and $E^{(1)}$ yields the Hartree-Fock energy (since H_0+V is the full Hamiltonian):

$$\begin{aligned}E^{(0)} + E^{(1)} &= \langle\psi^{(0)}|\mathbf{H}_0|\psi^{(0)}\rangle + \langle\psi^{(0)}|\mathbf{V}|\psi^{(0)}\rangle \\ &= \langle\psi^{(0)}|(\mathbf{H}_0 + \mathbf{V})|\psi^{(0)}\rangle = \langle\psi^{(0)}|\mathbf{H}|\psi^{(0)}\rangle = E^{HF}\end{aligned} \qquad [46]$$

We'll begin examining the third relation in Equation 39 in the same way:

$$\begin{aligned} \langle\psi^{(0)}|(\mathbf{H}_0-E^{(0)})|\psi^{(2)}\rangle &= \langle\psi^{(0)}|(E^{(1)}-\mathbf{V})|\psi^{(1)}\rangle + E^{(2)}\langle\psi^{(0)}|\psi^{(0)}\rangle \Rightarrow \\ E^{(2)} &= \langle\psi^{(0)}|(\mathbf{V}-E^{(1)})|\psi^{(1)}\rangle = \langle\psi^{(0)}|\mathbf{V}|\psi^{(1)}\rangle \end{aligned} \qquad [47]$$

We need to find $\psi^{(1)}$ before we can determine $E^{(2)}$. We will form it as a linear combination of substituted wavefunctions and solve for the coefficients:

$$\psi^{(1)} = \sum_s a_s \psi_s \ni \mathbf{H}_0\psi_s = E_s\psi_s \qquad [48]$$

We will return to the second relation in Equation 39, and this time use it to find the coefficients for $\psi^{(1)}$:

$$(\mathbf{H}_0-E^{(0)})\sum_s a_s\psi_s = (E^{(1)}-\mathbf{V})\psi^{(0)} \qquad [49]$$

We will form the inner product of both sides of Equation 49 with an arbitrary substituted wavefunction ψ_t, and then solve for a_t:

$$\begin{aligned} \langle\psi_t|(\mathbf{H}_0-E^{(0)})\Big|\sum_s a_s\psi_s\rangle &= \langle\psi_t|(E^{(1)}-\mathbf{V})|\psi^{(0)}\rangle \Rightarrow \\ \sum_s a_s\langle\psi_t|(\mathbf{H}_0-E^{(0)})|\psi_s\rangle &= E^{(1)}\langle\psi_t|\psi^{(0)}\rangle - \langle\psi_t|\mathbf{V}|\psi^{(0)}\rangle \Rightarrow \\ \sum_s a_s\Big(\langle\psi_t|\mathbf{H}_0|\psi_s\rangle - \langle\psi_t|E^{(0)}|\psi_s\rangle\Big) &= E^{(1)}\langle\psi_t|\psi^{(0)}\rangle - \langle\psi_t|\mathbf{V}|\psi^{(0)}\rangle \end{aligned} \qquad [50]$$

The left side of the final Equation 50 is nonzero only when $s=t$, yielding:

$$\begin{aligned} a_t(E_t-E^{(0)}) &= -\langle\psi_t|\mathbf{V}|\psi^{(0)}\rangle \Rightarrow \\ a_t &= \frac{\langle\psi_t|\mathbf{V}|\psi^{(0)}\rangle}{E^{(0)}-E_t} \end{aligned} \qquad [51]$$

The result in Equation 51 indicates that substitutions close in energy to the ground state make larger contributions to the perturbation. Similarly, the more strongly mixed a state is with the ground state, the larger its contribution to the perturbation. Both of these observations are in line with (quantum mechanical) intuition.

These coefficients result in the following expression for $\psi^{(1)}$:

$$\psi^{(1)} = \sum_t \left(\frac{\langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle}{E^{(0)} - E_t} \right) \psi_t \qquad [52]$$

We can now return to the expression for $E^{(2)}$:

$$\begin{aligned} E^{(2)} &= \langle \psi^{(0)} | \mathbf{V} | \psi^{(1)} \rangle = \langle \psi^{(0)} | \mathbf{V} | \sum_t a_t \psi_t \rangle = \sum_t a_t \langle \psi^{(0)} | \mathbf{V} | \psi_t \rangle \\ &= \sum_t \frac{\langle \psi^{(0)} | \mathbf{V} | \psi_t \rangle \langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle}{E^{(0)} - E_t} = -\sum_t \frac{\left| \langle \psi^{(0)} | \mathbf{V} | \psi_t \rangle \right|^2}{E_t - E^{(0)}} \end{aligned} \qquad [53]$$

The two factors in the numerator of the first expression in the second line are one another's complex conjugates, and so reduce to the square of its modulus in the final expression.

Note that both the numerator and denominator in the final expression are always positive expressions; in the case of the denominator, we know this because $E^{(0)}$ is the lowest energy eigenvalue of the unperturbed system. (The denominator reduces to a difference in orbital energies.)

In addition, the numerator will be nonzero only for double substitutions. Single substitutions are known to make this expression zero by Brillouin's theorem. Triple and higher substitutions also result in zero value since the Hamiltonian contains only one and two-electron terms (physically, this means that all interactions between electrons occur pairwise).

Thus, the value of $E^{(2)}$, the first perturbation to the Hartree-Fock energy, will always be negative. Lowering the energy is what the exact correction should do, although the Møller-Plesset perturbation theory correction is capable of overcorrecting it, since it is not variational (and higher order corrections may be positive).

By a similar although more elaborate process, the third and fourth order energy corrections can be derived. For further details, consult the references.

Density Functional Theory

Density functional theory-based methods ultimately derive from quantum mechanics research from the 1920's, especially the Thomas-Fermi-Dirac model, and from Slater's fundamental work in quantum chemistry in the 1950's. The DFT approach is based upon a strategy of modeling electron correlation via general functionals[†] of the electron density.

Such methods owe their modern origins to the Hohenberg-Kohn theorem, published in 1964, which demonstrated the existence of a unique functional which determines the ground state energy and density exactly. The theorem does not provide the form of this functional, however.

Following on the work of Kohn and Sham, the approximate functionals employed by current DFT methods partition the electronic energy into several terms:

$$E = E^T + E^V + E^J + E^{XC} \qquad [54]$$

where E^T is the kinetic energy term (arising from the motion of the electrons), E^V includes terms describing the potential energy of the nuclear-electron attraction and of the repulsion between pairs of nuclei, E^J is the electron-electron repulsion term (it is also described as the Coulomb self-interaction of the electron density), and E^{XC} is the exchange-correlation term and includes the remaining part of the electron-electron interactions.

All terms except the nuclear-nuclear repulsion are functions of ρ, the electron density. E^J is given by the following expression:

$$E^J = \frac{1}{2}\int\int \rho(\vec{\mathbf{r}}_1)\,(\Delta r_{12})^{-1}\,\rho(\vec{\mathbf{r}}_2)\,d\vec{\mathbf{r}}_1 d\vec{\mathbf{r}}_2 \qquad [55]$$

$E^T+E^V+E^J$ corresponds to the classical energy of the charge distribution ρ. The E^{XC} term in Equation 54 accounts for the remaining terms in the energy:

- The exchange energy arising from the antisymmetry of the quantum mechanical wavefunction.
- Dynamic correlation in the motions of the individual electrons.

[†] A *functional* is a function whose definition is itself a function: in other words, a function of a function.

Hohenberg and Kohn demonstrated that E^{XC} is determined entirely by the (is a functional of) the electron density. In practice, E^{XC} is usually approximated as an integral involving only the spin densities and possibly their gradients:

$$E^{XC}(\rho) = \int f(\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}), \nabla\rho_\alpha(\vec{r}), \nabla\rho_\beta(\vec{r}))\, d^3\vec{r} \qquad [56]$$

We use ρ_α to refer to the α spin density, ρ_β to refer to the β spin density, and ρ to refer to the total electon density ($\rho_\alpha + \rho_\beta$).

E^{XC} is usually divided into separate parts, referred to as the *exchange* and *correlation* parts, but actually corresponding to same-spin and mixed-spin interactions, respectively:

$$E^{XC}(\rho) = E^{X}(\rho) + E^{C}(\rho) \qquad [57]$$

All three terms are again functionals of the electron density, and functionals defining the two components on the right side of Equation 57 are termed *exchange functionals* and *correlation functionals*, respectively. Both components can be of two distinct types: *local* functionals depend on only the electron density ρ, while *gradient-corrected* functionals depend on both ρ and its gradient, $\nabla\rho$.[†]

We'll now take a brief look at some sample functionals. The local exchange functional is virtually always defined as follows:

$$E^{X}_{LDA} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\int \rho^{4/3} d^3\vec{r} \qquad [58]$$

where ρ is of course a function of $\vec{r}$. This form was developed to reproduce the exchange energy of a uniform electron gas. By itself, however, it has weaknesses in describing molecular systems.

Becke formulated the following gradient-corrected exchange functional based on the LDA exchange functional in 1988, which is now in wide use:

$$E^{X}_{Becke88} = E^{X}_{LDA} - \gamma\int \frac{\rho^{4/3}x^2}{(1 + 6\gamma\sinh^{-1}x)}\, d^3\vec{r} \qquad [59]$$

[†] Note that this use of the term "local" does not coincide with the use of the term in mathematics; both local and gradient-corrected functionals are local in the mathematical sense.

where $x = \rho^{-4/3}|\nabla\rho|$. γ is a parameter chosen to fit the known exchange energies of the inert gas atoms, and Becke defines its value as 0.0042 Hartrees. As Equation 59 makes clear, Becke's functional is defined as a correction to the local LDA exchange functional, and it succeeds in remedying many of the LDA functional's deficiencies.

Similarly, there are local and gradient-corrected correlation functionals. For example, here is Perdew and Wang's formulation[†] of the local part of their 1991 correlation functional:

$$
\begin{aligned}
E^C &= \int \rho\varepsilon_C(r_s(\rho(\hat{\mathbf{r}})), \zeta)\, d^3\hat{\mathbf{r}} \\
r_s &= \left[\frac{3}{4\pi\rho}\right]^{1/3} \\
\zeta &= \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta} \qquad [60] \\
\varepsilon_C(r_s, \zeta) &= \varepsilon_C(\rho, 0) + a_C(r_s)\frac{f(\zeta)}{f''(0)}(1-\zeta^4) + [\varepsilon_C(\rho, 1) - \varepsilon_C(\rho, 0)]\, f(\zeta)\,\zeta^4 \\
f(\zeta) &= \frac{[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2]}{(2^{4/3} - 2)}
\end{aligned}
$$

r_s is termed the density parameter. ζ is the relative spin polarization. $\zeta=0$ corresponds to equal α and β densities, $\zeta=1$ correponds to all α density, and $\zeta=-1$ corresponds to all β density. Note that $f(0)=0$ and $f(\pm1)=1$.

The general expression for ε_C involves both r_s and ζ. Its final term performs an interpolation for mixed spin cases.

The following function G is used to compute the values of $\varepsilon_C(r_s,0)$, $\varepsilon_C(r_s,1)$ and $-a_C(r_s)$:

$$
G(r_s, A, \alpha_1, \beta_1, \beta_2, \beta_3, \beta_4, P) = -2A(1+\alpha_1 r_s)\ln\left(1 + \frac{1}{2A(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^{P+1})}\right) \qquad [61]
$$

In Equation 61, all of the arguments to G except r_s are parameters chosen by Perdew and Wang to reproduce accurate calculations on uniform electron gases. The parameter sets differ for G when it is used to evaluate each of $\varepsilon_C(r_s,0)$, $\varepsilon_C(r_s,1)$ and $-a_C(r_s)$.

In an analogous way to the exchange functional we examined earlier, a local correlation functional may also be improved by adding a gradient correction.

[†] Which is very closely related to Vosko, Wilk and Nusair's local correlation functional (VWN).

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Pure DFT methods are defined by pairing an exchange functional with a correlation functional. For example, the well-known BLYP functional pairs Becke's gradient-corrected exchange functional with the gradient-corrected correlation functional of Lee, Yang and Parr.

Hybrid Functionals

In actual practice, self-consistent Kohn-Sham DFT calculations are performed in an iterative manner that is analogous to an SCF computation. This similarity to the methodology of Hartree-Fock theory was pointed out by Kohn and Sham.

Hartree-Fock theory also includes an exchange term as part of its formulation. Recently, Becke has formulated functionals which include a mixture of Hartree-Fock and DFT exchange along with DFT correlation, conceptually defining E^{XC} as:

$$E^{XC}_{hybrid} = c_{HF}E^{X}_{HF} + c_{DFT}E^{XC}_{DFT} \qquad [62]$$

where the c's are constants. For example, a Becke-style three-parameter functional may be defined via the following expression:

$$E^{XC}_{B3LYP} = E^{X}_{LDA} + c_0(E^{X}_{HF} - E^{X}_{LDA}) + c_X\Delta E^{X}_{B88} + E^{C}_{VWN3} + c_C(E^{C}_{LYP} - E^{C}_{VWN3}) \qquad [63]$$

Here, the parameter c_0 allows any admixture of Hartree-Fock and LDA local exchange to be used. In addition, Becke's gradient correction to LDA exchange is also included, scaled by the parameter c_X. Similarly, the VWN3 local correlation functional is used, and it may be optionally corrected by the LYP correlation correction via the parameter c_C. In the B3LYP functional, the parameters values are those specified by Becke, which he determined by fitting to the atomization energies, ionization potentials, proton affinities and first-row atomic energies in the G1 molecule set: c_0=0.20, c_X=0.72 and c_C=0.81. Note that Becke used the the Perdew-Wang 1991 correlation functional in his original work rather than VWN3 and LYP. The fact that the same coefficients work well with different functionals reflects the underlying physical justification for using such a mixture of Hartree-Fock and DFT exchange first pointed out by Becke.

Different functionals can be constructed in the same way by varying the component functionals—for example, by substituting the Perdew-Wang 1991 gradient-corrected correlation functional for LYP—and by adjusting the values of the three parameters.

Integration Grids and DFT Calculations

In general, DFT calculations proceed in the same way as Hartree-Fock calculations, with the addition of the evaluation of the extra term, E^{XC}. This term cannot be evaluated analytically for DFT methods, so it is computed via numerical integration.

These calculations employ a grid of points in space in order to perform the numerical integration. Grids are specified as a number of radial shells around each atom, each of which contains a set number of integration points. For example, in the (75,302) grid, 75 radial shells each contain 302 points, resulting in a total of 22,650 integration points.

Uniform and *pruned* versions of many grids have been defined. Uniform grids contain the same number of angular points at each radial distance, while pruned grids are reduced from their full form so that fewer points are used on the shells near the core and far from the nucleus, where less density is needed for a given level of computational accuracy. Put another way, pruned grids are designed to be densest in the region of the atom where properties are changing most rapidly.

For example, the pruned (75,302) grid, denoted "(75,302)p" contains about 7,500 integration points per atom. In general, pruning reduces the size of a uniform grid by about 66%.

As of this writing, (75,302)p[†] is the default grid in *Gaussian* for all but single point calculations using standard SCF convergence (including **SCF=Tight** calculations). The SG1 grid, a pruned (50,194) grid containing about 3,600 points per atom is used for lower-accuracy single point calculations.

(75,302)p produces more accurate results than SG1, and it is accordingly strongly recommended for final energy calculations (where **SCF=Tight** should also be used in general), and for all geometry optimizations and frequency calculations. (75,302)p also has better rotational invarience properties than SG1, and it is much more suitable for molecular systems involving transition metals and calculations using pseudopotentials. The following example illustrates the differences in accuracy that can result from employing different grids.

Example A.1: Comparing Integration Grids

files: **ea_01a** (Si_5H_{12})
ea_01b (Al_4P_4)
ea_01c (NoSymm)

We ran a BLYP/6-31G(d) single point energy calculation, using tight SCF convergence, on Si_5H_{12} and Al_4P_4 (119 and 152 basis functions, respectively), using the SG1 and (75,302)p pruned grids, and the unpruned (50,194) and (99,434) grids.

[†] Also referred to by the option **FineGrid**.

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Here are the predicted relative energies with respect to the results from the large (99,434) grid for each calculation:

	$\Delta E^{(99,434)}$ (kcal-mol^{-1})	
Grid (Option)	Si_5H_{12}	Al_4P_4
(50,194)p **Int=SG1**	0.292	-0.373
uniform (50,194) **Int(Grid=50194)**	0.277	-0.287
(75,302)p **Int=FineGrid**	-0.029	0.060

SG1 seems to have more trouble with second-row atoms than first-row atoms. The energy differences between the SG1 and the large (99,434) grids are small but significant. In contrast, the default (75,302)p grid reproduces the energy predictions of the larger grid very well. The energy differences between SG1 and the default grid are 0.321 and -0.313 for the Si_5H_{12} and Al_4P_4, respectively.

SG1 also suffers from substantial rotation invarience: changing the orientation of the molecule can substantially alter the predicted energy. All DFT methods using finite grids will exhibit some degree of rotational invarience, but SG1 is more sensitive than most grids—the effect is generally more pronounced with smaller grids—as the following results on Al_4P_4 indicate. This table gives the change in predicted energy when molecular symmetry is ignored in the calculation with respect to the default procedure (taking advantage of symmetry) for SG1 and the default grid:

Grid (Option)	ΔE^{NoSymm} (kcal-mol^{-1})
(50,194)p **Int=SG1**	0.354
(75,302)p **Int=FineGrid**	0.079

The default (75,302)p grid results in only minor changes in energy between the two molecular orientations. However, the SG1 grid's predicted energy is very different for the two orientations of the molecule.

The Complete Basis Set Extrapolation

As we noted in Chapter 7, the CBS family of methods all include a component which extrapolates from calculations using a finite basis set to the estimated complete basis set limit. In this section, we very briefly introduce this procedure.

The extrapolation to the complete basis set energy limit is based upon the Møller-Plesset expansion $E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} + \ldots$ as described earlier in this appendix. Recall that $E^{(0)} + E^{(1)}$ is the Hartree-Fock energy. We will denote $E^{(3)}$ and all higher terms as $E^{3\rightarrow\infty}$, resulting in this expression for E:

$$E = E^{HF} + E^{(2)} + E^{3\rightarrow\infty} \qquad [64]$$

Remember that the CBS models begin with a large enough SCF calculation to obtain the desired level of accuracy (see Chapter 7); therefore, no explicit extrapolation of the SCF energy is included. CBS extrapolation involves computing the second-order and infinite-order corrections to the energy.

Schwartz has shown that for a helium-like ion[†], the contribution to the second-order Møller-Plesset energy from the *l* angular momentum component can be approximated by the following expression:

$$\lim_{l\rightarrow\infty} \Delta E_l^{(2)} \approx -\frac{45}{256}\left(l+\frac{1}{2}\right)^{-4} \qquad [65]$$

This expression describes how the energy converges as we add successive s functions, p functions, d functions, f functions, and so on, to spherical atoms.

Petersson and coworkers have extended this two-electron formulation of asymptotic convergence to many-electron atoms. They note that the second-order Møller-Plesset correlation energy for a many-electron system may be written as a sum of pair energies, each describing the energetic effect of the electron correlation between that pair of electrons:

[†] In the limit of infinite nuclear charge.

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$$E^{(2)} = \sum_{i,j}^{occ} e_{ij}^{(2)} = \sum_{i,j}^{occ}\sum_{a,b}^{virt} C_{ij}^{ab} V_{ij}^{ab}$$
$$V_{ij}^{ab} = \langle ij|(\Delta r_{12})^{-1}|ab\rangle \qquad [66]$$
$$C_{ij}^{ab} = \frac{V_{ij}^{ab}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

where the V_{ij}^{ab} are Hamiltonian matrix elements coupling occupied orbitals i and j with virtual orbitals a and b. C_{ij}^{ab} are the coefficients of the first-order wavefunction.

For αβ electron pairs, the coefficient matrix C may be diagonalized, yielding the *pair natural orbital* (PNO) expansion of the pair energies:

$$^{\alpha\beta}e_{ij}^{(2)} = \sum_{a}^{PNO} C_{ij}^{aa} V_{ij}^{aa} \qquad [67]$$

In natural orbital form, the asymptotic convergence of $^{\alpha\beta}e_{ij}^{(2)}$ has been shown to have the following form, resulting in the CBS limit, $e_{ij}^{(2)}(\mathrm{CBS})$:

$$^{\alpha\beta}e_{ij}^{(2)}(\mathrm{CBS}) = \lim_{N\to\infty} {}^{\alpha\beta}e_{ij}^{(2)}(N) - \left(\tfrac{25}{512}\right) {}^{\alpha\beta}f_{ij}(N+\delta_{ij})^{-1}$$
$$^{\alpha\beta}e_{ij}^{(2)}(N) = \sum_{a=2}^{N} C_{ij}^{aa} V_{ij}^{aa} \qquad [68]$$

f is the *overlap factor*, and it provides the exact attenuation of the interorbital pairs relative to intraorbital pairs for a model involving two infinitely-separated helium-like ions.

The parameter δ_{ij} serves to retain size consistency in the CBS extrapolation for finite values of N. Full CI pair energies, $^{\alpha\beta}e_{ij}^{(\infty)}(N)$, may be obtained from the diagonalization of the pair CI Hamiltonian:

$$\langle \phi_{ij}^{ab} |\mathbf{H}| \phi_{ij}^{cd} \rangle \qquad [69]$$

where ϕ_{ij}^{ab} is a configuration in which occupied orbitals i and j are replaced by virtual orbitals a and b. It has been shown that the resulting infinite-order pair energies converge to the CBS limit according to the following expression:

$$^{\alpha\beta}e_{ij}^{(\infty)}(\mathrm{CBS}) \quad = \lim_{N \to \infty} {}^{\alpha\beta}e_{ij}^{(\infty)}(N) \; - \left[\sum_{a=1}^{N} C_{ij}^{a_i, a_j} \right]^2 \left(\tfrac{25}{512}\right) {}^{\alpha\beta}f_{ij} \, (N + \delta_{ij})^{-1} \qquad [70]$$

The sum over CI coefficients is an *interference factor* resulting from the fact that the full CI pair energies converge faster than the second-order pair energies.

CBS model chemistries make the correction resulting from these extrapolations to the second-order (MP2) correlation energy:

$$\Delta E^{(2)} = \sum_{ij} \left[e_{ij}^{(2)}(\mathrm{CBS}) - e_{ij}^{(2)}(N) \right] \qquad [71]$$

An infinite-order correction is similarly made to MP4 or QCISD(T) energies (approximate full CI energies):

$$\Delta E^{(\infty)} = \sum_{ij} \left\{ \left[\sum_{\mu_{ij}}^{N_{\mathrm{virt}}+1} C_{\mu_{ij}} \right]^2 \left[e_{ij}^{(2)}(\mathrm{CBS}) - e_{ij}^{(2)}(N) \right] \right\} \qquad [72]$$

Because the interelectronic cusp is difficult to describe well with one-electron basis functions, pair correlation energies converge much more slowly (as N^{-1})† than SCF energies (which converge as l^{-6}). This fact makes the use of CBS extrapolations of the correlation energy very beneficial in terms of both accuracy and computational cost.

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† $\alpha\alpha$ and $\beta\beta$ (triplet) pair energies converge as $N^{-5/3}$.

$f_{ij} (N + \delta_{ij})^{-1}$ [70]

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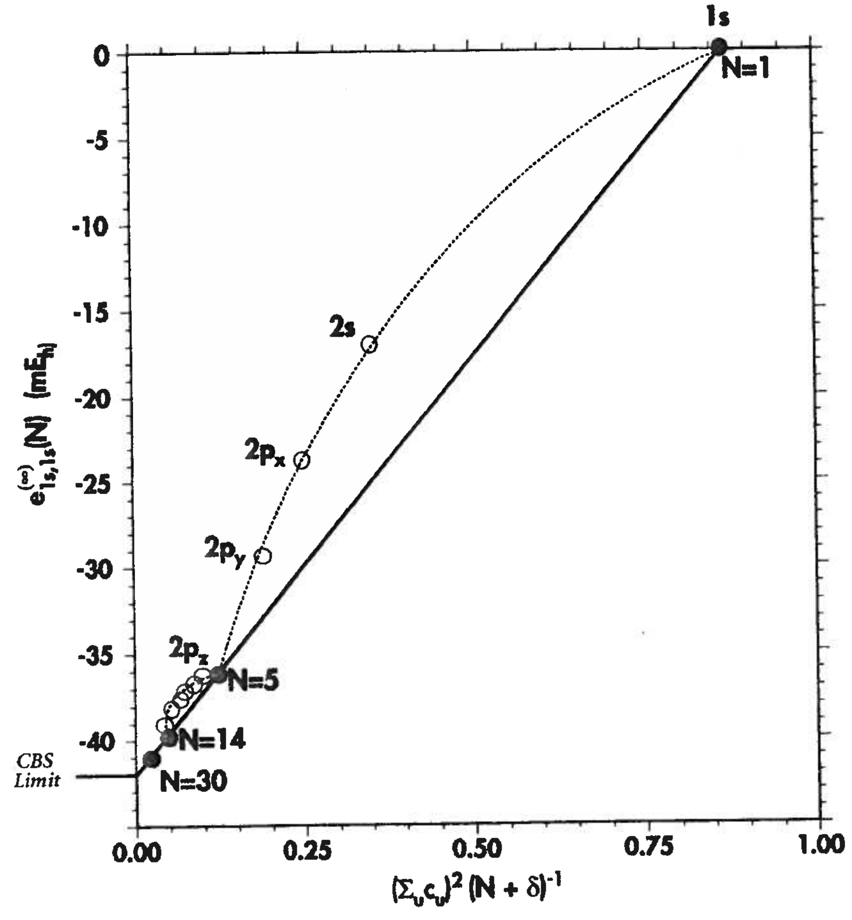
CBS extrapolation is illustrated in the following figure which depicts the extrapolation for the helium atom:



The filled and hollow circles indicate the contributions of each successive natural orbital. The filled circles correspond to complete shells. Only these points are useful for extrapolating to the complete basis set limit.

Consult the works listed in the references for a full discussion of CBS extrapolation.

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Appendix

B

Overview of Gaussian Input

In This Appendix:

Gaussian Input File Format

Constructing Z-matrices

We've already looked briefly at *Gaussian* input in the *Quick Start*. Here we present a more formal definition and discuss the various molecule specification options.

Gaussian input is designed to be free-format and extremely flexible. For example, it is not case-sensitive, and keywords and options may be shortened to a unique abbreviation.

Input File Sections

Gaussian input (which is the same for all versions of the program, including the Window version) has the basic structure described in the following table. Note that the input sections marked with an asterisk are required in every input file:

Input Section	Contents
Link 0 Commands	*Defines the locations of scratch files and job resource limits.*
*Route Section	*Specifies the job type and model chemistry.*
**blank line*	*Separates the route section from the title section.*
*Title Section	*Describes the job for the output and archive entry.*
**blank line*	
*Molecule Specification	*Gives the structure of the molecule to be studied.*
**blank line*	
Variables Section	*Specifies values for the variables used in the molecule specification.*
blank line	

Note that the separate input sections are separated from one another by blank lines. These blank lines are inserted automatically into input files created with the **Job Entry** window in the Windows version and need not be entered by the user. If you choose to create a *Gaussian* input file using an external Windows editor, however, you must follow the same rules for input as under other versions of *Gaussian*.

Note that some job types require additional sections not listed.

Input lines have a maximum length of 80 characters.

Appendix B Overview of Gaussian Input

The Route Section

The first line of the route section always begins with a pound sign (#) in the first column. This section specifies the theoretical procedure, basis set, and desired type of calculation. It may also include other keywords. The ordering of keywords is not important. Some keywords require options; the following input line illustrates the possible formats for keywords with options:

`#T RHF/6-31G(d)`	`SCF=Tight`	`Units=(Bohr,Radian)`	`Opt Test`
Keyword with:	**a single option**	**≥ 2 options**	**no options**

The amount of spacing between items is not significant in *Gaussian* input. In the route section, commas or slashes may be substituted for spaces if desired (except within parenthesized options, where slashes don't work). For example, the previous route section used a slash to separate the procedure and basis set, spaces to separate other keywords, and commas to separate the options to the **Units** keyword.

The route section may extend over more than one line if necessary. Only the first line need begin with a pound sign, although any others may. The route section is terminated by a blank line.

The Title Section

The title section consists of one or more lines of descriptive information about the job. It is included in the output and in the archive entry but is not otherwise used by *Gaussian*. This section is terminated by a blank line.

Specifying Molecular Structures

Gaussian accepts molecule specifications in several different formats:

- Cartesian coordinates
- Z-matrix format (internal coordinates)
- Mixed internal and Cartesian coordinates

All molecule specifications require that the *charge* and *spin multiplicity* be specified (as two integers) on the first line of this section. The charge is a positive or negative integer specifying the total charge on the molecule. Thus, 1 or +1 would be used for a singly-charged cation, -1 designates a singly-charged anion, and 0 represents a neutral molecule.

Spin Multiplicity

The *spin multiplicity* is given by the equation $2S + 1$, where S is the total spin for the molecule. Paired electrons contribute nothing to this quantity. They have a net spin of zero since an alpha electron has a spin of +½ and a beta electron has a spin of -½. Each unpaired electron contributes +½ to S. Thus, a singlet—a system with no unpaired electrons—has a spin multiplicity of 1, a doublet (one unpaired electron)

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has a spin multiplicity of 2, a triplet (two unpaired electrons of like spin) has a spin multiplicity of 3, and so on.

Units

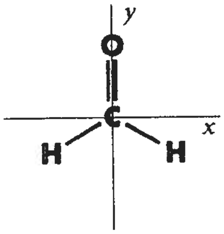
The units in a Z-matrix are angstroms for lengths and degrees for angles by default; the default units for Cartesian coordinates are angstroms. These are also the default units for lengths and angles used in *Gaussian* output. You can change them to bohrs and/or radians by including the **Units** keyword in the route section with one or both of its options: **Bohr** and **Radian.**

Cartesian Coordinate Input

Cartesian coordinate input consists of a series of lines of the form:

```
Atomic-symbol  X-coordinate  Y-coordinate  Z-coordinate
```

For example, here is the molecular structure for formaldehyde, given in Cartesian coordinates:

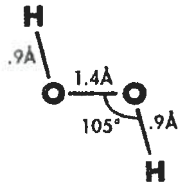


```
0 1
C  0.0    0.0  0.0
O  0.0    1.22 0.0
H  0.94 -0.54 0.0
H -0.94 -0.54 0.0
```

Z-Matrix Input

The other syntax for supplying molecular structures to *Gaussian 94* is the *Z-matrix.* A Z-matrix specifies the locations of and bonds between atoms using bond lengths, bond angles, and dihedral (torsion) angles.

Each atom in the molecule is described on a separate input line within the Z-matrix. As we consider the procedure for creating a Z-matrix, we'll use hydrogen peroxide as an example. These are the steps to do so:



1. Choose a starting atom in the molecule, and conceptually place it at the origin in three dimensional space.

The first line of the Z-matrix consists solely of the label for this atom. An atom label is made up of its atomic symbol optionally followed by an integer (no spaces), used to distinguish it from the other atoms of the same type (e.g. H1 for the first hydrogen, H2 for the second one, and so on).

We'll use the left oxygen atom in the illustration as our first atom:

```
O1
```

2. Choose another atom bonded to the first atom. Place it along the Z-axis, and specify the length of the bond connecting the two atoms.

This second input line will include the atom label of the second atom, the label of the atom it is bonded to (the first atom), and the bond length, in that order. Items may be separated by spaces, tabs or commas.

We'll use the hydrogen atom bonded to the first oxygen for our second atom:

```
O1
H1 O1 .9
```

3. Choose a third atom bonded to either of the previous two atoms and specify the angle formed by the two bonds.

This angle locates the molecule's position in the XZ-plane. This input line will include the new atom's label, the atom it is bonded to and the bond length, the label of the other atom forming the bond angle, and the angle's value.

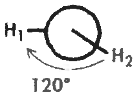
We have only one choice for the third atom in our Z-matrix, the second oxygen atom:

```
O1
H1 O1 0.9
O2 O1 1.4 H1 105.0
```

The new line illustrates an important point about numeric values within Z-matrices. Since they correspond to floating point quantities, they must include a decimal point, as in the value above. This is true even for a value of 0.

4. Describe the positions of all subsequent atoms by specifying:

- Its atom label.
- An atom it is bonded to and the bond length.
- A third atom bonded to it (or to the second atom), and the value of the resulting bond angle.
- A fourth atom bonded to either end of the previous chain, and the value of the dihedral (torsion) angle formed by the four atoms.



Dihedral angles describe the angle the fourth atom makes with respect to the plane defined by the first three atoms; their values range from 0 to 360 degrees, or from -180 to 180 degrees. Dihedral angles are easy to visualize using Newman projections. The illustration shows the Newman projection for hydrogen peroxide, looking down the O-O bond. Positive dihedral angles correspond to clockwise rotation in the Newman projection.

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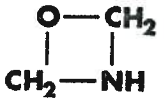
Obviously, we'll use the remaining hydrogen atom for the fourth line of our Z-matrix for hydrogen peroxide. Here is the completed molecule specification:

`0 1`	*Charge and multiplicity.*
`O1`	*Oxygen atom #1.*
`H1 O1 .9`	*Hydrogen #1, connected to oxygen #1 by a bond of 0.9 Å.*
`O2 O1 1.4 H1 105.`	*Oxygen #2: O2–O1 = 1.4 Å; ∠ H1–O1–O2 = 105°.*
`H2 O2 .9 O1 105. H1 120.`	*Hydrogen #2: H2–O2 bond =0.9 Å; ∠ H2–O2–O1 = 105°; dihedral angle H2–O2–O1–H1=120°.*

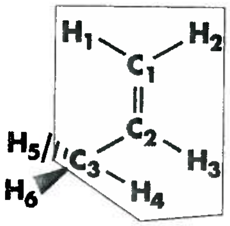
Sources for bond lengths, bond angles, and dihedral angles include the published literature, standard references like the CRC series, and previous calculations. Z-matrices may also be created by the **NewZMat** utility from data generated by a wide variety of drawing packages. Refer to the *Quick Start* for a sample conversion operation for your version of *Gaussian.*



Mixed Internal and Cartesian Coordinates

It is also possible to specify the molecular structure in a format which combines Cartesian coordinates and Z-matrix style input; this format is referred to as mixed internal and Cartesian coordinates. It is useful for systems where some parts of the molecule are more easily specified in Cartesian coordinates and others are more easily described as a Z-matrix. Consult Exercise C.2 (page 293) and Appendix B of the *Gaussian 94 User's Reference* for more information on this topic.

More Complex Z-Matrices



Constructing a Z-matrix for propene provides a more challenging example. Note that the atoms inside the red line in the illustration all lie in a plane. First we'll specify the carbon atoms:

`0 1`	*Charge and multiplicity.*
`C1`	*Carbon atom at the head of the double bond.*
`C2 C1 1.34`	*Carbon atom on the other end of the double bond.*
`C3 C2 1.52 C1 120.`	*Third carbon atom.*

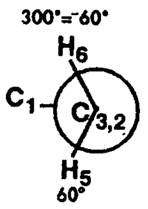
Next, we'll specify the hydrogens on C1 and C2. The bond angles formed with the double-bonded carbons and each of these hydrogens is 120°. We'll pick simple dihedral angles for each of them:

`H1 C1 1.09 C2 120. C3 0.`	*The dihedral with respect to the C-C single bond is 0°. Note that the decimal point must be included.*[†]
`H2 C1 1.09 C2 120. C3 180.`	*The dihedral with respect to the same bond is 180°, since it is on the opposite side of the double bond from carbon C3.*
`H3 C2 1.09 C1 120. H1 180.`	*This is an equivalent dihedral to the previous one, substituting H1 for the third carbon.*

The planar hydrogen on C3 is specified in a similar manner:

`H4 C3 1.09 C2 109.5 C1 180.`	*Just like the dihedral we formed for H2.*

The geometry of the carbon we've labelled C3 is tetrahedral; the bond angle of each of the hydrogens with respect to the C3-C2 bond is about 109.5°.



The dihedrals for the remaining two hydrogens are best visualized with a Newman projection. They are located above and below the plane of the C-C-C bond. H5 is the hydrogen below the plane, and its dihedral is 60°. The dihedral for H6 could be expressed as either 300° or -60°; we'll use the latter to express the symmetry of the molecule. Here are the Z-matrix lines for these atoms:

```
H5 C3 1.09 C2 109.5 C1  60.
H6 C3 1.09 C2 109.5 C1 -60.
```

Using Variables in a Z-matrix

Here is a complete input file for an optimization of this molecule:

```
#T RHF/6-31G(d) Opt Test

Propene Optimization

0 1
C1
C2 C1 CCD
C3 C2 CCS C1 A1
H1 C1 CH  C2 A1 C3 0.
H2 C1 CH  C2 A1 C3 180.
H3 C2 CH  C1 A1 H1 180.
H4 C3 CH  C2 A2 C1 180.
H5 C3 CH  C2 A2 C1  D
H6 C3 CH  C2 A2 C1 -D
```

Z-matrix with variables.

[†] Note that there are no blank lines within the Z-matrix, despite its appearance here. The extra spacing in this example is simply an artifact of the commentary.

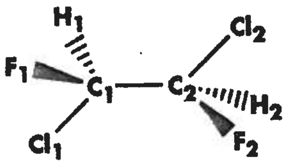
`Variables:`	
`CCD=1.34`	*C-C double bond length.*
`CCS=1.52`	*C-C single bond length.*
`CH=1.09`	*C-H bond length.*
`A1=120.0`	*C-C-C and some C-C-H bond angles.*
`A2=109.5`	*C-C-H bond angles for hydrogens on C3.*
`D=60.0`	*Magnitude of the dihedral angle for non-planar hydrogens.*

This file introduces the concept of *variables* within the molecule specification. Here, variables are simply named constants; variable names are substituted for literal values within the Z-matrix, and their values are defined in a separate section following it. The two sections are separated by a blank line, or a line with a blank in the first column and the label `Variables:` placed elsewhere on it (this is one exception *Gaussian* makes in its requirement for completely blank lines).[†]

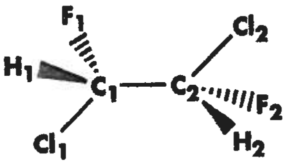
Notice that we used `D` and `-D` respectively for the dihedral angles for the non-planar hydrogens, as opposed to two separate variables. This is done to ensure symmetry within the molecule.

Exercise B.1: Z-Matrices for 1,2-Dichloro-1,2-Difluoroethane Isomers

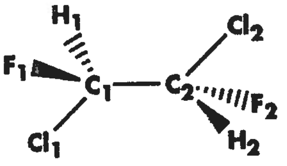
Try your hand at constructing Z-matrices for these three isomers of 1,2-Dichloro-1,2-Difluoroethane:



RR



SS



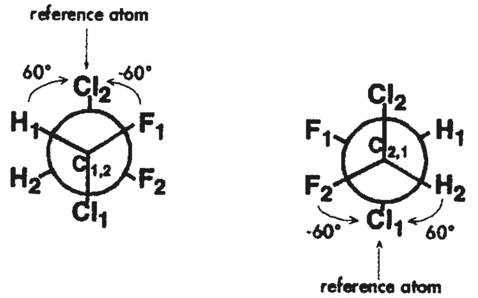
meso

Solution We'll construct the Z-matrix for the RR form first. We'll use the Cl-C-C-Cl plane as our major reference. Here are the lines for the carbons and chlorines:

`C1`	
`C2 C1 1.53`	*Bonded to C1 at a distance of 1.53A.*
`Cl1 C1 1.76 C2 109.5`	*Bonded to C1 at 1.76Å; ∠Cl-C-C=109.5°.*
`Cl2 C2 1.76 C1 109.5 Cl1 180.`	*Bonded to C2 (1.76A); ∠C-C-Cl =109.5°; and Cl-C-C-Cl dihedral angle is 180° (the 2 chlorines are on opposite sides of the carbon chain).*

[†] Variables represent labels for the internal degrees of freedom being specified for the structure. As we note, the values of the variables are defined in a separate section below the Z-matrix. It is also possible to specify a third section for *constants*, which immediately follows the variables section; its separator line is either blank or it contains the label `Constants:` preceded by one or more spaces. In traditonal **Opt=Z-Matrix** geometry optimizations, the values of variables are optimized while the values of constants remain fixed throughout.

Newman projections are helpful in determining the proper dihedral angles for the fluorines and hydrogens. Here are diagrams for the RR isomer, looking down the C-C bond in both directions:



The left diagram places the C_1 carbon in front, and indicates the angles for the fluorine and hydrogen attached to it, using the two carbons and the chlorine attached to the other carbon (Cl_2) to form the dihedral angle:

```
F1 C1 1.37 C2 109.5 Cl2 -60.
H1 C1 1.09 C2 109.5 Cl2  60.
```

A similar process, using the Newman projection diagram on the right, which places C_2 in front of C_1, and uses Cl_1 as the third atom for the dihedral angles, results in the last two lines of the Z-matrix:

```
F2 C2 1.37 C1 109.5 Cl1 -60.
H2 C2 1.09 C1 109.5 Cl1  60.
```

Here is the complete Z-matrix for the RR form:

```
0 1
C1
C2  C1 1.53
Cl1 C1 1.76 C2 109.5
Cl2 C2 1.76 C1 109.5 Cl1 180.
F1  C1 1.37 C2 109.5 Cl2 -60.
H1  C1 1.09 C2 109.5 Cl2  60.
F2  C2 1.37 C1 109.5 Cl1 -60.
H2  C2 1.09 C1 109.5 Cl1  60.
```

In the SS form, the positions of the fluorine and the hydrogen on each carbon are interchanged. This results in a corresponding exchange of their dihedral angles, while

dihedral angles for the
, looking down the C-C

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on each carbon are
lihedral angles, while

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all other values in the Z-matrix remain the same. Here is the complete Z-matrix for the SS form:

```
0 1
C1
C2  C1 1.53
Cl1 C1 1.76 C2 109.5
Cl2 C2 1.76 C1 109.5 Cl1 180.
F1  C1 1.37 C2 109.5 Cl2  60.
H1  C1 1.09 C2 109.5 Cl2 -60.
F2  C2 1.37 C1 109.5 Cl1  60.
H2  C2 1.09 C1 109.5 Cl1 -60.
```

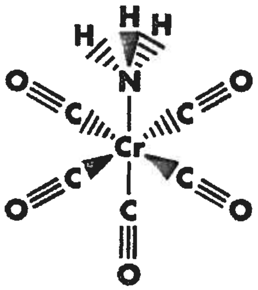
The meso form swaps the hydrogen and fluorine on only one of the carbons, leaving the other two unchanged with respect to the RR form. This will result in the dihedral angles for the hydrogens and fluorines having different signs on the two carbons:

```
0 1
C1
C2  C1 1.53
Cl1 C1 1.76 C2 109.5
Cl2 C2 1.76 C1 109.5 Cl1 180.
F1 C1 1.37 C2 109.5 Cl2 -60.
H1 C1 1.09 C2 109.5 Cl2  60.
F2 C2 1.37 C1 109.5 Cl1  60.
H2 C2 1.09 C1 109.5 Cl1 -60.
```

Exercise B.2: Mixed Cartesian and Internal Coordinates

Here is a molecule specification for $Cr(CO)_6$, expressed in Cartesian coordinates:

```
0   1
Cr  0.00  0.00  0.00
C   1.93  0.00  0.00
C  -1.93  0.00  0.00
C   0.00  1.93  0.00
C   0.00 -1.93  0.00
C   0.00  0.00  1.93
C   0.00  0.00 -1.93
O   3.07  0.00  0.00
O  -3.07  0.00  0.00
O   0.00  3.07  0.00
O   0.00 -3.07  0.00
O   0.00  0.00 -3.07
O   0.00  0.00  3.07
```



Replace one of the carbonyls with an ammonia group, and construct a new molecule specification.

Solution We replace the final carbon atom with a nitrogen, specifying the Cr-N bond length as 2.27, and then express the three hydrogen atoms via a Z-matrix. Note that Cartesian coordinates are included within a Z-matrix by specifying the bonded-to-atom as **0**:

```
0   1
Cr 0 0.00  0.00  0.00
C 0  1.93  0.00  0.00
C 0 -1.93  0.00  0.00
C 0  0.00  1.93  0.00
C 0  0.00 -1.93  0.00
C 0  0.00  0.00  1.93
O 0  3.07  0.00  0.00
O 0 -3.07  0.00  0.00
O 0  0.00  3.07  0.00
O 0  0.00 -3.07  0.00
O 0  0.00  0.00 -3.07
N 0  0.00  0.00  2.27
H 12 R 1 A  2  0.
H 12 R 1 A 13  D
H 12 R 1 A 13 -D

R 1.02
A 115.0
D 120.0
```

See Appendix B of the *Gaussian 94 User's Reference* for more information about and examples of constructing Z-matrices. ■

Multi-Step Jobs

Multiple *Gaussian* calculations may be combined within a single input file. The input for each successive job is separated from that of the preceding job step by a line of the form:

```
--Link1--
```

Here is an example input file containing two job steps:

`#T RHF/6-31G(d) Test`	*Route section for the first job step*
`Formaldehyde Energy`	*Title section for the first jobstep*
`0 1`	*Molecule specification section*
`...`	
`H2 O 1. H1 120.`	*End of Z-matrix*
	Blank line ending the molecule specification section
`--Link1--`	*Starts a new job step*

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b step by a line of the

ification section

```
#T RHF/6-31G(d) Test          Route section for the second job step

Peroxide Energy               Title section for the second job step
...                           Input continues...
```

When placing multiple jobs within a single input file, it is imperative that the final section of each job end with a blank line, a requirement that is not always strictly enforced for single-step jobs. If you want to run a single job from a multistep input file, you must copy the relevant lines to a new file, and then execute *Gaussian 94* using the new file.

Here is an example of an input file containing two job steps in which the second calculation depends upon and uses the results of the first job step:

```
%Chk=freq                     First job step
#T HF/6-31G(d) Freq

Frequencies at STP

Molecule specification

--Link1--                     Separator line
%Chk=freq                     Second job step
%NoSave
#T HF/6-31G(d) Geom=Check Guess=Read Freq=(ReadFC,ReadIsotopes)

Frequencies at 300 K

charge and multiplicity

300.0  2.0
Isotope specifications
```

This input file computes vibrational frequencies and performs thermochemical analysis at two different temperatures and pressures: first at 298.15 K and 1 atmosphere, and then again at 300 K and 2 atmospheres. Note that a blank line *must* precede the **--Link1--** line.

The **%Chk** command in each job step specifies the name for the checkpoint file—one of *Gaussian*'s scratch files—and it tells the program to save the file after the job finishes (normally, all scratch files are deleted automatically). The **%NoSave** command in the second job step tells the program to delete the checkpoint file after that step concludes even though **%Chk** has been included.

The most common purpose for specifying and saving the checkpoint file is so that molecular structures and other calculation results can be retrieved from it for use in a subsequent calculation. For example, in the second job step, the molecular structure, SCF initial guess, and frequency results are retrieved from the checkpoint file and used to predict thermochemical properties at a different temperature and pressure.

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Exploring Chemistry with Electronic Structure Methods

Second Edition

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