

MOPAC: A semiempirical molecular orbital program

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1. INTRODUCTION

1.1 What is MOPAC?

Before we start, we need a working definition for MOPAC. The following description has been used many times to describe MOPAC: MOPAC is a general-purpose, semiempirical molecular orbital program for the study of chemical reactions involving molecules, ions, and linear polymers. It implements the semiempirical Hamiltonians MNDO, AM1, MINDO/3, and MNDO-PM3, and combines the calculations of vibrational spectra, thermodynamic quantities, isotopic substitution effects, and force constants in a fully integrated program. Elements parameterized at the MNDO level include H, Li, Be, B, C, N, O, F, Al, Si, P, S, Cl, Ge, Br, Sn, Hg, Pb, and I; at the PM3 level the elements H, C, N, O, F, Al, Si, P, S, Cl, Br, and I are available. Within the electronic part of the calculation, molecular and localized orbitals, excited states up to sextets, chemical bond indices, charges, etc. are computed. Both intrinsic and dynamic reaction coordinates can be calculated. A transition-state location routine and two transition-state optimizing routines are available for studying chemical reactions.

Over the past two decades computational chemistry has undergone a considerable change. During the 70s, there was a chaos of untested methods of decidedly questionable accuracy and very limited applicability. This was a time in which myriad new methods, particularly in the field of semiempirical theory, would suddenly appear. Enthusiastically advocated by their authors, they would, as often as not, die with equal rapidity. For many experimental chemists, the lesson learned during this era was that computational chemists – a title which few would admit to for many years – were not to be heeded, but to be tacitly ignored.

Since then computational chemistry has become respectable. Today, three main branches enjoy considerable popularity: molecular mechanics, semiempirical, and ab initio or Gaussian methods [1]. Each branch has carved out a niche within which it is supreme, and from which it can recognize the eminence of the other two. Thus, the conformations of macromolecules are most effectively studied using the techniques of molecular mechanics, while the electronic properties of small molecules are most accurately calculated using ab initio methods. In the middle lie the semiempirical methods, of which MNDO [2], MINDO/3 [3] and AM1 [4], developed by Michael J.S. Dewar, are the most popular. These methods are not particularly fast; in fact, they are very slow when compared with molecular mechanics. Nor are they particularly rigorous: this is rightfully

the province of the ab initio methods. As with *Homo sapiens*, a creature without specialization, the semiempirical methods are not particularly good at any one thing. A consequence of this is that such methods, again as with *Homo sapiens*, have become extremely versatile.

It is not sufficient to develop a useful computational chemistry technique; as a series of mathematical formulae, new methods have no practical use. Such techniques must first have an algorithmic body to inhabit in order to have any corporeal existence. Currently several such bodies exist. In this section we will look at one of these implementations, MOPAC. This description of MOPAC is not intended to serve as an instruction set for using the program (the Manual is provided for that purpose), but rather as an overview of the program, along with indications of its application.

MOPAC is a single program which incorporates many separate functions, almost all of which were developed by individual groups prior to the writing of MOPAC. As a result, while the current formulation was written almost entirely by the author, MOPAC really represents the cumulative effort of a very large number of individuals. The individual algorithms they contributed each represent many man-years of effort. However, by concentrating on writing a single coherent program to implement all these different methods at the expense of advancing computational techniques, the author has been able to generate a single program which is, in the words of Michael Dewar, 'impressively easy to use' and 'contains options for nearly all the applications where our procedures have been found to be useful'.*

Although MOPAC was written for use on a VAX computer, the fact that it would be transferred to other machines was recognized at the onset. Thus MOPAC was written from its inception in almost pure FORTRAN-77. This policy proved prophetic. MOPAC has since been converted to run on many machines, including those made by CDC, CRAY, ETA, GOULD, IBM, NEC, PRIME, and ZENITH, with little difficulty. These range in size from the supercomputers, such as the CRAY-2, to the micros, such as the IBM PC-AT and -XT and Zenith 100.

MOPAC is wholly in the public domain. The source code and documentation can be obtained from the Quantum Chemistry Program Exchange. Over the past five years it has been developed at the Frank J. Seiler Research Laboratory of the Air Force Academy, and, as a product of government work, cannot be copyrighted. This is not to say that some versions of MOPAC have not been copyrighted – versions specific to individual machines have been – but all versions produced at the Frank J. Seiler Research Laboratory are public domain and may be obtained without restriction from the Quantum Chemistry Program Exchange.

In order to remain current, a new version of MOPAC has been produced at the rate of one per year. This rate was chosen as the best compromise between keeping users current and not asking users to continuously update their files. As far as is possible, updates have been checked for errors and for compatibility with previous versions. There have been six versions published so far, and these versions have been converted to run on between 15 and 20 different types of computer. This has resulted in a large number of 'official' programs. When all the modifications individual users have made are taken into consideration, it is obvious that there is a very high potential for confusion. Thus users are recommended to obtain copies of MOPAC from QCPE, and to stay as current as possible.

* Foreword to MOPAC Version 4.00 Manual.

1.2 DRAW

Concurrent with the development of MOPAC, Major Donn M. Storch of the U.S. Air Force Academy's Department of Chemistry, wrote a graphics package to act as a general purpose data manipulation program. This program, called DRAW [5], is very useful for generating and checking the input data for MOPAC. It's main use, however, is in the graphical interpretation of the results of a MOPAC calculation. As the author of DRAW paraphrased da Vinci, 'A picture is worth a thousand pieces of information'. Users of MOPAC are strongly encouraged to also acquire DRAW, again from QCPE.

2. SEMIEMPIRICAL METHODS

There are four distinct methods available within MOPAC: MINDO/3, MNDO, AM1, and PM3. All are semiempirical, and have roughly the same structure. A complete knowledge of these methods is not necessary in order to use MOPAC; however, a superficial understanding of these methods and their relationship to *ab initio* methods is important for using MOPAC and particularly for interpreting the results.

The four methods within MOPAC have many features in common. They are all self-consistent field (SCF) methods, they take into account electrostatic repulsion and exchange stabilization, and, in them, all calculated integrals are evaluated by approximate means. Further, they all use a restricted basis set of one *s* orbital and three *p* orbitals (p_x , p_y , and p_z) per atom and ignore overlap integrals in the secular equation. Thus, instead of solving

$$|\mathbf{H} - \mathbf{E}\mathbf{S}| = 0$$

the expression

$$|\mathbf{H} - \mathbf{E}| = 0$$

in which \mathbf{H} is the secular determinant, \mathbf{S} is the overlap matrix, and \mathbf{E} is the set of eigenvalues, is solved. These approximations considerably simplify quantum mechanical calculations on systems of chemical interest. As a result, larger systems can be studied. Computational methods are only models, and there is no advantage in rigorously solving Schrödinger's equation for a large system if that system has had to be abbreviated in order to make the calculations tractable. Semiempirical methods are thus seen to be well balanced: they are accurate enough to have useful predictive powers, yet fast enough to allow large systems to be studied. Of course some systems, e.g., enzymes, are so large that only a part of the system can be included in the model.

All four semiempirical methods contain sets of parameters. For MINDO/3 atomic and diatomic parameters exist, while MNDO, AM1 and PM3 use only single-atom parameters. Not all parameters are optimized for all methods; for example, in MINDO/3, MNDO and AM1 the two-electron one-center integrals are normally taken from atomic spectra. In the list given on the next page, parameters optimized for a given method are indicated by *. A + indicates that the value of the parameter was obtained from experiment (not optimized). Where neither symbol is given, the associated parameter is not used in that method.

Parameters used in semiempirical methods

Parameter	Description	MINDO/3	MNDO	AM1	PM3
U_s and U_p	s and p atomic orbital one-electron one-center integrals	+	*	*	*
β_s and β_p	s and p atomic orbital one-electron two-center resonance integral terms		*	*	*
I_s	s atomic orbital ionization potential for two-center resonance integral term	+			
I_p	p atomic orbital ionization potential for two-center resonance integral term	+			
β_{AB}	diatomic two-center one-electron resonance integral multiplier	*			
ζ_s	s-type Slater atomic orbital exponent	*	*	*	*
ζ_p	p-type Slater atomic orbital exponent	*	*	*	*
α_A	atom A core-core repulsion term		*	*	*
α_{AB}	atoms A and B core-core repulsion term	*			
G_{ss}	s-s atomic orbital one-center two-electron repulsion integral	+	+	+	*
G_{sp}	s-p atomic orbital one-center two-electron repulsion integral	+	+	+	*
G_{pp}	p-p atomic orbital one-center two-electron repulsion integral	+	+	+	*
G_{p2}	p-p' atomic orbital one-center two-electron repulsion integral	+	+	+	*
H_{sp}	s-p atomic orbital one-center two-electron exchange integral	+	+	+	*
K_{n_A} or a_{n_A}	Gaussian multiplier for nth Gaussian of atom A			*	*
L_{n_A} or b_{n_A}	Gaussian exponent multiplier for nth Gaussian of atom A			*	*
M_{n_A} or c_{n_A}	radius of center of nth Gaussian of atom A.			*	*

All four semiempirical methods also use two experimentally determined constants per atom: the atomic mass of the most abundant isotope and the heat of atomization.

3. THE DATA FILE

A MOPAC calculation involves supplying a data file defining the system being studied to MOPAC. The MOPAC program reads the file and generates an output file containing the results of the calculation. The input file has a highly standardized format. This consists of three lines of text followed by a geometry specification.

Example of data file

```

Line 1  SYMMETRY BONDS LOCALIZE VECTORS
Line 2  Ethane
Line 3
Line 4  C
Line 5  C      1.5  1
Line 6  H      1.1  1      109  1
Line 7  H      1.1  0      109  0      120  0      2  1  3
Line 8  H      1.1  0      109  0      240  0      2  1  3
Line 9  H      1.1  0      109  0      180  0      1  2  3
Line 10 H      1.1  0      109  0      120  0      1  2  6
Line 11 H      1.1  0      109  0      240  0      1  2  7
Line 12
Line 13  3      1      4  5  6  7  8
Line 14  3      2      4  5  6  7  8

```

The first line of text specifies the type of calculation. This is achieved via the use of descriptive keywords: thus, a unipositive cation would be specified by the keyword 'CHARGE = 1'. Lines two and three are text describing the calculation for the user's benefit only.

4. GEOMETRY SPECIFICATION

Molecular geometries are specified in one of two ways. The more common specification involves internal coordinates in which each atom is related to previously specified atoms by a bond length, an angle and a dihedral angle: i.e., a connectivity list. Sometimes it is convenient to use reference mathematical points in the definition of the geometry: these are allowed and are called dummy atoms. Dummy atoms are ignored during any quantum mechanical calculation. The internal coordinate definition can also be assisted by the use of what are called symmetry functions. These allow two or more bond lengths, angles or dihedrals to be related in a simple manner, typically by forcing them to be equivalent throughout a calculation.

Although geometries are no longer commonly specified by Cartesian coordinates the option to allow such a specification is supported. The position of each atom is defined by three Cartesian coordinates: these are the x, y and z values of the atom's position from an arbitrary origin. Cartesian coordinates are distinguished from internal coordinates by the absence of a connectivity list.

Regardless of the method of specifying the geometry, MOPAC normally proceeds via internal coordinates. The most common geometry operation is geometry optimization. Originally the Davidon-Fletcher-Powell [6] method was used. However, a few systems were found for which the DFP optimization terminated at a significant distance from a stationary point. As a result, the DFP optimization has been replaced by the BFGS or Broyden-Fletcher-Goldfarb-Shanno [7] method. This method is faster and less likely to produce flawed results. All methods use the same general approach. Using the derivatives of the energy with respect to coordinates, the geometry is changed so as to lower the heat of formation. When no further change can significantly lower the heat of formation, the optimization is stopped. The geometry then corresponds to a stationary point on the potential surface. Except for small systems, this will be one of many possible conformers or isomers.

5. PRECISION

Few computer programs work to the limiting precision of the host. Many operations involve iterative approximations to an exact result; this limits the precision of the final results. Of course, precision should not be confused with accuracy: MOPAC is only as accurate as the underlying methods. The level of precision is determined fully by the algorithm, however, and this can be varied over a considerable range. Within MOPAC there are two principal operations where the level of precision is important: passing the SCF criterion and satisfying the geometry optimization criteria.

5.1 SCF criterion

The heat of formation and the density matrices are the principal results of an SCF calculation. The precision with which these SCF properties are calculated is determined by the SCF criterion.

The SCF criterion is very flexible. For routine use the default criterion will ensure a heat of formation within less than 0.1 calories of the correct semiempirical answer. For more critical work the SCF criterion can be tightened by a factor ranging from 10^1 to 10^{15} ; this allows SCF properties to be determined with extreme precision. Of course, increasing the precision will result in an increase in the time necessary to complete the SCF. Even worse, many systems which achieve an SCF as defined by the default criterion will fail to go self-consistent with a more stringent test. In general, however, few systems which would otherwise go self-consistent will fail to achieve an SCF if the criterion is tightened by a factor of about 10–100.

5.2 Geometry optimization criteria

Strictly speaking, *the* optimized geometry is the one for which no distortion of the geometry would lead to a decrease in the heat of formation. Such a geometry is not generally realizable; instead, geometry optimization is terminated when one of several tests is passed. Details of these tests are given in the Manual (q.v.), but a summary can be given here. The geometry is considered optimized if one or more of the following calculated quantities is *sufficiently* small: (a) the predicted change in the geometry; (b) the predicted change in heat of formation; or (c) the current gradient norm, i.e., the scalar of the vector of derivatives of the energy with respect to coordinates.

The definition of ‘sufficiently’ small is given in both the MOPAC program and Manual. However, the user can specify the degree of optimization by specifying a gradient norm in the keyword line of the data file. The calculation is stopped when the calculated gradient norm drops below the specified limit. In order to allow users this option, when a gradient norm is specified, all other geometry tests are suspended.

5.3 Why specify high precision?

Routine work on rigid systems such as formaldehyde or naphthalene does not warrant high precision. Unfortunately, many applications involve flexible molecules and for these systems increased precision is necessary. Increased precision is also needed when following a reaction path as large geometry changes can occur with very small changes in heat of formation. This point

is not trivial: computational chemistry calculations have now achieved the status of experiments and are routinely reported in the literature. As such they must be reproducible. Since optimized geometries, much less initial geometries, are not normally published, anyone reproducing published work must be able to optimize geometries in the confidence that the program will give the same results as those reported.

For many organic systems, particularly those of biological interest, high precision is necessary in order to achieve this degree of reproducibility. For such systems the gradient norm should be forced below about 1 kcal/mol/Å, and preferably below 0.5.

Note that while calculations on simple organics and inorganics would suggest that a gradient of 2–3 kcal/mol/Å is acceptable, this is not the case for flexible organics. For the former group the force constants are so high that minor geometric changes are sufficient to reduce the gradient norm to zero. On the other hand flexible molecules have such low force constants, sometimes called flat surfaces, that large geometry changes may be necessary in order to reduce the gradient norm, in which case, quite large energy changes can result.

This is not to imply that very high precision is always wanted or even desirable. An intelligent choice of geometric and SCF criteria should be made, one which balances computer time against tolerable imprecision. At present there are no hard-and-fast rules for making this choice. The SCF criterion should be sufficiently stringent to allow the geometry optimization to function effectively, while the geometry criterion should allow heats of formation to be precise within a given limit, say 0.1 kcal/mol.

6. RESULTS OF SCF CALCULATIONS

MOPAC SCF calculations generate three kinds of results: (1) results that can be compared with experiment; (2) quantum mechanical predictions which cannot be compared with experiment; and (3) quantities which are used in subsequent calculations but which are not normally made available to users.

The first set of results are the observables such as heat of formation, dipole moment, ionization potential, and unpaired spin density distribution. When fully optimized geometries are used, these results can be compared with experimental values. Comparison with experiment forms one criterion by which any method which is advocated for its predictive power should be judged.

Some methods, such as the Gaussian *ab initio* methods, attempt to predict properties from first principles. This is a much more difficult task than that addressed by the semiempirical methods. Specifically, *ab initio* methods must not only predict accurately but must also carry out the calculation starting from first principles. As a result, semiempirical methods may be more accurate than *ab initio* for systems similar to those for which they are parameterized, but *ab initio* methods are likely to be more accurate for other systems, systems for which experimental evidence is currently lacking. This last class includes transition states, excited states, and exotic systems not likely to be found experimentally.

SCF calculations, being quantum mechanical in nature, allow molecular orbitals, charges, bond orders [8] and valencies [8] etc. to be calculated. These quantities are not experimentally verifiable. Chemists may have a good idea what the values of certain quantities are, thus the C–C bond orders in ethane, ethylene and acetylene are likely to be about 1.0, 2.0, and 3.0, respectively. However, these are only informed guesses – there is no experimental technique for determining

these quantities. A consequence of this is that different computational methods can produce different values for these quantum mechanical artifacts. The quality of a method should not be determined by how well it predicts these quantities.

The last set of results of an SCF calculation are quantities used internally, such as the density matrix. These quantities are used in subsequent calculations and are not normally printed (although they can be printed upon keyword request).

7. GEOMETRY OPTIMIZATION

Only very seldom are users satisfied with a single SCF calculation on a guessed geometry. In order to allow comparison with experiment and with calculations on other systems, the geometry must be modified from the input geometry. The most common operation is energy minimization. This gives rise to a stationary point on the potential surface. Note that this is not necessarily the global minimum, i.e., the most stable conformer for the most stable structural isomer for the input collection of atoms. There is currently no algorithmic method for consistently locating global minima for complicated molecular systems; rather, the optimized geometry will correspond to an isomer or conformer. It is easy to see that a method which located the global minimum would not only be unnecessary, but also undesirable.

Consider the system $\text{C}_2\text{H}_6\text{O}$. If the program located the global minimum every time it was run then it would always predict that ethanol ($\Delta H_f = -56.2$ kcal/mol) was the stable isomer and dimethyl ether ($\Delta H_f = -44.0$ kcal/mol) would not be predicted to exist. In fact, a global optimization method would, by definition, produce only one geometry and one heat of formation. The existence of conformers would not be envisioned by such a program, much less isomers. To summarize, MOPAC, in common with all other large computational chemistry packages, does not and can not infallibly locate the global minimum, but only local minima. While this is occasionally a source of unnecessary concern, it is how MOPAC was designed to operate.

Geometry optimization proceeds by calculating the resultant forces on each atom in the system and then moving the atoms in a direction determined by these forces so as to lower the energy of the system. When the geometry is within a preset distance or energy of the local minimum, the optimization is stopped.

8. REACTIONS

Few calculations are complete after the geometry has been optimized. A common next step is to model a reaction. In its simplest form this involves identifying a reaction coordinate connecting two stable systems A and B and monitoring the system as it is progressively translated along this coordinate. In this context, a reaction coordinate is a curved line representing the path between reactants and products on a $3n-6$ -dimensional geometry surface. Since reaction coordinates are artifacts of the model, no conclusions can be drawn about any points along the coordinate with the important exception of the highest energy point (call this C). The energy of activation is the difference in energy between compounds A and C. If the highest point reached is on a smooth surface, then C corresponds to a transition state, a second kind of stationary point which is independent of both the choice of reaction coordinate and coordinate system used.

Refinement of the geometry of C is not as easy as optimization of A or B. To refine the geome-

try of C, the gradient norm is minimized [9], i.e., the geometry of C is changed in such a way as to minimize the sum of the resultant forces acting on all the atoms of C.

This operation, locating transition states, is considerably more difficult than locating minima. If a system is optimized to locate a specific minimum, it is normally sufficient for the starting geometry to lie anywhere within the potential energy valley of that minimum in order to be sure that the optimization procedure will converge on that minimum. With transition states, the criterion for specifying the initial geometry in order to converge on a specific transition state is much more stringent. In this case, the initial geometry must lie between the multidimensional surface of inflection and the desired transition state. As points of inflection are located between maxima and minima, the volume within which the initial geometry must lie in order to locate a specific transition state is much smaller than that for simple geometry optimization, in which a specific conformer has to be optimized.

Once a stationary point, either ground state or transition state, has been refined, it should be characterized by calculating the force constants. A stable minimum or conformer will have no negative force constants, while a transition state will have exactly one negative force constant; any stationary point with two or more negative force constants is almost certainly chemically meaningless.

In rare cases the system cannot be refined. This will occur whenever the starting geometry is in a domain bounded by inflection surfaces and which does not contain a stationary point – a one-dimensional example would be a shoulder on a curve. There does not appear to be any easy way to recover from such a situation. The best course appears to be to start again and try to avoid entering the offending domain.

More sophisticated methods of locating the domain of a saddle point exist. An example of such a method is the ‘eigenvector following’ procedure [10], in which information regarding the local gradient is used to systematically proceed up the bottom of a valley to the transition state. At present, such methods are not available in MOPAC. It is likely that these absences will be corrected in the future.

9. VIBRATIONAL FREQUENCIES

After calculating the force constants, it is a trivial matter to mass-weight the force matrix and calculate the vibrational frequencies. By altering individual atomic masses the effect of isotopic substitution can also be investigated.

Special routines have been written to make the task of analyzing the vibrational modes easier [11]. Those pairs of atoms which are most strongly involved in each vibration are indicated along with information about the relative motion. Transition dipoles, reduced masses, and a measure of the distance all the atoms move through during half a vibrational cycle are also displayed.

10. REACTION COORDINATES

The reaction coordinate used in getting from the ground state to the transition state has no physical meaning, because it is dependent on the particular coordinate system used. However, there are two different paths on the potential surface leading from the transition state to reactants and products which have limited physical meaning.

The first of these paths is the Intrinsic Reaction Coordinate [12], which defines the path the atoms would follow if the system was allowed to relax, starting from the transition state. The resultant forces on each atom are used, together with the isotopic mass of each atom, to calculate which direction to move the atoms in order to move downhill in energy. In other words, in a mass-weighted $3n-6$ -dimensional coordinate space, the atoms are moved a small distance in a direction perpendicular to the local energy contours. By making a large number of such movements, a path is traced out to either the reactants or products. This path is a fully-damped path in that all energy acquired by the atoms in the course of the descent is lost at each point.

The other extreme is the Dynamic Reaction Coordinate (DRC), in which the energy of motion acquired by the atoms as they descend is not shed. Instead, the acquired velocity is used in the prediction of the next step. A system following this trajectory is unlikely to ever achieve the geometries of either reactants or products. Even if such geometries were realized they would only be specific points on a trajectory, points when the instantaneous acceleration drops to zero and for which the velocity is a maximum. The DRC is a time-dependent calculation for the study of reaction dynamics. For example, the time-dependent behavior (system geometry, heat of formation, etc.) for phenomena such as the Berry pseudorotation and molecular collisions can be obtained. Trajectories can be followed for up to several thousand femtoseconds.

The DRC for a vibration of a ground state system can be calculated. Vibration cycle times can be compared with those obtained from force calculations. In general, the agreement is very good. However, in cases where atomic excursions take the system out of the parabolic domain, anharmonic effects become important and marked differences between DRC and force constant vibrational lifetimes do occur.

11. EXTENDED SYSTEMS

In addition to molecules, radicals, and ions, MOPAC can also efficiently calculate polymer properties. Conventionally, polymers have been studied using solid state methods such as tight-binding theory. In this approach, a Brillouin zone is constructed and sampled using a regular mesh of points. This produces a number of complex density matrices, from which the real density matrix can be derived. Such methods are quite time consuming, but are also quite rigorous and allow calculation of the band structure of Brillouin zones.

MOPAC is intended primarily for use by chemists, so the approach to the calculation of polymer structures is quite different. Instead of sampling the Brillouin zone, only a single point is used. The use of a single point requires the unit cell or repeat distance to be large enough for the associated Brillouin zone to be so small that all bands are essentially flat. In practical terms, this means that unit cells need to be greater than about 10 Å.

Polymer calculations require about 50% more time than calculation on molecules equivalent in size to the unit cell used. Results are exactly as accurate as the results for equivalent molecules.

12. SUMMARY OF MOPAC CAPABILITIES

Most users use only a very small range of MOPAC's capabilities. For example, a user may be interested only in heats of formation, and have little interest in geometries or charges, etc. This is possibly a result of having learned how to request certain functions and how to interpret the

results. Having learned to trust a certain aspect of the program, a user may be reluctant to investigate other, less familiar, aspects. One consequence of this is that the user is denied information which may be useful to his or her research effort. The following list summarizes the more important quantities which can be calculated using MOPAC. Note that this list does not include capabilities which do not actually calculate values, such as the restart function or shutdown operation. Users are encouraged to investigate the effect of all keywords, and to familiarize themselves with the full range of operations of MOPAC.

12.1 Calculable quantities

The main quantities calculated by MOPAC are:

Atomic charges (Q)	Molecular orbitals (P)
Atomic velocities (in DRCs) (V)	M.O. bonding indices (Q)
Bond orders and valencies (Q)	Molecular polarizabilities (\AA^3)
Density matrices (Q)	Moments of inertia (I)
Dipole moments (De)	Mulliken populations (Q)
Effective masses (M)	Optimized geometries (G)
Entropy (C/T)	Partition functions (N)
Excitation energies (E)	Reaction coordinates (G)
Force constants (Dy)	Spin matrices (Q)
Heat capacity (C/T)	State eigenvectors (P)
Heat of formation (K)	Total spin states (S)
Hyperpolarizability	Transition dipole moments (De)
Internal energies (K)	Unit cell lengths (G)
Ionization potentials (E)	Unpaired spin densities (Q)
Localized orbitals (P)	Vibrational frequencies (CM)
Molecular geometries (G)	Zero point energies (K)

12.2 Units

Units given in parentheses in section 12.1 are:

\AA^3 :	cubic Angstroms
C:	calories per degree
CM:	cm^{-1}
De:	Debye
Dy:	dynes per centimeter
E:	electron volts
G:	distances in Angstroms, angles in degrees
I:	gram-centimeter ²
K:	kcal/mol
M:	atomic mass units
N:	a ratio, therefore no units
P:	normalized wave-function
Q:	charge on electron

S: spin units (electron = $\frac{1}{2}$)
 T: degrees Kelvin
 V: centimeters per second.

12.3 Conversion factors

The following conversion factors may be used to convert calculated energy units into other units.

Conversion factors for energy					
$e_2 \backslash e_1$	a_0	eV	kcal/mol	kJ/mol	cm^{-1}
a_0	1.0000000				
eV	27.211652	1.000000			
kcal/mol	627.47237	23.05896	1.000000		
kJ/mol	2625.3444	96.47868	4.184000	1.000000	
cm^{-1}	219474.63	8065.465	349.7758	83.59842	1.000000

To convert energies in units of e_1 into units of e_2 , multiply by factor. The conversion factors are based on the assumption that Avogadro's number is 6.022045×10^{23} . Note that the conversion factors used within MOPAC are very slightly different from those given here. This is a result of the historical development of MOPAC. As the differences are small, and as substituting the more recent conversion factors would lead to incompatibility with earlier versions, the original conversion factors have been retained.

13. THEORY USED IN MOPAC

This appendix describes in detail some of the operations of MOPAC. Its objective is to bridge the gap between theory, as it is usually presented in a textbook, and the actual algorithm used. In most instances the style is simply descriptive, but in certain cases, like the overlap integral, a brief derivation of the equations used is presented. In these latter cases, readers are encouraged to follow the derivation step by step.

13.1 Geometry optimization

The most common use of MOPAC is for geometry optimization. This involves starting with an approximation to the desired geometry and, by calculating the forces acting on the system, changing the geometry so as to lower the total energy. Because force constants or second derivatives are not known at this time, the initial steps in optimizing the geometry have to be conservative.

The heat of formation minimization routine in MOPAC is a modified Broyden-Fletcher-Goldfarb-Shanno or BFGS method [7]. Minor changes were made necessary by the presence of phenomena peculiar to chemical systems.

In the following discussion of the geometry optimization theory, a matrix or tensor will be indicated by upper case bold type, e.g. \mathbf{H} , and a vector by lower case bold type, e.g., \mathbf{x} . All other symbols represent scalar quantities. Starting with a user-supplied geometry \mathbf{x}_0 , MOPAC computes an estimate to the inverse Hessian \mathbf{H}_0 . The geometry optimization proceeds by

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \alpha \mathbf{d}_k$$

where

$$\mathbf{d}_k = \mathbf{H} \mathbf{g}_k$$

and each element of \mathbf{H} is defined by

$$\mathbf{H}_{k+1} = \mathbf{H}_k - \frac{\mathbf{H} \mathbf{y}_k \mathbf{p}_k^t + \mathbf{p}_k \mathbf{y}_k^t \mathbf{H}}{\mathbf{S}} + \frac{\mathbf{Q}(\mathbf{p}_k \mathbf{p}_k^t)}{\mathbf{S}}$$

where

$$\mathbf{Q} = \mathbf{I} + \frac{\mathbf{y}_k^t \mathbf{H} \mathbf{y}_k}{\mathbf{p}_k^t \mathbf{y}_k}$$

$$\mathbf{S} = \mathbf{p}_k^t \mathbf{y}_k$$

$$\mathbf{p}_k = \mathbf{x}_{k+1} - \mathbf{x}_k = \alpha \mathbf{d}_k$$

$$\mathbf{y}_k = \mathbf{g}_{k+1} - \mathbf{g}_k$$

and

$$\mathbf{g}_k = \frac{dE_k}{d\mathbf{x}_k}$$

Two different methods are used to calculate the displacement of \mathbf{x} in the direction \mathbf{d} . During the initial stages of geometry optimization, a line search is used. This proceeds as follows:

The geometry is displaced by $(\alpha/4)\mathbf{d}$ and the energy evaluated via an SCF calculation. If this energy is lower than the original value, then a second step of the same size is made. If it is higher, then a step of $-(\alpha/2)\mathbf{d}$ is made. The energy is then re-evaluated. Given the three energies, a prediction is made as to the value of α which will yield the minimum value of the energy in the direction \mathbf{d} . Of course, the size of the steps is constrained so that the system would not suddenly become unrealistic (e.g., break bonds, superimpose atoms, etc.). Similarly, the contingency in which the energy versus α function is inverse parabolic is considered, as are rarely-encountered curves, e.g., almost perfectly linear regressions. The line search is stopped when the drop in energy on any step becomes less than 5% of the total drop or 0.5 kcal/mol, whichever is smaller.

As the geometry converges on a local minimum, the prediction of the search direction becomes less accurate. There are many reasons for this. For example, the finite precision of the SCF calculation may lead to errors in the density matrix, or finite step sizes in the derivative calculation

(if analytical derivatives are not used) may result in errors in the derivatives. For whatever reason, the gradient norm and energy minimum may not coincide. The difference is typically less than 0.00001 kcal/mol and less than 0.05 units of gradient norm.

Reduction of the gradient norm below about 1.0 is difficult using the line-minimization method just outlined. A better procedure is to use a binary search. This is used whenever the gradient norm drops below 1.0 and the scalar of \mathbf{d} is less than 0.001. The steps involved are as follows:

α , the step size, is set to 1.0 if the scalar of $\mathbf{d}_k \mathbf{g}_k$ is positive, otherwise α is set to -1.0 . If $\mathbf{x}_k + \alpha \mathbf{d}_k$ lowers the energy of the system, then \mathbf{x}_{k+1} is defined for this step, otherwise α is halved and the energy re-evaluated. Once the energy is lower than $E_k + 0.00001$, where E_k is the heat of formation on step k , \mathbf{x}_{k+1} is defined.

Normally, the initial guess to \mathbf{H} , the inverse Hessian, is the unit matrix. However, in chemical systems where the second derivatives are very large, use of the unit matrix would result in large changes in the geometry. Thus a slightly elongated bond length could, in the first step, change from, e.g., 1.6 Å to -6.5 Å. To prevent this catastrophe, the initial geometry is perturbed by a small amount, thus

$$\mathbf{x}_1 = \mathbf{x}_0 + 0.01 * \text{sign}(\mathbf{g}_0)$$

from which a trial inverse Hessian can be constructed:

$$H_1(i,i) = 0.01 * \text{sign}(g_0(i)) / y_1(i)$$

$$H_1(i,j) = 0.0$$

A negative value for $H_1(i,i)$ would lead to difficulties within the BFGS optimization. To avoid this, $H_1(i,i)$ is set to $0.06 / \text{abs}(g(i))$ whenever $\text{sign}(g_0(i)) / y_1(i)$ is negative.

As the optimization proceeds, the inverse Hessian matrix becomes more accurate. However, as the geometry steadily changes, the inverse Hessian will contain information which does not reflect the current point. This can lead to the predicted search direction vector making an angle of more than 90° with the gradient vector. In other words, the search direction vector may point uphill in energy. To guard against this, the inverse Hessian is re-initialized whenever the cosine of the angle between the search direction and the gradient vector drops below 0.05.

Originally the Davidon–Fletcher–Powell [6] technique was used, but in rare instances it failed to work satisfactorily. The BFGS formula appears to work as well as or better than the DFP method most of the time. In the infrequent case when the DFP is more efficient, the increase in efficiency of the DFP can usually be traced to a fortuitous choice of a search direction. Small changes in starting conditions can destroy this accidental increased efficiency and make the BFGS method appear more efficient. A keyword is provided to allow the DFP optimizer to be used.

13.2 Electronic section

Because this section involves a large number of symbols, it is convenient to have a common set. Throughout the theory section, therefore, the same symbols are used to denote the same quantities; exceptions will be indicated wherever they occur.

Glossary of symbols

Symbol	Meaning
H	One-electron matrix
F	Two-electron or Fock matrix
φ	Atomic orbital
$\mu, \nu, \lambda, \sigma$	Atomic orbital indices
ψ	Molecular orbital
i, j, k, l	Molecular orbital indices
A, B	Atom indices
α	Alpha spin
β	Beta spin
ζ	Atomic orbital exponent
S	Overlap matrix
P	Density matrix
s, p_x, p_y, p_z	s, p_x, p_y and p_z atomic orbitals
$\langle \text{expression} \rangle$	Dirac integral symbols
$\langle \mu\nu \lambda\sigma \rangle$	Two-electron integral
$\langle \mu \nu \rangle$	Overlap integral
$\delta(\lambda, \sigma)$	Kronecker delta, 1 if $\lambda = \sigma$, otherwise 0
ε_i	Eigenvalues
Z	Nuclear or core charge

Combinations of these symbols are allowed, thus $P_{\lambda\sigma}^\beta$ represents the β density matrix element between atomic orbitals φ_λ and φ_σ .

13.2.1 Approximations used in MNDO, MINDO/3, AM1 and PM3

All four methods are similar enough to describe simultaneously. In the following discussion, applications specific to each method will be indicated in the text. This will allow easy comparison among the methods, a comparison which is not obvious from their names. MINDO/3 [3] stands for Modified Intermediate Neglect of Differential Overlap, version 3, MNDO [2] stands for Modified Neglect of Diatomic Overlap. AM1 [4] is Austin Model 1, and MNDO-PM3 [13], a very new method, is the Modified Neglect of Diatomic Overlap, Parametric Method Number 3, MNDO and AM1 being the first two ‘MNDO’-type methods. In these methods all terms arising from the overlap of two atomic orbitals which are on different centers or atoms are set to zero. As this is not the forum for developing the ideas of Hartree–Fock theory, the derivation of the Roothaan–Hall equations will be assumed, and our description of the methods will start with the final Roothaan [14]–Hall [15] equations.

Basic Roothaan–Hall equations

Secular equation:

$$c_i[F - \varepsilon_i S]c_i = 0$$

Total electronic energy of system:

$$E = \frac{1}{2} \mathbf{P}(\mathbf{H} + \mathbf{F})$$

Fock matrix element:

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu} + \sum_{\lambda} \sum_{\sigma} [P_{\lambda\sigma}^{\alpha+\beta} \langle \mu\nu | \lambda\sigma \rangle - P_{\lambda\sigma}^{\alpha} \langle \mu\lambda | \nu\sigma \rangle]$$

Or, spin-free:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} [\langle \mu\nu | \lambda\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \nu\sigma \rangle]$$

The methods all use a minimum basis set consisting of a maximum of one atomic orbital for each angular quantum number. The normal basis set for any atom consists of one *s* and three *p* orbitals, p_x , p_y and p_z .

13.2.1.1 Neglect of diatomic overlap integral

All overlap integrals arising from the overlap of two different atomic orbitals are neglected. This reduces the overlap matrix to a unit matrix. The secular equation thus reduces to

$$c_i [\mathbf{F} - \varepsilon_i] c_i = 0$$

13.2.1.2 Neglect of three- and four-center integrals

Continuing with the neglect of differential overlap, all two-electron integrals involving charge clouds arising from the overlap of two atomic orbitals on different centers are ignored. Since no rotation can convert a two-center two-electron integral into a set of integrals involving three- and four-center terms, rotational invariance is not compromised by this approximation. The effects of this approximation on the Roothaan equations are as follows:

In the Fock matrix, if φ_{μ} and φ_{ν} are on different centers the MNDO, AM1, and PM3 matrix element $F_{\mu\nu}^{\alpha}$ reduces to

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu} - \sum_{\lambda}^A \sum_{\sigma}^B P_{\lambda\sigma}^{\alpha} \langle \mu\lambda | \nu\sigma \rangle$$

while the MINDO/3 matrix element becomes

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu} - P_{\mu\nu}^{\alpha} \langle \mu\nu | \mu\nu \rangle$$

where

$$P_{\lambda\sigma}^{\alpha} = \sum_{i}^{\text{occ}} c_{\lambda i}^{\alpha} c_{\sigma i}^{\alpha}$$

is summed over all occupied orbitals. Equivalent expressions exist for $F_{\mu\nu}^\beta$ and $P_{\lambda\sigma}^\beta$. Thus no Coulombic terms are present in the two-center Fock matrix elements.

If φ_μ and φ_ν are different but on the same center, then, since a minimal basis set is used, all integrals of the type $\langle\mu\nu|\lambda\sigma\rangle$ are zero by the orthogonality of the atomic orbitals unless $\mu = \nu$ and $\lambda = \sigma$ or $\mu = \lambda$ and $\nu = \sigma$. The off-diagonal one-center MNDO and AM1 Fock matrix elements become

$$F_{\mu\nu}^\alpha = H_{\mu\nu} + 2P_{\mu\nu}^{\alpha+\beta} \langle\mu\nu|\mu\nu\rangle - P_{\mu\nu}^\alpha (\langle\mu\nu|\mu\nu\rangle + \langle\mu\mu|\nu\nu\rangle)$$

while the MINDO/3 element becomes

$$F_{\mu\nu}^\alpha = -P_{\mu\nu}^\alpha \langle\mu\nu|\mu\nu\rangle$$

If φ_μ is the same as φ_ν then, because of the symmetry of the two-electron integrals, the diagonal MNDO, AM1, and PM3 Fock matrix elements reduce to

$$F_{\mu\mu}^\alpha = H_{\mu\mu} + \sum_v^A (P_{\nu\nu}^{\alpha+\beta} \langle\mu\mu|\nu\nu\rangle - P_{\nu\nu}^\alpha \langle\mu\nu|\mu\nu\rangle) + \sum_B \sum_{\lambda}^B \sum_{\sigma}^B P_{\lambda\sigma}^{\alpha+\beta} \langle\mu\mu|\lambda\sigma\rangle$$

and the corresponding MINDO/3 element becomes:

$$F_{\mu\mu}^\alpha = H_{\mu\mu} + \sum_v^A (P_{\nu\nu}^{\alpha+\beta} \langle\mu\mu|\nu\nu\rangle - P_{\nu\nu}^\alpha \langle\mu\nu|\mu\nu\rangle) + \sum_B \langle AA|BB \rangle \sum_{\lambda}^B P_{\lambda\lambda}^{\alpha+\beta}$$

13.2.1.3 One-center two-electron integrals

The MNDO and AM1 one-center two-electron integrals are derived from experimental data on isolated atoms. Most were taken from Oleari's [16] work, but a few were obtained by optimization to fit molecular properties. The values of PM3 one-center two-electron integrals were optimized to reproduce experimental molecular properties.

For each atom there are a maximum of five one-center two-electron integrals. These are $\langle ss|ss \rangle$, $\langle ss|pp \rangle$, $\langle sp|sp \rangle$, $\langle pp|pp \rangle$, and $\langle pp|p'p' \rangle$, where p and p' are two different p -type atomic orbitals. In the original formulation [17] there was a sixth integral, $\langle pp'|pp' \rangle$, but it can be shown that this integral is related to two of the other integrals by

$$\langle pp'|pp' \rangle = \frac{1}{2}(\langle pp|pp \rangle - \langle pp|p'p' \rangle)$$

Proof:

If the molecular frame is rotated by 45 degrees about the z axis the atomic bases mix thus:

$$R(45^\circ)p_x = \frac{1}{2}(p_x + p_y)$$

$$R(45^\circ)p_y = \frac{1}{2}(p_y - p_x)$$

$$\begin{aligned} R(45^\circ)\langle p_x p_y | p_x p_y \rangle &= \frac{1}{4} \langle (p_x + p_y)(p_y - p_x) | (p_x + p_y)(p_y - p_x) \rangle \\ &= \frac{1}{4} (\langle p_x p_x | p_x p_x \rangle + \langle p_y p_y | p_y p_y \rangle - \langle p_x p_x | p_y p_y \rangle - \langle p_y p_y | p_x p_x \rangle) \end{aligned}$$

or

$$R(45^\circ) \langle p_x p_y | p_x p_y \rangle = \frac{1}{2} (\langle p_x p_x | p_x p_x \rangle - \langle p_x p_x | p_y p_y \rangle)$$

For convenience these five integrals are given the following names

$$\begin{array}{ll} \langle ss | ss \rangle & G_{ss} \\ \langle pp | pp \rangle & G_{pp} \\ \langle sp | sp \rangle & H_{sp} \\ \langle pp | pp \rangle & G_{pp} \\ \langle pp | p' p' \rangle & G_{p2} \end{array}$$

Using these definitions, the two-electron one-center contributions to the Fock matrix become

$$\begin{aligned} F_{ss}^\alpha &: P_{ss}^\beta G_{ss} + (P_{px}^{\alpha+\beta} + P_{py}^{\alpha+\beta} + P_{pz}^{\alpha+\beta}) G_{sp} - (P_{px}^\alpha + P_{py}^\alpha + P_{pz}^\alpha) H_{sp} \\ F_{sp}^\alpha &: 2P_{sp}^{\alpha+\beta} H_{sp} - P_{sp}^\alpha (H_{sp} + G_{sp}) \\ F_{pp}^\alpha &: P_{ss}^{\alpha+\beta} G_{sp} - P_{ss}^\alpha H_{sp} + P_{pp}^\beta G_{pp} + (P_{p'}^{\alpha+\beta} + P_{p''}^{\alpha+\beta}) G_{p2} - \frac{1}{2} (P_{p'}^\alpha + P_{p''}^\alpha) (G_{pp} - G_{p2}) \\ F_{pp'}^\alpha &: P_{pp'}^{\alpha+\beta} (G_{pp} - G_{p2}) - \frac{1}{2} P_{pp'}^\alpha (G_{pp} + G_{p2}) \end{aligned}$$

These expressions are common to all methods.

13.2.1.4 MNDO, AM1, and PM3 two-electron two-center integrals

In a local diatomic frame there are 22 unique two-electron two-center integrals for each pair of heavy (non-hydrogen) atoms. These are shown below:

Two-electron two-center integrals (Local Frame)

1	$\langle ss ss \rangle$	12	$\langle sp_\sigma p_\pi p_\pi \rangle$
2	$\langle ss p_\pi p_\pi \rangle$	13	$\langle sp_\sigma p_\sigma p_\sigma \rangle$
3	$\langle ss p_\sigma p_\sigma \rangle$	14	$\langle ss sp_\sigma \rangle$
4	$\langle p_\pi p_\pi ss \rangle$	15	$\langle p_\pi p_\pi sp_\sigma \rangle$
5	$\langle p_\sigma p_\sigma ss \rangle$	16	$\langle p_\sigma p_\sigma sp_\sigma \rangle$
6	$\langle p_\pi p_\pi p_\pi p_\pi \rangle$	17	$\langle sp_\pi sp_\pi \rangle$
7	$\langle p_\pi p_\pi p_\pi p'_\pi \rangle$	18	$\langle sp_\sigma sp_\sigma \rangle$
8	$\langle p_\pi p_\pi p_\sigma p_\sigma \rangle$	19	$\langle sp_\pi p_\pi p_\sigma \rangle$
9	$\langle p_\sigma p_\sigma p_\pi p_\pi \rangle$	20	$\langle p_\pi p_\sigma sp_\pi \rangle$
10	$\langle p_\sigma p_\sigma p_\sigma p_\sigma \rangle$	21	$\langle p_\pi p_\sigma p_\pi p_\sigma \rangle$
11	$\langle sp_\sigma ss \rangle$	22	$\langle p_\pi p'_\pi p_\pi p_\pi \rangle$

Each integral represents the energy of an electron density distribution (electron 1) arising from the product of the first two atomic orbitals interacting with the electron density distribution (electron 2), which arises from the product of the second two atomic orbitals. Only if the first two a.o.'s are the same and the second two a.o.'s are the same will the interaction energy have to be positive, in which case the integral represents an electron–electron repulsion term. In all other cases the sign of the integral value may be positive or negative.

With the exception of integral 22, all the integrals can be calculated using different techniques without loss of rotational invariance. That is, no integral depends on the value of another integral, except for number 22. As with the H_{pp} monocentric integral, it is easy to show that

$$\langle p_{\pi} p'_{\pi} | p_{\pi} p'_{\pi} \rangle = \frac{1}{2} (\langle p_{\pi} p_{\pi} | p_{\pi} p_{\pi} \rangle - \langle p_{\pi} p_{\pi} | p'_{\pi} p'_{\pi} \rangle)$$

The electron density distributions are approximated by a series of point charges. There are four possible types of distribution. These are as follows:

<i>Types of electron density distribution</i>	
Monopole (1 charge)	Unit negative charge centered on the nucleus
Dipole (2 charges)	$+\frac{1}{2}$ charge located at position (x,y,z), $-\frac{1}{2}$ charge located at position ($-x, -y, -z$)
Linear quadrupole (3 charges)	$+\frac{1}{2}$ charge located at the nucleus, $-\frac{1}{4}$ charge at positions (x,y,z) and at ($-x, -y, -z$)
Square quadrupole (4 charges)	Four charges of magnitude $+\frac{1}{4}, -\frac{1}{4}, +\frac{1}{4}$ and $-\frac{1}{4}$ forming a square centered on the nucleus.

These are used to represent the four types of atomic orbital products.

Density distributions arising from pairs of atomic orbitals

Atomic orbitals	Multipole distribution	Number of charges
$\langle ss $	Monopole	1
$\langle sp $	Dipole	2
$\langle pp $	Monopole plus linear quadrupole	4
$\langle pp' $	Square quadrupole	4

Each two-electron interaction integral is the sum of all the interactions arising from the charge distribution representing one pair of atomic orbitals with the charge distribution representing the second pair of atomic orbitals. Thus, in the simplest case, the $\langle ss | ss \rangle$ interaction is represented by the repulsion of two monopoles, while a $\langle p_{\pi} p_{\pi} | p'_{\pi} p'_{\pi} \rangle$, a much more complicated interaction, is represented by 16 separate terms, arising from the four charges representing the monopole and linear quadrupole on one center interacting with the equivalent set on the second center.

While the repulsion of two like charges is proportional to the inverse distance separating the charges, boundary conditions preclude using this simple expression to represent the interelectronic interactions. Instead, the interaction energy is approximated by

$$\langle ss | ss \rangle = \frac{27.21}{\sqrt{\left(R + c_A + c_B\right)^2 + \frac{1}{4} \left(\frac{1}{A_A} + \frac{1}{A_B}\right)^2}}$$

All that remains is to specify functional forms for the terms c and A . c , the distance of a multipole charge from its nucleus, is a simple function of the atomic orbitals; in the case of a $s-p$ product, this is a vector of length D_1 Bohr pointing along the p axis, where

$$D_1 = \frac{(2n+1)(4\xi_s\xi_p)^{(n+\frac{1}{2})}}{3^{\frac{1}{2}}(\xi_s + \xi_p)^{(2n+2)}}$$

and n is the principal quantum number. The principal quantum number is always the same in these methods for s and p orbitals on any given atom.

The corresponding distances of the charges from the nucleus for the linear and square quadrupoles are $2D_2$ and $\sqrt{2}D_2$ Bohr, respectively, where

$$D_2 = \left(\frac{4n^2 + 6n + 2}{20} \right)^{1/2} \frac{1}{\xi_p}$$

Now that the distances of the charges from the nucleus have been defined, the upper boundary condition can be set. In the limit, when $R = 0.0$, the value of the two-electron integral should equal that of the corresponding monocentric integral. Three cases can be identified:

- (1) a monopole-monopole interaction, in which case the integral must converge on G_{ss} .
- (2) a dipole-dipole interaction, where the integral must converge on H_{sp} .
- (3) the quadrupole-quadrupole interaction where the integral must converge on H_{pp} .

For convenience, the A_A terms are given special names. These are:

Additive terms for two-electron integrals

Multipole	Monocentric equivalent	Name
Monopole	G_{ss}	AM
Dipole	H_{sp}	AD
Quadrupole	$H_{pp} = \frac{1}{2}(G_{pp} - G_{p2})$	AQ

In practice, $\frac{1}{2}(G_{pp} - G_{p2})$ is used instead of H_{pp} . This eliminates any possibility of loss of rotational invariance due to an incorrect value of H_{pp} .

In the literature, different units have been used to report the derived parameters. To date, units of derived MNDO parameters which have been published are:

Units of derived parameters

Element	Units stated		Units used		Ref.	Element	Units stated		Units used		Ref.
	D_n	A_n	D_n	A_n			D_n	A_n	D_n	A_n	
H		A		A	18	P	A	A	A	A	25
Li		(No lit. Ref.)			19	S	Bohr	Bohr	Bohr	Bohr ⁻¹	26
Be	A	A	A	A	20	Cl	A	A	A	A	27
B	A	A	A	A	21	Ge	Bohr	Bohr	Bohr	Bohr ⁻¹	28
C	A	A	A	A	18	Br	Bohr	Bohr	Bohr	Bohr ⁻¹	29
N	A	A	A	A	18	Sn	None	None	Bohr	Bohr ⁻¹	30
O	A	A	A	A	18	I	Bohr	Bohr	Bohr	Bohr ⁻¹	31
F	A	A	A	A	22	Hg	None	None	Bohr	Bohr ⁻¹	32
Al	A	A	A	A	23	Pb	None	None	Bohr	Bohr ⁻¹	33
Si	Bohr	Bohr	Bohr	Bohr ⁻¹	24						

In order to maintain consistency, inverse Bohr or a_0^{-1} are to be preferred for AM, AD and AQ, and Bohr or a_0 for D_1 and D_2 . The other derived parameters reported may be converted into inverse Bohr or into Bohr by one of the following two relationships:

for D_1 and D_2 , if the units are Ångstroms, divide by 0.529167.

for AM, AD, and AQ, if the units are Ångstroms, take the reciprocal and multiply by 0.529167/2.

These conversion factors should work for all currently reported derived parameters, with the exception of DQ_{Be} and DQ_{Cl} , where the reported values, in Å, are 0.684928 and 0.435988, respectively; these should be 0.6878779 and 0.4370799.

While AM is given simply by $G_{ss}/27.21$, AD and AQ are complicated functions of one-center terms and the orbital exponents – recall that, in the limit, the associated charges are not all coincident. AD and AQ are solved iteratively. Given an initial estimate of AD of

$$AD = \left[\frac{H_{sp}}{27.21 D_1^2} \right]^{1/3}$$

then by iterating, an exact value of AD can be found. On iteration n the value of AD is given by

$$AD_n = AD_{n-2} + (AD_{n-1} - AD_{n-2}) \frac{\left(\frac{H_{sp}}{27.21} - a_{n-2} \right)}{a_{n-1} - a_{n-2}}$$

where

$$a_n = 2AD_n - 2(4D_1^2 + AD_n^{-2})^{-\frac{1}{2}}$$

About 5 iterations are needed in order to get AD specified with acceptable accuracy.

Similarly, for AQ an initial estimate of $\left[\frac{H_{pp}}{27.21 (3D_2^4)} \right]^{1/5}$ is made and, again, by iterating using

$$AQ_n = AQ_{n-2} + (AQ_{n-1} - AQ_{n-2}) \frac{\left(\frac{H_{pp}}{27.21} - a_{n-2} \right)}{a_{n-1} - a_{n-2}}$$

where, now,

$$a_n = 4AQ_n - 8(4D_2^2 + AQ_n^{-2})^{-\frac{1}{2}} + 4(8D_2^2 + AQ_n^{-2})^{-\frac{1}{2}}$$

an exact value of AQ can be obtained. About 5 iterations are necessary.

Note that these equations are intrinsically unstable on finite-precision computers. The denominator $(a_{n-1} - a_{n-2})$ rapidly becomes vanishingly small; this is necessary in order to accurately define AD and AQ.

Final assembly of two-electron two-center integrals

With all the component parts defined, the two-electron two-center integrals are assembled from the sum of all the interactions of the charges on one center with those on the other center. The distance between the two charges must be determined – this is the vector addition of R , the interatomic distance in Bohr, and the two c terms defining the location of the charges from the nucleus – as well as the appropriate additive terms, AM, AD or AQ selected. Two examples will illustrate this assembly:

$\langle ss|ss \rangle$: This is represented by a single term. For monopoles, $c = 0$ and $A_A = AM_A$, $A_B = AM_B$ giving

$$\langle ss|ss \rangle = \frac{14.399}{\left(R_{AB}^2 + \frac{1}{2} \left[\frac{1}{AM_A} + \frac{1}{AM_B} \right]^2 0.529167^2 \right)^{1/2}}$$

$\langle ss|p_\pi p_\pi \rangle$: $p_\pi p_\pi$ is expressed as the sum of a monopole and a linear quadrupole. This gives rise to a total of four charges, hence four terms. However, since the interaction of the monopole with each of the two negative charges of the dipole are the same, only three terms need to be evaluated. In general, symmetry considerations lower the total number of terms that need to be evaluated, so the maximum number in any integral is 8. The full integral is then represented as

$$\begin{aligned} \langle ss|p_\pi p_\pi \rangle = & \frac{14.399}{\left(R_{AB}^2 + \frac{1}{2} \left[\frac{1}{AM_A} + \frac{1}{AM_B} \right]^2 0.529167^2 \right)^{1/2}} \\ & + \frac{\frac{1}{2} 14.399}{\left(R_{AB}^2 + (2D_2^B)^2 + \frac{1}{2} \left[\frac{1}{AM_A} + \frac{1}{AQ_B} \right]^2 0.529167^2 \right)^{1/2}} \\ & - \frac{\frac{1}{4} 14.399}{\left(R_{AB}^2 + \frac{1}{4} \left[\frac{1}{AM_A} + \frac{1}{AQ_B} \right]^2 0.529167^2 \right)^{1/2}} \end{aligned}$$

13.2.1.5 MINDO/3 two-electron two-center integrals

In marked contrast to the other methods, MINDO/3 Coulomb and exchange integrals are simple. The integral is a function of the atom types and the interatomic distance only, and is of form

$$\langle AA|BB \rangle = \frac{14.399}{\left(R_{AB}^2 + \frac{1}{2} \left[\frac{14.399}{A_A} + \frac{14.399}{A_B} \right]^2 \right)^{1/2}}$$

where A_A and A_B are the averages of the appropriate one-center two-electron integrals. All finite integrals over atomic orbitals on two centers are set equal. Thus, $\langle s_A s_A | s_B s_B \rangle = \langle s_A s_A | p_B p_B \rangle = \langle p_A p_A | p_B p_B \rangle = \langle AA|BB \rangle$.

13.2.1.6 The one-center one-electron integral $H_{\mu\mu}$

This represents the energy an electron in atomic orbital ϕ_μ would have if all electrons were removed from the system. This is approximated by adding on to the one-electron energy of the atomic orbital in the fully ionized atom the potential due to all the other nuclei in the system. The one-electron energy is obtained parametrically, and is given the symbol $U_{\mu\mu}$. $H_{\mu\mu}$ is derived from the fundamental equation

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} Z_B \langle \mu\mu | BB \rangle$$

by equating the core-electron integral $\langle \mu\mu | BB \rangle$ to the corresponding two-electron integral, thus

(a) MNDO and AM1 and PM3:

$$\langle \mu\mu | BB \rangle = Z_B \langle \mu\mu | ss \rangle$$

(b) MINDO/3:

$$\langle \mu\mu | BB \rangle = Z_B \langle AA | BB \rangle$$

13.2.1.7 The two-center one-electron integral $H_{\mu\nu}$

Sometimes called the resonance integral, $H_{\mu\nu}$ is approximated using the overlap integral, $S_{\mu\nu}$. Note that this violates the NDO approximation, but since resonance integrals are large, this integral is retained. This is the origin of Modified in the MNDO and MINDO/3 names. Using Slater atomic orbitals of type

$$\phi_\mu = N r^{\zeta_\mu - 1} e^{-\zeta_\mu r}$$

the overlap integral is given by

$$S_{\mu\nu} = \langle \phi_\mu \phi_\nu \rangle$$

Within MNDO, AM1, and PM3, $H_{\mu\nu}$ is approximated by

$$H_{\mu\nu} = S_{\mu\nu} \frac{1}{2} (\beta_\mu + \beta_\nu)$$

while MINDO/3 has a very different form:

$$H_{\mu\nu} = S_{\mu\nu} \beta_{AB} (I_\mu + I_\nu)$$

This use of a diatomic parameter is the most distinctive difference between the MNDO/AM1/PM3 philosophies and that of MINDO/3. Because of the difficulty in parameterizing an element at the MINDO/3 level – the number of β -parameters rises as the square of the number of elements parameterized – it is unlikely that any further development of MINDO/3 will be made.

13.2.1.8 Core-core repulsion integrals

From simple electrostatics the core–core repulsion integral in eV is

$$E_N(A,B) = \frac{14.399 Z_A Z_B}{R_{AB}}$$

However, the electron–electron and electron–core integrals do not collapse to the form c/R_{AB} (R_{AB} in Å) for distances beyond the van der Waals' radii. If the simple term given above is used, there would be a net repulsion between two neutral atoms or molecules. To correct for this the core–core repulsion is approximated by

$$E_N(A,B) = Z_A Z_B \langle AA|BB \rangle$$

13.2.1.9 MINDO/3 modification to the core–core term

In addition to this term, account must be taken of the decreasing screening of the nucleus by the electrons as the interatomic distance becomes very small. At very small distances the core–core term should approach the classical form. To account for this, an additional term is added to the basic core–core repulsion to give

$$E_N(A,B) = Z_A Z_B \left[\langle AA|BB \rangle + \left(\frac{14.399}{R_{AB}} - \langle AA|BB \rangle \right) e^{(-\alpha_{AB} R_{AB})} \right]$$

Here α_{AB} is a diatomic parameter. In the case of N–H and O–H interactions only, this expression is replaced by

$$E_N(A,B) = Z_A Z_B \left[\langle AA|BB \rangle + \left(\frac{14.399}{R_{AB}} - \langle AA|BB \rangle \right) \alpha_{AB} e^{-R_{AB}} \right]$$

13.2.1.10 MNDO modification to the core–core term

The MNDO approximation to the screening effect is similar to that of MINDO/3 in practice, but has a different functional form:

$$E_N(A,B) = Z_A Z_B \langle s_A s_A | s_B s_B \rangle [1 + e^{(-\alpha_A R_{AB})} + e^{(-\alpha_B R_{AB})}]$$

Again, O–H and N–H interactions are treated differently. For these interactions, use

$$E_N(A,B) = Z_A Z_B \langle s_A s_A | s_B s_B \rangle \left[1 + \left(\frac{e^{(-\alpha_B R_{AH})}}{R_{AH}} \right) + e^{(-\alpha_H R_{AH})} \right]$$

13.2.1.11 AM1 and PM3 modifications to the core–core term

These modifications are the same as that for MNDO with the addition of an extra term to reduce the excessive core–core repulsions just outside bonding distances. The additional term may be considered as a van der Waals' attraction term. The AM1 and PM3 core–core terms are:

$$E_N(A,B) = E_N^{MNDO}(A,B) + \left(\frac{Z_A Z_B}{R_{AB}} \right) \left[\sum_k a_{kA} e^{-b_{kA}(R_{AB} - c_{kA})^2} + \sum_k a_{kB} e^{-b_{kB}(R_{AB} - c_{kB})^2} \right]$$

The extra terms define spherical Gaussian functions, the a , b , and c are adjustable parameters. PM3 has two Gaussians per atom, while AM1 has between two and four.

13.3 Heat of formation calculation

The SCF calculation produces a density, \mathbf{P} , and Fock matrix, \mathbf{F} . These, together with the one-electron matrix, \mathbf{H} , allow the total electronic energy to be calculated via

$$E_{\text{elect}} = \frac{1}{2} \sum_{\mu} \sum_{\nu} \mathbf{P}_{\mu\nu} (\mathbf{H}_{\mu\nu} + \mathbf{F}_{\mu\nu})$$

The total core-core repulsion energy is given by

$$E_{\text{nuc}} = \sum_{A < B} \sum E_{\text{N}}(A, B)$$

The addition of these two terms represents the energy released when the ionized atoms and valence electrons combine to form a molecule. A more useful quantity is the heat of formation of the compound from its elements in their standard state. This is obtained when the energy required to ionize the valence electrons of the atoms involved (calculated using semiempirical parameters), $E_{\text{el}}(A)$, and heat of atomization, $\Delta H_{\text{f}}(A)$, are added to the electronic plus nuclear energy. This yields

$$\Delta H_{\text{f}} = E_{\text{elect}} + E_{\text{nuc}} + \sum_A E_{\text{el}}(A) + \sum_A \Delta H_{\text{f}}(A)$$

13.4 Overlap integrals

The particular technique used for the evaluation of the overlap integral depends on the atoms involved and whether analytic derivatives are used. All four semiempirical methods use Slater-type orbitals, STOs, although when analytic derivatives are involved [34], a Gaussian expansion [34] of STOs is normally used.

Specific expressions for various of the overlap integrals have appeared in the literature. These are normally used for those overlaps which involve only small principal quantum numbers, PQN, n , and a low angular quantum number, l . For the general case, however, in which any PQN may be encountered, the general overlap integral is used. As the final expression is rather ungainly, a simple derivation of the overlap integral will be given.

Slater atomic orbitals are of form

$$\varphi = \frac{(2\xi)^{n+\frac{1}{2}}}{(2n)!^{\frac{1}{2}}} r^{n-1} e^{-\xi r} Y_l^m(\theta, \phi)$$

where the $Y_l^m(\theta, \phi)$ are the normalized complex spherical harmonics. Complex spherical harmonics are chosen for convenience; (θ, ϕ) real orbitals have a similar behavior, but require more manipulation. The θ dependence of spherical harmonics are the Laguerre polynomials, of form

$$Y_l^m(\theta, \phi) = \frac{e^{im\phi}}{(2\pi)^{\frac{1}{2}}} \left[\frac{(2l+1)(l-m)!}{2(l+m)!} \right]^{1/2} \frac{\sin^m \theta d^{l+m}(\cos^2 \theta - 1)^l}{2^l l! (d \cos \theta)^{l+m}}$$

For convenience the phase factor is set to +1; this varies according to which source is used and the purpose for which the Laguerre polynomials are used.

Solving the differential gives

$$\frac{d^{l+m}}{(d \cos \theta)^{l+m}} (\cos^2 \theta - 1)^l = \sum_j \frac{l!(2j)! (-1)^{l+j}}{j!(l-j)! (2j-l-m)!} (\cos \theta)^{2j-l-m}$$

which, on rearranging to have the summation start at zero, becomes

$$\frac{d^{l+m}}{(d \cos \theta)^{l+m}} \cos^2 (\theta - 1)^l = \sum_{j=0}^{1/2(l-m)} \frac{l!(2(l-j))! (-1)^j}{j!(l-j)! (l-m-2j)!} (\cos \theta)^{l-m-2j}$$

Substituting this into the STO yields

$$\begin{aligned} \varphi &= \frac{(2\xi)^{n+\frac{1}{2}}}{(2n)!^{\frac{1}{2}}} \left[\frac{(2l+1)(l-m)!}{2(l+m)!} \right]^{1/2} \left[\frac{\sin^m \theta}{2^l} r^{n-1} e^{-\xi r} \frac{e^{im\phi}}{(2\pi)^{\frac{1}{2}}} \right] \\ &\quad \sum_{j=0}^{1/2(l-m)} \frac{(2(l-j))! (-1)^j}{j!(l-j)! (l-m-2j)!} (\cos \theta)^{l-m-2j} \end{aligned}$$

At this point it is convenient to collect some of the constants together; thus,

$$C_{lmj} = \left[\frac{(l-m)!}{(l+m)!} \right]^{1/2} \frac{(2(l-j))! (-1)^j}{2^l j!(l-j)!(l-m-2j)!}$$

which allows us to represent the STO in a considerably simplified form:

$$\varphi = \frac{(2\xi)^{n+\frac{1}{2}}}{(2n)!^{\frac{1}{2}}} \frac{(2l+1)^{\frac{1}{2}}}{2^{\frac{1}{2}}} \sin^m \theta r^{n-1} e^{-\xi r} \frac{e^{im\phi}}{(2\pi)^{\frac{1}{2}}} \sum_{j=0}^{1/2(l-m)} C_{lmj} (\cos \theta)^{l-m-2j}$$

The overlap integral of two STOs can then be represented as

$$\begin{aligned} \langle \varphi_a \varphi_b \rangle &= \frac{(2\xi_a)^{n_a+\frac{1}{2}} (2\xi_b)^{n_b+\frac{1}{2}} ((2l_a+1)(2l_b+1))^{\frac{1}{2}}}{((2n_a)! (2n_b)!)^{\frac{1}{2}}} \frac{2}{2} \\ &\quad \int_0^\infty \sin^m \theta_a \sin^m \theta_b r_a^{n_a-1} r_b^{n_b-1} e^{-r_a \xi_a} e^{-r_b \xi_b} \frac{e^{im\phi} e^{im\phi*}}{2\pi} \\ &\quad \sum_{j_a=0}^{1/2(l_a-m)} C_{l_a m j_a} (\cos \theta_a)^{l_a-m-2j_a} \sum_{j_b=0}^{1/2(l_b-m)} C_{l_b m j_b} (\cos \theta_b)^{l_b-m-2j_b} dv \end{aligned}$$

It is impractical to solve this integral using polar coordinates. Instead, a prolate spheroidal coordinate system is used. Using the identities:

$$r_a = \frac{R(\mu + v)}{2}; \quad \cos\theta_a = \frac{(1 + \mu v)}{(\mu + v)};$$

$$r_b = \frac{R(\mu - v)}{2}; \quad \cos\theta_b = \frac{(1 - \mu v)}{(\mu - v)};$$

$$\sin\theta_a = \frac{((\mu^2 - 1)(1 - v^2))^{\frac{1}{2}}}{(\mu + v)}$$

and

$$\sin\theta_b = \frac{((\mu^2 - 1)(1 - v^2))^{\frac{1}{2}}}{(\mu - v)}$$

this gives $dv = \frac{R^3}{8} (\mu + v)(\mu - v) d\mu dv d\phi$.

Substituting these identities into the previous expression we get:

$$\begin{aligned} \langle \varphi_a \varphi_b \rangle &= \int_0^{2\pi} \int_{-1}^1 \int_1^\infty \xi^{n_a + \frac{1}{2}} \xi^{n_b + \frac{1}{2}} \left[\frac{(2l_a + 1)(2l_b + 1)}{(2n_a)!(2n_b)!} \right]^{1/2} 2^{n_a + n_b} \\ &\quad \frac{((\mu^2 - 1)(1 - v^2))^m}{(\mu + v)^m (\mu - v)^m} \frac{R^{n_a - 1}}{2^{n_a - 1}} (\mu + v)^{n_a - 1} \frac{R^{n_b - 1}}{2^{n_b - 1}} (\mu - v)^{n_b - 1} \frac{e^{-R\xi_a(\mu + v)/2} e^{-R\xi_b(\mu - v)/2}}{2\pi} \\ &\quad \sum_{j_a=0}^{(l_a - m)/2} \sum_{j_b=0}^{(l_b - m)/2} C_{l_a m j_a} C_{l_b m j_b} \frac{(1 + \mu v)^{l_a - m - 2j_a}}{(\mu + v)^{l_a - m - 2j_a}} \frac{(1 - \mu v)^{l_b - m - 2j_b}}{(\mu - v)^{l_b - m - 2j_b}} \frac{R^3}{8} (\mu + v)(\mu - v) d\mu dv d\phi \end{aligned}$$

which, on integrating over ϕ and rearranging, gives:

$$\begin{aligned} \langle \varphi_a \varphi_b \rangle &= \int_{-1}^1 \int_1^\infty \frac{\xi^{n_a + \frac{1}{2}} \xi^{n_b + \frac{1}{2}}}{2} \left[\frac{(2l_a + 1)(2l_b + 1)}{(2n_a)!(2n_b)!} \right]^{1/2} R^{n_a + n_b + 1} \\ &\quad \sum_{j_a=0}^{1/2(l_a - m)} \sum_{j_b=0}^{1/2(l_b - m)} C_{l_a m j_a} C_{l_b m j_b} (\mu^2 - 1)^m (1 - v^2)^m (\mu + v)^{n_a - l_a + 2j_a} \\ &\quad (\mu - v)^{n_b - l_b + 2j_b} (1 + \mu v)^{l_a - m - 2j_a} (1 - \mu v)^{l_b - m - 2j_b} e^{-\frac{1}{2}R\xi_a(\mu + v)} e^{-\frac{1}{2}R\xi_b(\mu - v)} d\mu dv \end{aligned}$$

This is a product of six simple expressions of type $(a + b)^n$. Expanding each term as a binomial generates six summations:

$$\begin{aligned}
\langle \varphi_a \varphi_b \rangle = & \int_{-1}^1 \int_1^\infty \frac{\xi^{n_a + \frac{1}{2}} \zeta^{n_b + \frac{1}{2}}}{2} \left[\frac{(2l_a + 1)(2l_b + 1)}{(2n_a)!(2n_b)!} \right]^{1/2} R^{n_a + n_b + 1} \\
& \sum_{j_a=0}^{1/2(l_a-m)} \sum_{j_b=0}^{1/2(l_b-m)} C_{l_a m j_a} C_{l_b m j_b} \sum_{k_a=0}^m \sum_{k_b=0}^m \sum_{p_a=0}^{n_a-l_a+2j_a} \sum_{p_b=0}^{n_b-l_b+2j_b} \sum_{q_a=0}^{l_a-m-2j_a} \sum_{q_b=0}^{l_b-m-2j_b} \\
& \frac{(l_b-m-2j_b)!}{(l_b-m-2j_b-q_b)!q_b!} \frac{(l_a-m-2j_a)!}{(l_a-m-2j_a-q_a)!q_a!} \frac{(n_b-l_b+2j_b)!}{(n_b-l_b+2j_b-p_b)!p_b!} \\
& \frac{(n_a-l_a+2j_a)!}{(n_a-l_a+2j_a-p_a)!p_a!} \frac{m!^2}{(m-k_b)!k_b!(m-k_a)!k_a!} (-1)^{k_a+k_b+m+p_b+q_b} \\
& \mu^{2k_a+p_a+p_b+q_a+q_b} \nu^{2k_b+n_a-l_a+2j_a+n_b-l_b+2j_b-p_a-p_b+q_a+q_b} e^{-\frac{1}{2}R\xi_a(\mu+\nu)} e^{-\frac{1}{2}R\zeta_b(\mu-\nu)} d\mu d\nu
\end{aligned}$$

Using integration by parts, and making use of the following integrals

$$\begin{aligned}
\int_1^\infty x^n e^{-ax} dx &= e^{-a} \sum_{\mu=1}^{n+1} \frac{n!}{a^\mu(n-\mu+1)!} = A_n(a) \\
\int_{-1}^1 x^n e^{-ax} dx &= -e^{-a} \sum_{\mu=1}^{n+1} \frac{n!}{a^\mu(n-\mu+1)!} - e^a \sum_{\mu=1}^{n+1} \frac{n(-1)^{n-\mu}}{a^\mu(n-\mu+1)!} = B_n(a)
\end{aligned}$$

the overlap integral becomes

$$\begin{aligned}
\langle \varphi_a \varphi_b \rangle = & \frac{\xi_a^{n_a + \frac{1}{2}} \zeta_b^{n_b + \frac{1}{2}}}{2} \left[\frac{(2l_a + 1)(2l_b + 1)}{(2n_a)!(2n_b)!} \right]^{1/2} R^{n_a + n_b + 1} \sum_{j_a=0}^{1/2(l_a-m)} C_{l_a m j_a} \sum_{j_b=0}^{1/2(l_b-m)} C_{l_b m j_b} \sum_{k_a=0}^m \\
& \sum_{k_b=0}^m \sum_{p_a=0}^{n_a-l_a+2j_a} \sum_{p_b=0}^{n_b-l_b+2j_b} \sum_{q_a=0}^{l_a-m-2j_a} \sum_{q_b=0}^{l_b-m-2j_b} \frac{(l_b-m-2j_b)!}{(l_b-m-2j_b-q_b)!q_b!} \frac{(l_a-m-2j_a)!}{(l_a-m-2j_a-q_a)!q_a!} \\
& \frac{(n_b-l_b+2j_b)!}{(n_b-l_b+2j_b-p_b)!p_b!} \frac{(n_a-l_a+2j_a)!}{(n_a-l_a+2j_a-p_a)!p_a!} \frac{m!^2}{(m-k_b)!k_b!(m-k_a)!k_a!} (-1)^{k_a+k_b+m+p_b+q_b} \\
& B_{2k_b+n_a-l_a+2j_a+n_b-l_b+2j_b-p_a-p_b+q_a+q_b} \left(\frac{R(\xi_a - \zeta_b)}{2} \right) A_{2k_a+p_a+p_b+q_a+q_b} \left(\frac{R(\xi_a + \zeta_b)}{2} \right)
\end{aligned}$$

in which the coefficients C_{lmj} have the numerical values

l	m	j	C_{lmj}	l	m	j	C_{lmj}
0	0	0	1.0	3	0	0	5/2
1	0	0	1.0	3	1	0	$(225/48)^{\frac{1}{2}}$
1	1	0	$(1/2)^{\frac{1}{2}}$	3	2	0	$(15/8)^{\frac{1}{2}}$
2	0	0	3/2	3	3	0	$(5/16)^{\frac{1}{2}}$
2	1	0	$(3/2)^{\frac{1}{2}}$	3	0	1	-3/2
2	2	0	$(3/8)^{\frac{1}{2}}$	3	1	1	$-(3/16)^{\frac{1}{2}}$
2	0	1	-1/2				

which is the most convenient form for algorithmic use.

13.5 Configuration interaction

For some systems a single determinant is insufficient to describe the electronic wave function. For example, square cyclobutadiene and twisted ethylene require at least two configurations to describe their ground states. More than one configuration is also needed if an excited state is required – the RHF SCF converges on a ground state or, if half-electron methods are used, on a mixture of states, while the excited state involves a different configuration. Radicals also present a difficulty at the RHF level in that the SCF wavefunction corresponds to an equal mixture of the two doublets, with a corresponding error in the total energy. This error can most easily be corrected by performing a MECI calculation. To allow several configurations to be used, a Multi-Electron Configuration Interaction technique has been developed [36].

MECI is a completely general C.I. The resulting states are space- and spin-quantized, there is no restriction on total spin, the starting wavefunction can be closed or open shell, and even or odd electron systems are allowed, although for simplicity the starting configuration is assumed to be closed-shell in the description of the MECI. As MECI requires the space parts of the α and β molecular orbitals to be identical, only RHF wavefunctions are used.

Each configuration which can be generated in a molecule may be represented by a single Slater determinant; this is called a microstate. The final states will be linear combinations of these microstates. In general, microstates will not be eigenfunctions of the total spin operator, but will be mixtures of different spin states.

The initial configuration used to generate the SCF is arbitrary; for half-electron systems it will not even correspond to a microstate, each M.O. having a fractional electron occupancy. Even if the starting wavefunction is a closed shell it would still correspond to only one of a large number of microstates to be used in the MECI. As a result, before the MECI is started all electronic terms arising from the electrons in the initial configuration, which will be used by MECI, are removed. The starting wavefunction will thus consist of a low-lying doubly occupied set of M.O.s and a high-lying empty set of M.O.s, neither of which will be involved in the MECI, and in between a small set of M.O.s from which the electrons have been removed. This set of M.O.s will be involved in the MECI.

Microstates are normally written as an antisymmetrized product of p α and q β electrons,

$$\Psi_g = [(p+q)!]^{-\frac{1}{2}} \sum_p (-1)^p P[\psi_1^{(1)}\alpha(1)\psi_2^{(2)}\alpha(2)\dots\psi_p^{(p)}\alpha(p)\psi_1^{(p+1)}\beta(p+1)\dots\psi_q^{(p+q)}\beta(p+q)]$$

where $[(p+q)!]^{-\frac{1}{2}}$ is the normalization constant, P is an operator which permutes the electron coordinates, and $(-1)^P$ assumes the values -1 or +1 for odd and even permutations, respectively. Rather than having all the α electrons appearing first in a microstate it is more convenient to order the one-electron wavefunctions in order of their indices as they occur in the full set of M.O. If both α and β M.O.s of the same index occur, then α precedes β , thus:

$$\Psi_g = [(p+q)!]^{-\frac{1}{2}} \sum_P (-1)^P P[\psi_1^{(1)}\alpha(1)\psi_1^{(2)}\beta(2)\psi_2^{(3)}\alpha(3)\psi_2^{(4)}\beta(4)\dots\psi_j^{(p+q)}\beta(p+q)]$$

Only those M.O.s involved in the MECI are of interest, thus from the full set of M.O.s, filled and empty

$$\begin{bmatrix} \psi_1(1)\alpha(1) & \psi_2(3)\alpha(3)\dots \\ \psi_1(2)\beta(2) & \psi_2(4)\beta(4)\dots \end{bmatrix}$$

the ground-state configuration (assumed to be closed shell for simplicity) can be represented by

$$\begin{bmatrix} 1 & 1 & 1 & 1 & \dots & 1 & 1 & 1 & 0 & 0 & 0 & \dots & 0 & 0 \\ 1 & 1 & 1 & 1 & \dots & 1 & 1 & 1 & 0 & 0 & 0 & \dots & 0 & 0 \end{bmatrix}$$

where a 1 represents a spin molecular orbital occupied by one electron and 0 represents an empty M.O. Denoting the lower bound of the M.O.s involved in the C.I. by B and the upper bound by A,

$$\begin{bmatrix} 1 & 1 & 1 & \dots & \vdots & 1 & 1 & 1 & 0 & 0 & \dots & 0 & 0 & 0 & \vdots & \dots & 0 & 0 \\ 1 & 1 & 1 & \dots & \vdots & 1 & 1 & 1 & 0 & 0 & \dots & 0 & 0 & 0 & \vdots & \dots & 0 & 0 \end{bmatrix}$$

B A

all M.O.s below (to the left of) B can be considered as part of the core while those above (to the right of) A are empty and can likewise be ignored. We can thus focus our attention on the M.O.s in the range B-A.

For convenience, microstates will be expressed as a sum of molecular orbital occupancies, so that

$$\Psi_p = \sum_{i=B}^A (O_i^{\alpha p} + O_i^{\beta p})$$

For example, if the ground state configuration Ψ_g is closed shell, then the occupancy of the M.O.s would be

$$O^{\alpha g} = O^{\beta g} = O^g = |1, \dots, 1, 0, \dots, 0|$$

The electronic energy, E_r , of any microstate Ψ_r is the sum on the one- and two-electron energies:

$$E_r = \sum_i^p H_{ii} + \sum_i^q H_{ii} + \frac{1}{2} \sum_{ij}^p (J_{ij} - K_{ij}) + \frac{1}{2} \sum_{ij}^q (J_{ij} - K_{ij}) + \sum_i^p \sum_j^q J_{ij}$$

where H_{ii} is the one-electron energy of M.O. ψ_i

J_{ii} is the two-electron Coulomb integral $\langle \psi_i \psi_i | \psi_j \psi_j \rangle$

and K_{ii} is the two-electron exchange integral $\langle \psi_i \psi_j | \psi_i \psi_j \rangle$

In this section it is more convenient to express it in terms of molecular orbital occupancies:

$$E_r = \sum_{i=B}^A H_{ii}(O_i^{\alpha r} + O_i^{\beta r}) + \sum_{ij} (\frac{1}{2}(J_{ij} - K_{ij})(O_i^{\alpha r} O_j^{\alpha r} + O_i^{\beta r} O_j^{\beta r}) + J_{ij} O_i^{\alpha r} O_j^{\beta r})$$

Similarly, the orbital energies can be written

$$\epsilon_{ii}^{\alpha r} = H_{ii} + \sum_j^p (J_{ij} - K_{ij}) + \sum_j^q J_{ij}$$

or, in terms of orbital occupancies

$$\epsilon_{ii}^{\alpha r} = H_{ii} + \sum_{j=B}^A (J_{ij} - K_{ij}) O_j^{\alpha r} + \sum_{j=B}^A J_{ij} O_j^{\beta r}$$

As stated above, all electronic terms arising from the electrons of the M.O.s involved in the starting configuration must be removed. This lowers the orbital energies thus:

$$\epsilon_{ii}^+ = \epsilon_{ii} - \sum_{j=B}^A (2J_{ij} - K_{ij}) O_j^{\beta}$$

The total energy of the system after removal of these electrons is given by

$$E_g^+ = E_g - \sum_{i=B}^A 2\epsilon_{ii}^+ O_i^{\beta} + J_{ii}(O_i^{\beta})^2 + \sum_{i=B}^A \sum_{j=B}^{i-1} 2(2J_{ij} - K_{ij}) O_i^{\beta} O_j^{\beta}$$

By redefining the system so that those filled M.O.s which are not used in the MECI are considered part of an unpolarizable core, the new energy levels ϵ_i^+ can be identified with the one-electron energies H_{ii} and the total electronic energy E_r of any microstate is set equal to the sum of the energy of the electrons considered in the microstate plus E_g^+ .

13.5.1 Construction of secular determinant

Microstates can be generated by permuting available electrons among the available levels. Elements of the C.I. matrix are then defined by

$$\langle \Psi_a | H | \Psi_b \rangle$$

Evaluation of these matrix elements is difficult. Each microstate is a Slater determinant, and the Hamiltonian operator involves all electrons in the system. Fortunately, most matrix elements are zero because of the orthogonality of the M.O.s. Only the non-zero elements need be evaluated; three types of interaction are possible:

(a) $\Psi_a = \Psi_b$. Since the two wavefunctions are the same, this corresponds to the energy of a microstate. As the electronic energy of the closed shell is common to all configurations considered in the C.I., it is sufficient to add on to E_g^+ the energy terms which are specific to the microstate, thus

$$\langle \Psi_p | H | \Psi_p \rangle = E_g^+ + \sum_{i=B}^A \left(\varepsilon_{ii} + \sum_{j=B}^i (J_{ij} - K_{ij}) O_j^{\alpha p} \right) O_i^{\alpha p} + \sum_{i=B}^A \left(\varepsilon_{ii} + \sum_{j=B}^i (J_{ij} - K_{ij}) O_j^{\beta p} \right) O_i^{\beta p} + \sum_{i=B}^A \sum_{j=B}^A J_{ij} O_i^{\alpha p} O_j^{\beta p}$$

(b) Except for ψ_i in Ψ_a and ψ_j in Ψ_b ; $\Psi_a = \Psi_b$. Assuming ψ_i and ψ_j to be α -spin the interaction energy is

$$\langle \Psi_a | F | \Psi_b \rangle = (-1)^w (\varepsilon_{ij}^+ + \sum_k (\langle ij|kk \rangle - \langle ik|jk \rangle) O_k^{\alpha a} + \langle ij|kk \rangle O_k^{\beta a})$$

This presents a problem. Unlike ε_{ii}^+ , which has already been defined, there is no easy way to calculate ε_{ij}^+ . Rather than undertake this calculation, use can be made of the fact that, for the starting configuration

$$\varepsilon_{ij} = \langle \Psi_g | F | \Psi_g \rangle = H_{ij} + \sum_k (\langle ij|kk \rangle - \langle ik|jk \rangle) O_k^{\alpha g} + \sum_k \langle ij|kk \rangle O_k^{\beta g}$$

or

$$\varepsilon_{ij} = \varepsilon_{ij}^+ + \sum_{k=B}^A (\langle ij|kk \rangle - \langle ik|jk \rangle) O_k^{\alpha g} + \sum_{k=B}^A \langle ij|kk \rangle O_k^{\beta g}$$

ε_{ij}^+ corresponds to an off-diagonal term in the Fock matrix, which at self-consistency is, by definition, zero. Therefore

$$\varepsilon_{ij}^+ = - \sum_{k=B}^A [\langle ij|kk \rangle - \langle ik|jk \rangle] O_k^{\alpha g} - \sum_{k=B}^A \langle ij|kk \rangle O_k^{\beta g}$$

which can be substituted directly into the expression for $\langle \Psi_a | F | \Psi_b \rangle$ to give

$$\langle \Psi_a | F | \Psi_b \rangle = (-1)^w \sum_k [\langle ij|kk \rangle - \langle ik|jk \rangle] (O_k^{\alpha a} - O_k^{\alpha g}) + \sum_k \langle ij|kk \rangle (O_k^{\beta a} - O_k^{\beta g})$$

All that remains is to determine the phase factor. One of the microstates is permuted until the two unmatched M.O.s occupy the same position. The number of permutations needed to do this when the two M.O.s are of α spin is

$$w = \sum_{k=i+1}^{j-1} (O_k^{\alpha p} + O_k^{\beta p})$$

assuming $j > i$; otherwise

$$w = O_j^{\alpha p} + \sum_{k=i+1}^{j-1} (O_k^{\alpha p} + O_k^{\beta p})$$

(c) Except for ψ_i and ψ_j in Ψ_a and ψ_k and ψ_l in Ψ_b ; $\Psi_a = \Psi_b$. Two situations exist: (i) when all four M.O.s are of the same spin; and (ii) when two are of each spin. Thus,

(i) All four M.O.s are of the same spin. The interaction energy is

$$\langle \Psi_a | F | \Psi_b \rangle = (-1)^w [\langle ik|jl \rangle - \langle il|jk \rangle]$$

in which the phase factor is

$$w = \sum_{m=i+1}^{j-1} (O_m^{\alpha a} + O_m^{\beta a}) + \sum_{m=k+1}^{l-1} (O_m^{\alpha a} + O_m^{\beta a}) + O_i^{\beta a} + O_k^{\beta a}$$

if the four M.O.s are of α spin; otherwise,

$$w = \sum_{m=i+1}^{j-1} (O_m^{\alpha a} + O_m^{\beta a}) + \sum_{m=k+1}^{l-1} (O_m^{\alpha a} + O_m^{\beta a}) + O_j^{\alpha a} + O_l^{\alpha a}$$

Two M.O.s are of each spin. In this case there is no exchange integral, therefore the interaction energy is

$$\langle \Psi_a | F | \Psi_b \rangle = (-1)^w \langle ik|jl \rangle$$

and the phase factor is

$$w = \sum_{m=k}^i (O_m^{\alpha a} + O_m^{\beta a}) + \sum_{m=j}^l (O_m^{\alpha a} + O_m^{\beta a})$$

if $i > k$, then $w = w + O_k^{\alpha a} + O_i^{\beta a}$,

if $j > l$, then $w = w + O_k^{\alpha b} + O_i^{\beta b}$,

finally if $i > k$ and $j > l$ or $i < k$ and $j < l$, then $w = w + 1$.

All other matrix elements are zero. The completed secular determinant is then diagonalized. This yields the state vectors and state energies, relative to the starting configuration. In turn, the state vectors can be used to generate unpaired spin density (at the RHF level) for pure spin states. If the density matrix for the state is of interest, such as in the calculation of transition dipoles for vibrational modes of excited or open shell systems, or for other use, the perturbed density matrix is reconstructed.

13.6 Spin angular momentum

State functions are eigenvalues of the S_z and S^2 operators. The derivation of the expectation value of the S^2 operator is given in this section.

The fundamental spin operators have the following effects:

$$\begin{aligned} S_x\alpha &= 1/2\beta & S_x\beta &= 1/2\alpha \\ S_y\alpha &= i/2\beta & S_y\beta &= -i/2\alpha \\ S_z\alpha &= 1/2\alpha & S_z\beta &= -1/2\beta \end{aligned}$$

Using these expressions, various useful identities can be established:

$$\begin{aligned} S^2 &= S_x^2 + S_y^2 + S_z^2 \\ I^+ &= (S_x + iS_y) & I^+\beta &= \alpha \\ I^- &= (S_x - iS_y) & I^-\alpha &= \beta \\ S_x^2 + S_y^2 &= (I^+I^-) + i(S_xS_y - S_yS_x) \\ &= (I^-I^+) + i(S_yS_x - S_xS_y) \\ &= \frac{1}{2}(I^+I^- + I^-I^+) \end{aligned}$$

and finally $i(S_yS_x - S_xS_y) = S_z$

For any microstate, Ψ , the expectation value of the S^2 operator is given by

$$\langle S^2 \rangle = \langle \Psi(S_z^2 + S_y^2 + S_x^2)\Psi \rangle$$

The first part of this expression is obvious, viz.:

$$\langle \Psi|S_z^2|\Psi \rangle = \frac{1}{4}(N^\alpha - N^\beta)$$

However, the effect of $S_y^2 + S_x^2$ is not so simple. By making use of the fact that the operators involve two electrons, a large number of integrals resulting from the expansion of the Slater determinants can be readily eliminated. The only integrals which are not zero due to the orthogonality of the eigenvectors, i.e., those which may be finite due to the spin operators, are

$$\langle \Psi|S_y^2 + S_x^2|\Psi \rangle = 2 \sum_{i < j} [\langle \psi_i\psi_i|S^2|\psi_j\psi_j \rangle - \langle \psi_i\psi_j|S^2|\psi_i\psi_j \rangle]$$

Using the relationships already defined, this expression simplifies as follows:

$$\begin{aligned} S_1S_2 &= S_{1z}S_{2z} + \frac{1}{2}(I_1^+I_2^- + I_1^-I_2^+) \\ \langle \Psi(S^2)\Psi \rangle &= 2 \sum_{i < j} [\frac{1}{4}(2\delta(m_{Si}m_{Sj}) - 1 - \frac{1}{2}(1 - \delta(m_{Si}m_{Sj})))\langle \psi_i\psi_j \rangle^2] \end{aligned}$$

or,

$$\begin{aligned} \langle \Psi(S^2)\Psi \rangle &= \frac{3(p+q)}{4} + \frac{p(p-1)}{2} + \frac{q(q-1)}{2} - \frac{(p+q)(p+q-1)}{4} - \sum_{ij}^{pq} \langle \psi_i\psi_j \rangle^2 \\ \langle \Psi(S^2)\Psi \rangle &= \frac{1}{2}(p+q) + \frac{1}{4}(p-q)^2 - \sum_{ij}^{pq} \langle \psi_i\psi_j \rangle^2 \end{aligned}$$

For the general case, in which the state function is a linear combination of microstates, the expectation value of S is more complicated:

$$\langle \Phi_k S^2 \Phi_k \rangle = \sum_{ij} C_{ik} C_{jk} \langle \Psi_i S^2 \Psi_j \rangle$$

As with the construction of the C.I. matrix, the elements of this expression can be divided into a small number of different types:

- (a) $\Psi_a = \Psi_b$: Since the two wavefunctions are the same, this corresponds to the expectation value of a microstate, and has already been derived.
- (b) Except for ψ_i in Ψ_a and ψ_j in Ψ_b ; $\Psi_a = \Psi_b$: Assuming ψ_i and ψ_j to have alpha-spin the expectation value is

$$\langle \Psi_a | S_y^2 + S_x^2 | \Psi_b \rangle = (-1)^w \sum_k (\langle ij|kk \rangle - \langle ik|jk \rangle) O_k^{\alpha\alpha} + \langle ij|kk \rangle O_k^{\beta\alpha}$$

The effect of the spin operator is to change the spin of the electrons but leave the space part unchanged. All integrals vanish identically due to one or more of the following identities:

$$\begin{aligned} \langle \psi_i \psi_j \rangle &= 0 & \langle m_i m_j \rangle &= \delta(i, j) \\ \langle \psi_i \psi_k \rangle &= \delta(i, k) & \langle \psi_j \psi_k \rangle &= \delta(j, k) \end{aligned}$$

Therefore, $\langle S^2 \rangle = 0$

- (c) Except for ψ_i and ψ_j in Ψ_a and ψ_k and ψ_l in Ψ_b ; $\Psi_a = \Psi_b$: Two situations exist: (i) when all four M.O.s are of the same spin; and (ii) when two are of each spin.

When all four M.O.s have the same spin, the effect of the spin operator is to reverse the spin of two M.O.s in the ket half of the integral. By spin orthogonality this results in an integral value of zero.

In the case where two M.O.s are of α spin and two are of β spin the matrix elements, after elimination of those terms which are zero due to space orthogonality, are

$$\langle S^2 \rangle = (-1)^w (\langle \psi_i \psi_k | S^2 | \psi_j \psi_l \rangle - \langle \psi_i \psi_l | S^2 | \psi_j \psi_k \rangle)$$

The effect of S^2 on ψ_k and ψ_l is to reverse the spin of these functions; this gives

$$\langle S^2 \rangle = (-1)^w (\langle \psi_i \psi'_k \rangle \langle \psi_j \psi'_l \rangle - \langle \psi_i \psi'_l \rangle \langle \psi_j \psi'_k \rangle)$$

where ψ' has the opposite spin to that of ψ .

Thus, only if ψ_i and ψ_j are spatially identical with ψ_k and ψ_l will $\langle S^2 \rangle$ be non-zero. The phase-factor w is such that if $i = k$ and $j = l$ then $w = 0$, and if $i = l$ and $j = k$ then $w = 1$, for all other cases the matrix element is zero, so the phase of w is irrelevant. For these two cases, the matrix element is

$$\langle S^2 \rangle = 1 \quad \text{if} \quad (I^+ + I^-)(\psi_i + \psi_j) = (\psi_k + \psi_l)$$

otherwise $\langle S^2 \rangle = 0$.

- (d) If more than two differences exist, $\langle S^2 \rangle = 0$.

14. AN SCF CALCULATION

Semiempirical calculations can be run on computers using readily available programs. It is possible to use such programs for research without having any knowledge of their workings. This does not imply any failing on the part of the researcher; after all, it is possible to write extensive computer programs while having little knowledge of how a computer works. However, in order to more efficiently use such programs, a more than casual knowledge of the theory involved is desirable. In the following section the details of a very simple calculation will be described. This calculation can be carried out as a ‘black box’ calculation, but the following exercise may help to satisfy the intellectual curiosity of users of semiempirical methods regarding the mechanics of carrying out an SCF calculation.

So far we have looked at the theory used in semiempirical methods. In order to understand how an SCF calculation works, we will now carry out a very simple example. We will use the MNDO method because it currently is the most popular of the ‘NDO’ methods. The CNDO/2 method is very similar, and the example we will look at will emphasize the similarity. The system to be examined is a regular hexagon of hydrogen atoms in which the H–H distance is 0.98314 Å. Of course, a regular hexagon of hydrogen atoms is not a stable system; the only reason we are using it here is to demonstrate the working of an SCF calculation. The optimized geometry was obtained by defining all bond lengths to be equal, constraining all bond angles to be 120 degrees and defining the system as being planar.

We will need various reference data in order to follow the calculation. By reference to the MOPAC source file BLOCK.FOR we find that:

$$\begin{aligned}
 G_{ss}(H) &= \langle \varphi_s \varphi_s | 1/r | \varphi_s \varphi_s \rangle &= 12.848 \text{ eV} \\
 U_{ss}(H) &= \langle \varphi_s | H | \varphi_s \rangle &= -11.906276 \text{ eV} \\
 \xi_s & &= 1.331967 \text{ Bohr} \\
 \beta_s & &= -6.989064 \text{ eV} \\
 E_{\text{iso1}} & &= -11.906276 \text{ eV} \\
 E_{\text{atom}} & &= 52.102 \text{ kcal/mol}
 \end{aligned}$$

This exercise is designed to allow the reader to reproduce each step. All that is needed in order to follow the working is a hand calculator.

<i>Interatomic distance matrix (Å)</i>						
Atom	1	2	3	4	5	6
1	0.0000					
2	0.9831	0.0000				
3	1.7029	0.9831	0.0000			
4	1.9663	1.7029	0.9831	0.0000		
5	1.7029	1.9663	1.7029	0.9831	0.0000	
6	0.9831	1.7029	1.9663	1.7029	0.9831	0.0000

The overlap integral of two Slater orbitals between two hydrogen atoms is particularly simple:

$$\langle \varphi | \varphi \rangle = (e^{-a})(a^2/3 + a + 1)$$

where $a = \xi R/a_0$

At the optimum H–H distance of 0.983143 Å, this yields an overlap integral of 0.4643. The nearest-neighbor one-electron integral is thus

$$H(1,2) = S_{1,2}(\beta_s + \beta_p)/2 = -3.2457 \text{ eV}$$

In general, overlap integrals are more complicated and also involve angular components, but the principles involved are the same. You may want to check other off-diagonal terms in the one-electron matrix, or you may accept the results given here.

One-electron matrix (eV)						
Atom	1	2	3	4	5	6
1	– 51.7112					
2	– 3.2457	– 51.7112				
3	– 1.0970	– 3.2457	– 51.7112			
4	– 0.6992	– 1.0970	– 3.2457	– 51.7112		
5	– 1.0970	– 0.6992	– 1.0970	– 3.2457	– 51.7112	
6	– 3.2457	– 1.0970	– 0.6992	– 1.0970	– 3.2457	– 51.7112

On-diagonal one-electron integrals are more complicated than the off-diagonal terms. The one-electron energy of an electron in an atomic orbital is the sum of its kinetic energy and stabilization due to the positive nucleus of its own atom, U_{ss} or U_{pp} , plus the stabilization due to all the other nuclei in the system.

Each electron on a hydrogen atom experiences a stabilization due to the five other unipositive nuclei in the system. Within semiempirical theory the electron-nuclear interaction is related to the electron–electron interaction via

$$E_{e,n} = -Z_n \langle \varphi_s \varphi_s | \varphi_s \varphi_s \rangle$$

Given the two-electron two-center integral matrix the calculation of the diagonal terms of the one-electron matrix is straightforward:

$$H_{n,n} = -11.9063 - 2(9.6583) - 2(7.0632) - 6.3620$$

For interactions between an atomic orbital and a non-hydrogen atom there will be 10 terms; these arise from all permutations of the basis set, s, p_x, p_y, p_z with the atomic orbital under the neglect of differential overlap approximation. The 10 integrals are $\langle ii|ss \rangle$, $\langle ii|sp_x \rangle$, $\langle ii|p_x p_x \rangle$, $\langle ii|sp_y \rangle$, $\langle ii|p_x p_y \rangle$, $\langle ii|p_y p_y \rangle$, $\langle ii|sp_z \rangle$, $\langle ii|p_x p_z \rangle$, $\langle ii|p_y p_z \rangle$, and $\langle ii|p_z p_z \rangle$.

Two-electron integrals (eV)

Atom	1	2	3	4	5	6
1	12.8480					
2	9.6583	12.8480				
3	7.0632	9.6583	12.8480			
4	6.3620	7.0732	9.6583	12.8480		
5	7.0632	6.3620	7.0732	9.6583	12.8480	
6	9.6583	7.0632	6.3620	7.0732	9.6583	12.8480

14.1 Starting density matrix

The density matrix is necessary in order to calculate the Fock matrix, but, in turn, the Fock matrix is necessary in order to calculate the density matrix. To break this impasse, a guessed density matrix is used. The guess is very crude: all off-diagonal matrix elements are set to zero, and all on-diagonal terms on any atom are set equal to the core charge of that atom divided by the number of atomic orbitals. Our starting guess for H_6 consists of a unit matrix.

Each iteration of the SCF calculation consists of assembling a Fock matrix from the one-electron matrix, the two-electron integrals, and the density matrix, diagonalizing it to obtain the eigenvectors, and finally reassembling the density matrix. At some point the change in density matrix drops below a preset limit. When this happens we say that the field is self-consistent. We will now carry out these steps for the H_6 system.

14.2 Assembly of the starting Fock matrix

In the first iteration this is particularly simple, as there are no off-diagonal terms in the density matrix. Only the on-diagonal terms are affected. Each on-diagonal term in the Fock matrix F_{aa} is modified by the electrostatic field of all the electrons in the system except the electron or fraction of an electron in the atomic orbital φ_a . Consider $F(1,1)$. The total initial population of φ_1 is 1.0, composed of equal amounts of α and β electron density. An electron in φ_1 would therefore experience the electrostatic repulsion of half an electron. An electron cannot repel itself, however it will be repelled by its partner electron of opposite spin.

In addition, each electron will be affected, normally repelled, by the electrostatic field of all the electrons on all the other atoms. Each atom has one electron, so the total energy of an electron, i.e., the diagonal Fock matrix element, is given by

$$F(1,1) = 51.7112 + \frac{1}{2}(12.848) + 2(9.6583 + 7.0632) + 6.3620$$

The Fock matrix is obtained by adding the two-electron terms to the one-electron matrix. The elements of the Fock matrix represent the sum of the one- and two-electron interactions. For the system of six hydrogen atoms, this has the following form:

Initial Fock matrix (eV)

Atom	1	2	3	4	5	6
1	-5.4823					
2	-3.2457	-5.4823				
3	-1.0970	-3.2457	-5.4823			
4	-0.6992	-1.0970	-3.2457	-5.4823		
5	-1.0970	-0.6992	-1.0970	-3.2457	-5.4823	
6	-3.2457	-1.0970	-0.6992	-1.0970	-3.2457	-5.4823

14.3 Diagonalization of the Fock matrix

The Fock matrix is then diagonalized to yield the following set of eigenvalues and eigenvectors:

Energy level		Molecular orbital coefficients					
		1	2	3	4	5	6
6	-0.4857	0.4082	-0.4082	0.4082	-0.4082	0.4082	-0.4082
5	-1.8388	0.5774	-0.2887	-0.2887	0.5774	-0.2887	-0.2887
4	-1.8388	0.0000	0.5000	-0.5000	0.0000	0.5000	-0.5000
3	-6.9317	0.5774	0.2887	-0.2887	-0.5774	-0.2887	0.2887
2	-6.9317	0.0000	0.5000	0.5000	0.0000	-0.5000	-0.5000
1	-14.8669	0.4082	0.4082	0.4082	0.4082	0.4082	0.4082

14.4 Exercises involving eigenvectors

In the following exercises ‘verify’ means using a hand calculator. They are intended to confirm understanding of the theory involved. Work through one or more examples to confirm the validity of the statement that follows.

- 1 Verify that the eigenvectors are normalized.
- 2 Verify that the eigenvectors are orthogonal to each other.
- 3 Verify that the eigenvalues are correct.
- 4 Verify that the eigenvectors diagonalize the Fock matrix.
- 5 Verify that the diagonal sum rule is obeyed, i.e., that the sum of the eigenvalues is equal to the sum of the diagonal matrix elements (the trace) of the Fock matrix.

14.5 Iterating density matrix

The density matrix is then reformed using the occupied set of eigenvectors, i.e., the lowest three levels. This yields:

<i>Density matrix</i>						
	1	2	3	4	5	6
1	1.0000					
2	0.6667	1.0000				
3	0.0000	0.6667	1.0000			
4	-0.3333	0.0000	0.6667	1.0000		
5	0.0000	-0.3333	0.0000	0.6667	1.0000	
6	0.6667	0.0000	-0.3333	0.0000	0.6667	1.0000

Verify that the density matrix is correct.

14.6 Iterating Fock matrix

The second Fock matrix can then be constructed using this density matrix. The on-diagonal terms are identical to those in the first Fock matrix, since the atomic orbital electron densities are unchanged, but the off-diagonal terms are now changed. The off-diagonal terms are modified to allow for exchange interactions. (Note that not all exchange terms are stabilizing.)

Let us evaluate the matrix element $F(1,2)$:

$$F(1,2) = -3.2457 - \frac{1}{2}(0.6667)(9.6583) \text{ eV}$$

The second Fock matrix is given below.

<i>Second Fock matrix (eV)</i>						
Atom	1	2	3	4	5	6
1	-5.4823					
2	-6.4651	-5.4823				
3	-1.0970	-6.4651	-5.4823			
4	+0.3611	-1.0970	-6.4651	-5.4823		
5	-1.0970	+0.3611	-1.0970	-6.4651	-5.4823	
6	-6.4651	-1.0970	+0.3611	-1.0970	-6.4651	-5.4823

Diagonalization of this matrix yields the same set of eigenvectors as we had initially. In general, several iterations are necessary in order to obtain an SCF; however, a few systems exist for which symmetry restrictions on the form of the eigenvectors allow them to achieve an SCF in one iteration. Hexagonal H_6 is one such system. Although the eigenvectors are the same, the eigenvalues obviously have to be different.

Exercise: Verify that the SCF energy levels of H_6 are -20.2455 , -11.2115 , -11.2115 , 2.4410 , 2.4410 , and 4.8928 eV.

Once an SCF is achieved we need to calculate the heat of formation.

14.7 Calculation of heat of formation

The heat of formation is defined as

$$\Delta H_f = E_{\text{elect}} + E_{\text{nuc}} + E_{\text{isol}} + E_{\text{atom}}$$

where E_{elect} is the electronic energy, E_{nuc} is the nuclear-nuclear repulsion energy, E_{isol} is the energy required to strip all the valence electrons off all the atoms in the system, and E_{atom} is the total heat of atomization of all the atoms in the system.

E_e is calculated from $\frac{1}{2}\mathbf{P}(\mathbf{H} + \mathbf{F})$, or

$$E_e = \frac{1}{2} \sum_{\lambda=1}^6 \sum_{\sigma=1}^6 P_{\lambda\sigma} (H_{\lambda\sigma} + F_{\lambda\sigma})$$

Using the data we have already derived, we can calculate E_{elect} as

$$\begin{aligned} E_{\text{elect}} = & 3(+1.0000)(-51.7112 + -5.4823) \\ & + 6(+0.6667)(-3.2457 + -6.4651) \\ & + 3(-0.3333)(-0.6992 + -0.3611) \end{aligned}$$

or

$$E_{\text{elect}} = -210.0858 \text{ eV}$$

E_{nuc} is a relatively straightforward calculation, and is equal to 130.2864 eV. The total energy of the system is thus -79.7990 eV.

We are now ready to calculate the ΔH_f . As the total energy and E_{isol} are in eV, we must first convert them into kcal/mol.

$$\Delta H_f = 23.061(-79.7990 + 71.4377) + 6(52.1020) \text{ kcal/mol}$$

or

$$\Delta H_f = 119.792 \text{ kcal/mol}$$

It is convenient to combine E_{isol} and E_{atom} together so as to simplify this calculation. In order to convert any total energy ($E_{\text{elect}} + E_{\text{nuc}}$) into a ΔH_f , the following operation must be performed:

$$\Delta h_f = 23.061 \left(E_{\text{elect}} + E_{\text{nuc}} - \sum_i E_{\text{isol} + \text{atom}} \right)$$

in which the index 'i' is over all atoms in the system.

Users of MOPAC may wish to verify this calculation for a system of their own choice. To facilitate this, the following table may prove useful.

Element	Values of $E_{\text{isol} + \text{atom}}$			
	$E_{\text{isol} + \text{atom}}$ (eV/atom)			
	MINDO/3	MNDO	AM1	PM3
Hydrogen	− 14.764312	− 14.165588	− 13.655739	− 15.332633
Lithium		− 6.793583		
Beryllium		− 27.541992		
Boron	− 67.584394	− 70.200344	− 69.601659	
Carbon	− 126.880346	− 127.910952	− 128.226140	− 118.640263
Nitrogen	− 192.410048	− 207.466249	− 207.307791	− 162.513823
Oxygen	− 309.652672	− 320.451178	− 318.682192	− 291.924879
Fluorine	− 475.817831	− 477.502913	− 483.109715	− 438.336301
Aluminum		− 47.931017		− 50.311708
Silicon	− 95.576505	− 87.539565	− 83.701885	− 72.488357
Phosphorus	− 154.270388	− 156.236921	− 124.436836	− 121.236135
Sulfur	− 231.996798	− 228.891710		− 186.333060
Chlorine	− 347.185366	− 354.374768	− 373.455532	− 316.452049
Chromium		− 138.938301		
Zinc		− 31.231065		
Germanium		− 80.129955		
Bromine		− 347.840783	− 353.473742	− 353.699430
Tin		− 95.454929		
Iodine		− 341.704860	− 347.970786	− 289.422586
Mercury		− 29.456154		
Lead		− 107.856099		

These numbers may be used in conjunction with the semiempirical electronic and nuclear energies to calculate the heat of formation.

15. ACCURACY OF SEMIEMPIRICAL CALCULATIONS

The following tables illustrate the relative accuracy of three semiempirical methods: MNDO, AM1, and MNDO-PM3. MNDO-PM3 is a recent [13] re-parameterization of the MNDO method, in which the AM1 form of the core-core interaction is used. In cases where two sets of MNDO parameters have been published, the more recent set will be used. Only 11 of the 12 elements surveyed here have been parameterized at the AM1 level: these are H [4], C [4], N [4], O [4], F [37], Si [38], P [39], S [40], Cl [37], Br [37], and I [37]. In addition, boron has been parameterized at the AM1 level [41].

As MNDO-PM3 is very new, a word or two about it is in order. In parameterizing MNDO and AM1, only a very few molecules could be used. This was a natural constraint imposed by the software and equipment available at the time these methods were being developed. MNDO-PM3 was parameterized using a radically different optimization procedure, and used about 400–500 experimental reference data in order to define the values of the parameters.

Average ΔH_f errors are given in Table 2 and geometry errors are summarized in Table 9. Reference geometry data are taken from many sources, mainly from X-ray and microwave structures.

No differentiation is made between these various sources, although microwave structures are preferred to X-ray. Further, no differentiation is made between various definitions of bond lengths. Thus the bond length corresponding to the bottom of the harmonic well, r_0 , is not distinguished from the equilibrium bond length, or from the bond length corresponding to the system in which the zero point energy is included. For semiempirical methods, the average error in bond lengths is large relative to the differences between the bond lengths obtained using the various definitions.

Average dipole errors are 0.45D (MNDO), 0.35 (AM1), and 0.38 (PM3), while average ionization errors are 0.78 (MNDO), 0.61 (AM1), and 0.57 (PM3).

Users of MNDO-PM3 are cautioned that, at the time of going to press, little information is available as to the accuracy of PM3 in predicting activation barriers, higher ionization potentials, or vibrational frequencies. In consequence, results of such calculations should be treated with caution, until a suitable survey can be done.

15.1 Limitations of MNDO

MNDO is the oldest of the three methods surveyed here, and as a direct result, is the least accurate. MNDO has many advantages over earlier semiempirical methods, but as MNDO is such a large improvement over those methods, enumeration of MNDO's good points would be invidious to the other methods. Instead, only the limitations likely to be encountered by users will be mentioned. The principal drawbacks to MNDO are:

- 1 Sterically crowded molecules are too unstable
Example: neopentane
- 2 Four-membered rings are too stable
Example: cubane
- 3 The hydrogen bond is virtually non-existent
Example: water dimer
- 4 Hypervalent compounds are too unstable
Example: sulfuric acid
- 5 Activation barriers are generally too high
- 6 Non-classical structures are predicted to be unstable relative to the classical structure
Example: ethyl radical
- 7 Oxygenated substituents on aromatic rings are out-of-plane
Example: nitrobenzene
- 8 The peroxide bond is systematically too short by about 0.17 Å
- 9 The C-O-C angle in ethers is too large by about 9°.

15.2 Accuracy of AM1

AM1 is a distinct improvement over MNDO, in that the overall accuracy is considerably improved. Specific improvements are:

- 1 The strength of the hydrogen bond in the water dimer is 5.5 kcal/mol, in accordance with experiment.
- 2 Activation barriers for reaction are markedly better than those of MNDO.
- 3 Hypervalent phosphorus compounds are considerably improved relative to MNDO.

- 4 In general, errors in ΔH_f obtained using AM1 are about 40% less than those given by MNDO.

Unfortunately, with this improvement a few deficiencies were introduced. The most important of these are:

- 1 AM1 phosphorus has a spurious and very sharp potential barrier at 3.0 Å. The effect of this is to distort otherwise symmetric geometries and to introduce spurious activation barriers. A vivid example is given by P_4O_6 , in which the notionally equal P-P bonds are predicted by AM1 to differ by 0.4 Å. This is by far the most severe limitation of AM1.
- 2 Alkyl groups have a systematic error due to the heat of formation of the CH_2 fragment being too negative by about 2 kcal/mol.
- 3 Nitro compounds, although considerably improved relative to MNDO, are still systematically too positive in energy.
- 4 The peroxide bond is still systematically too short by about 0.17 Å.

15.3 Accuracy of PM3

The author believes that PM3 is a distinct improvement over AM1. Evidence of this is:

- 1 Hypervalent compounds are predicted with considerably improved accuracy.
- 2 Overall errors in ΔH_f are reduced by about 40% relative to AM1.

Although PM3 is more accurate in predicting the ΔH_f of many systems than either AM1 or MNDO, it does have some limitations. The more important of these are:

- 1 There is currently a paucity of information regarding the limitations of PM3! This should be corrected naturally as results of PM3 calculations are reported.
- 2 The barrier to rotation in formamide is practically non-existent. In part, this can be corrected by the use of the MMOK option (described in the MOPAC Manual).

Users of PM3 should be aware that PM3 has other defects. The only reason they are not enumerated here is that PM3 is a very recently developed method. As a result, these defects have not yet been identified.

The tables given here have been carefully checked for accuracy. In many instances the calculated results differ from those of earlier publications. In most cases, the difference has been investigated and found to be due to errors in the earlier work. This does not, of course, mean that the tables are fully accurate, only that care has been taken to minimize error.

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TABLE 1
COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF FORMATION FOR ORGANIC MOLECULES

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
CH ₄	Methane	-17.9	-13.0	4.9	5.9	9.1	a
C ₂ H ₂	Acetylene	54.2	50.7	-3.5	3.7	0.6	b
C ₂ H ₄	Ethylene	12.4	16.6	4.2	2.9	4.0	a
C ₂ H ₆	Ethane	-20.2	-18.1	2.1	0.5	2.8	a
C ₃ H ₄	Allene	45.6	47.1	1.5	-1.7	0.5	a
C ₃ H ₄	Cyclopropene	66.2	68.2	2.0	2.1	8.6	c
C ₃ H ₄	Propyne	44.4	40.2	-4.2	-3.0	-1.0	a
C ₃ H ₆	Cyclopropane	12.7	16.3	3.5	-1.5	5.0	a
C ₃ H ₆	Propene	4.9	6.4	1.5	0.1	1.7	a
C ₃ H ₈	Propane	-24.8	-23.6	1.2	-0.1	0.5	a
C ₄ H ₂	Diacetylene	113.0	102.5	-10.5	-9.8	-6.9	d
C ₄ H ₄	Vinylacetylene	72.8	66.4	-6.4	-7.2	-4.9	d
C ₄ H ₆	1-Methylcycloprop-1-ene	58.2	57.4	-0.8	-4.5	6.5	a
C ₄ H ₆	Bicyclobutane	51.9	69.2	17.3	12.2	26.2	a
C ₄ H ₆	1,2-Butadiene	38.8	38.0	-0.8	-5.3	-1.7	a
C ₄ H ₆	1-Butyne	39.5	35.7	-3.8	-3.3	-2.0	a
C ₄ H ₆	2-Butyne	34.7	29.8	-4.9	-9.8	-2.7	a
C ₄ H ₆	Cyclobutene	37.5	37.7	0.2	-6.5	8.3	c
C ₄ H ₆	Methylenecyclopropane	47.9	44.5	-3.4	-10.0	-0.2	a
C ₄ H ₆	1,3-Butadiene	26.0	31.0	5.0	3.0	3.9	a
C ₄ H ₈	1-Butene	-0.2	1.8	2.0	0.6	0.6	a
C ₄ H ₈	cis-2-Butene	-1.9	-2.5	-0.6	-2.4	-0.3	a
C ₄ H ₈	Cyclobutane	6.8	-3.8	-10.6	-18.7	-7.8	a
C ₄ H ₈	Isobutene	-4.3	-3.3	1.0	2.3	3.1	a
C ₄ H ₈	trans-2-Butene	-3.0	-3.8	-0.8	-2.1	-0.3	a
C ₄ H ₁₀	n-Butane	-30.4	-29.1	1.3	0.7	-0.8	a
C ₄ H ₁₀	Isobutane	-32.4	-29.5	2.9	5.6	3.0	a
C ₅ H ₆	Cyclopentadiene	32.1	31.8	-0.3	0.0	5.0	c
C ₅ H ₈	1,2-Dimethylcyclopropene	46.4	46.7	0.3	-7.2	8.2	e
C ₅ H ₈	Methylene cyclobutane	29.1	19.7	-9.4	-18.2	-4.0	f
C ₅ H ₈	1,cis-3-Pentadiene	19.1	21.1	2.0	0.6	1.8	a
C ₅ H ₈	Cyclopentene	8.3	3.0	-5.3	-8.6	-5.3	c
C ₅ H ₈	Bicyclo(2.1.0)-pentane	37.3	37.8	0.5	-7.1	8.8	e
C ₅ H ₈	1,4-Pentadiene	25.3	26.6	1.3	-0.7	-0.5	a
C ₅ H ₈	Spiropentane	44.3	43.1	-1.2	-10.6	6.2	a
C ₅ H ₈	1,trans-3-Pentadiene	18.1	21.3	3.2	1.0	2.5	a
C ₅ H ₁₀	1-Pentene	-5.3	-4.0	1.3	0.3	-1.4	a
C ₅ H ₁₀	2-Methyl-1-butene	-8.6	-7.9	0.7	2.1	1.8	a
C ₅ H ₁₀	2-Methyl-2-butene	-10.1	-12.2	-2.1	-0.4	0.1	a
C ₅ H ₁₀	3-Methyl-1-butene	-6.6	-3.9	2.7	4.3	2.2	a
C ₅ H ₁₀	cis-2-Pentene	-7.0	-7.7	-0.7	-2.3	-1.9	a
C ₅ H ₁₀	cis-Dimethylcyclopropane	1.3	1.4	0.1	-3.4	3.5	e
C ₅ H ₁₀	Cyclopentane	-18.3	-23.9	-5.6	-12.2	-10.5	c
C ₅ H ₁₀	trans-2-Pentene	-7.9	-8.7	-0.8	-2.4	-1.8	a

TABLE 1 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₅ H ₁₂	2-Methylbutane	-36.8	-34.4	2.4	6.8	1.4	a
C ₅ H ₁₂	Neopentane	-40.3	-35.8	4.5	15.7	7.5	a
C ₅ H ₁₂	<i>n</i> -Pentane	-35.1	-34.5	0.6	0.7	-2.9	a
C ₆ H ₆	Benzene	19.8	23.5	3.6	1.5	2.2	a
C ₆ H ₆	Fulvene	47.5	56.2	8.7	6.2	15.2	a
C ₆ H ₈	1,3-Cyclohexadiene	25.4	20.4	-5.0	-10.9	-7.9	a
C ₆ H ₁₀	2,3-Dimethyl-1,3-butadiene	10.8	14.0	3.2	4.3	6.6	a
C ₆ H ₁₀	Cyclohexene	-1.1	-4.9	-3.8	-8.8	-9.0	a
C ₆ H ₁₀	1,5-Hexadiene	20.1	21.1	1.0	-0.5	-2.3	a
C ₆ H ₁₀	1,2-Dimethylcyclobutene	19.8	16.2	-3.6	-13.4	7.2	c
C ₆ H ₁₀	Bicyclopropyl	30.9	36.1	5.2	-2.2	8.6	a
C ₆ H ₁₂	Cyclohexane	-29.5	-31.0	-1.5	-5.3	-9.0	c
C ₆ H ₁₄	<i>n</i> -Hexane	-39.9	-39.9	0.0	0.8	-4.9	a
C ₇ H ₈	Cycloheptatriene	43.2	42.5	-0.7	-9.4	-4.9	c
C ₇ H ₈	Norbornadiene	59.7	58.8	-0.9	3.2	8.0	e
C ₇ H ₈	Toluene	12.0	14.1	2.1	1.6	2.4	a
C ₇ H ₁₂	Norbornane	-12.4	-13.7	-1.3	2.0	-2.0	g
C ₇ H ₁₆	<i>n</i> -Heptane	-44.9	-45.3	-0.5	1.0	-6.8	a
C ₈ H ₈	Cubane	148.7	113.8	-34.9	-49.6	2.5	a
C ₈ H ₈	Styrene	35.3	39.2	3.9	2.3	3.4	a
C ₈ H ₁₀	Ethylbenzene	7.2	9.5	2.3	1.6	1.5	a
C ₈ H ₁₄	Bicyclo(2.2.2)-octane	-24.1	-27.8	-3.7	-2.2	-11.9	g
C ₈ H ₁₈	<i>n</i> -Octane	-49.9	-50.8	-0.8	1.4	-8.6	a
C ₉ H ₂₀	<i>n</i> -Nonane	-54.7	-56.2	-1.5	1.5	-10.7	a
C ₁₀ H ₈	Azulene	73.5	81.3	7.8	-1.4	10.9	a
C ₁₀ H ₈	Naphthalene	36.1	40.7	4.6	2.2	4.5	a
C ₁₀ H ₁₆	Adamantane	-31.9	-34.6	-2.7	5.5	-11.3	h
C ₁₄ H ₁₀	Anthracene	55.2	61.7	6.5	3.6	7.7	a
C ₁₄ H ₁₀	Phenanthrene	49.5	55.0	5.5	6.2	7.9	a
CO	Carbon monoxide	-26.4	-19.7	6.7	20.5	20.7	b
CH ₂ O	Formaldehyde	-26.0	-34.1	-8.1	-6.9	-5.5	a
CH ₄ O	Methanol	-48.1	-51.9	-3.8	-9.3	-8.9	a
C ₂ H ₂ O	Ketene	-11.4	-9.2	2.2	4.6	5.7	a
C ₂ H ₄ O	Acetaldehyde	-39.7	-44.2	-4.5	-2.5	-1.8	a
C ₂ H ₄ O	Ethylene oxide	-12.6	-8.1	4.5	-2.9	3.6	a
C ₂ H ₆ O	Ethanol	-56.2	-56.8	-0.6	-6.8	-6.5	a
C ₂ H ₆ O	Dimethyl ether	-44.0	-48.3	-4.3	-7.2	-9.2	a
C ₃ H ₆ O	Acetone	-51.9	-53.3	-1.4	2.5	2.7	a
C ₃ H ₆ O	Propanal	-45.5	-49.3	-3.8	-2.5	-2.8	a
C ₃ H ₆ O	Trimethylene oxide	-19.3	-26.7	-7.5	-17.9	-6.3	a
C ₃ H ₈ O	Isopropanol	-65.1	-64.0	1.1	-0.3	-2.9	a
C ₃ H ₈ O	Propanol	-61.2	-63.6	-2.4	-6.3	-9.4	a
C ₄ H ₄ O	Furan	-8.3	-4.0	4.3	-0.3	11.3	a
C ₄ H ₆ O	2-Butenal	-24.0	-27.1	-3.1	-3.4	-1.6	a
C ₄ H ₆ O	Divinyl ether	-3.3	-0.7	2.5	0.5	4.1	a
C ₄ H ₈ O	2-Butanone	-57.0	-57.4	-0.4	2.9	1.9	i

TABLE I (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₄ H ₈ O	Butanal	-48.9	-54.7	-5.8	-3.9	-6.2	a
C ₄ H ₈ O	Tetrahydrofuran	-44.0	-51.3	-7.3	-15.3	-14.4	a
C ₄ H ₁₀ O	Diethyl ether	-60.3	-59.6	0.7	0.1	-4.7	a
C ₄ H ₁₀ O	<i>t</i> -Butanol	-74.7	-71.3	3.4	10.4	3.1	a
C ₅ H ₈ O	Cyclopentanone	-46.0	-37.2	8.8	9.6	9.9	a
C ₅ H ₁₀ O	Tetrahydropyran	-53.4	-57.4	-4.0	-8.6	-13.7	a
C ₅ H ₁₂ O	3-Pentanol	-75.2	-73.8	1.4	1.7	-5.5	a
C ₆ H ₆ O	Phenol	-23.0	-21.7	1.4	-3.6	0.8	a
C ₆ H ₁₀ O	Cyclohexanone	-54.0	-60.2	-6.1	-6.1	-9.3	a
C ₇ H ₆ O	Benzaldehyde	-8.8	-10.6	-1.8	-0.8	-0.1	a
C ₇ H ₈ O	Anisole	-17.3	-14.6	2.7	-0.4	1.4	a
C ₁₀ H ₈ O	1-Naphthol	-5.1	-4.1	1.0	-1.7	2.9	a
C ₁₀ H ₈ O	2-Naphthol	-10.1	-4.6	5.5	0.4	6.3	a
CO ₂	Carbon dioxide	-94.1	-85.0	9.0	19.0	14.2	b
CH ₂ O ₂	Formic acid	-90.5	-94.4	-3.9	-2.1	-6.9	j
C ₂ H ₂ O ₂	<i>trans</i> -Glyoxal	-50.7	-64.3	-13.6	-10.7	-8.0	a
C ₂ H ₄ O ₂	Acetic acid	-103.3	-102.0	1.3	2.2	0.3	a
C ₂ H ₄ O ₂	Methyl formate	-83.6	-87.0	-3.4	-1.9	-7.5	d
C ₂ H ₆ O ₂	Dimethyl peroxide	-30.1	-34.1	-4.0	1.8	3.1	a
C ₂ H ₆ O ₂	Ethylene glycol	-93.9	-95.2	-1.3	-12.2	-13.6	a
C ₃ O ₂	Carbon suboxide	-22.4	-24.0	-1.6	-1.1	7.8	a
C ₃ H ₄ O ₂	β -Propiolactone	-67.6	-70.6	-3.0	-3.3	-3.4	a
C ₃ H ₆ O ₂	Propionic acid	-108.4	-106.4	2.0	2.1	-0.7	a
C ₃ H ₆ O ₂	Methyl acetate	-97.9	-94.1	3.8	4.3	1.5	d
C ₃ H ₈ O ₂	Dimethoxymethane	-83.3	-87.4	-4.1	-11.1	-20.0	a
C ₄ H ₆ O ₂	Diacetyl	-78.2	-83.4	-5.2	-0.6	3.3	a
C ₄ H ₁₀ O ₂	Diethyl peroxide	-46.1	-40.0	6.1	7.0	7.7	a
C ₅ H ₈ O ₂	Acetylacetone	-90.5	-91.6	-1.1	6.3	4.8	a
C ₆ H ₄ O ₂	<i>p</i> -Benzoquinone	-29.3	-31.5	-2.3	-3.5	4.2	a
C ₇ H ₆ O ₂	Benzoic acid	-70.1	-66.2	3.9	2.4	2.1	a
C ₇ H ₆ O ₂	<i>o</i> -Salicylic acid	-70.1	-66.2	3.9	2.4	2.1	a
C ₄ H ₂ O ₃	Maleic anhydride	-95.2	-90.1	5.1	6.7	18.8	a
C ₄ H ₆ O ₃	Acetic anhydride	-137.1	-135.0	2.1	4.5	5.4	a
C ₂ H ₂ O ₄	Oxalic acid	-175.0	-174.0	1.0	-0.1	2.6	a
CHN	Hydrogen cyanide	32.3	33.0	0.7	3.0	-1.3	b
CH ₅ N	Methylamine	-5.5	-5.2	0.3	-2.1	-1.9	a
C ₂ H ₃ N	Acetonitrile	20.9	23.3	2.4	-1.7	-1.6	k
C ₂ H ₃ N	Methyl isocyanide	35.6	54.7	19.1	24.8	14.8	k
C ₂ H ₅ N	Ethyleneimine (Azirane)	30.2	31.6	1.4	-5.1	2.9	a
C ₂ H ₇ N	Ethylamine	-11.4	-12.5	-1.1	-1.8	-3.8	a
C ₂ H ₇ N	Dimethylamine	-6.6	-7.9	-1.3	0.0	1.0	a
C ₃ H ₃ N	Acrylonitrile	44.1	50.2	6.1	-0.3	0.9	a
C ₃ H ₅ N	Ethyl cyanide	12.1	18.5	6.4	1.7	0.9	d
C ₃ H ₉ N	Isopropylamine	-20.0	-18.8	1.3	3.7	0.7	a
C ₃ H ₉ N	Trimethylamine	-6.6	-10.9	-4.3	3.8	4.9	a
C ₃ H ₉ N	<i>n</i> -Propylamine	-16.8	-17.9	-1.1	-1.4	-5.3	a

TABLE 1 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₄ H ₅ N	Pyrrole	25.9	27.1	1.2	6.6	14.0	a
C ₄ H ₉ N	Pyrrolidine	-0.8	-12.0	-11.2	-15.0	-9.6	a
C ₄ H ₁₁ N	<i>t</i> -Butylamine	-28.9	-25.2	3.7	13.4	7.7	a
C ₅ H ₅ N	Pyridine	34.6	30.4	-4.2	-5.8	-2.6	a
C ₇ H ₅ N	Phenyl cyanide	51.5	58.5	7.0	0.5	1.9	a
CNO	NCO	38.1	32.4	-5.7	-1.0	0.8	b
CHNO	Hydrogen isocyanate	-24.3	-15.3	9.0	13.5	9.1	b
CH ₃ NO	Formamide	-44.5	-41.8	2.7	4.3	-0.3	l
C ₃ H ₇ NO	Dimethylformamide	-45.8	-44.6	1.2	8.4	8.9	a
CH ₃ NO ₂	Nitromethane	-17.9	-15.9	2.0	21.2	8.0	a
CH ₃ NO ₂	Methyl nitrite	-15.8	-9.1	6.7	-20.9	-16.0	a
C ₂ H ₅ NO ₂	Nitroethane	-23.5	-20.9	2.6	20.2	6.6	a
C ₂ H ₅ NO ₂	Glycine	-93.7	-96.0	-2.3	-2.0	-7.8	a
C ₃ H ₇ NO ₂	1-Nitropropane	-30.0	-26.8	3.2	21.9	6.2	a
C ₃ H ₇ NO ₂	2-Nitropropane	-33.2	-27.1	6.1	26.9	11.6	a
C ₃ H ₇ NO ₂	Alanine	-111.4	-101.1	10.3	12.7	6.4	a
C ₄ H ₉ NO ₂	1-Nitrobutane	-34.4	-32.1	2.3	21.6	4.0	a
C ₄ H ₉ NO ₂	2-Nitrobutane	-39.1	-31.9	7.2	29.0	10.9	a
C ₆ H ₅ NO ₂	Nitrobenzene	15.4	14.5	-0.9	20.4	9.9	d
C ₇ H ₇ NO ₂	2-Nitrotoluene	9.3	4.7	-4.6	20.6	7.9	a
C ₇ H ₇ NO ₂	3-Nitrotoluene	4.1	5.1	1.0	24.1	13.5	m
C ₇ H ₇ NO ₂	4-Nitrotoluene	7.4	4.7	-2.7	22.4	9.9	m
CH ₃ NO ₃	Methyl nitrate	-29.1	-32.4	-3.3	16.7	-2.2	a
C ₂ H ₅ NO ₃	Ethyl nitrate	-36.8	-36.4	0.5	18.9	-0.4	a
C ₂ H ₅ NO ₃	Nitroethanol	-75.1	-61.4	13.7	29.0	10.5	n
CH ₂ N ₂	Diazomethane	71.0	61.0	-10.0	-3.7	-8.4	a
CH ₂ N ₂	N = N-CH ₂ -	79.0	91.7	12.7	-6.6	7.8	o
CH ₆ N ₂	Methylhydrazine	22.6	17.9	-4.7	-8.2	-5.3	a
C ₂ N ₂	Cyanogen	73.8	77.5	3.7	-7.2	-5.9	a
C ₂ H ₈ N ₂	1,1-Dimethylhydrazine	20.0	15.1	-4.9	-1.9	4.0	a
C ₂ H ₈ N ₂	1,2-Dimethylhydrazine	22.0	15.6	-6.4	-7.0	-0.5	a
C ₄ N ₂	Dicyanoacetylene	126.5	128.1	1.6	-15.1	-6.7	a
C ₄ H ₂ N ₂	Fumaronitrile	81.3	86.0	4.7	-6.6	-5.3	a
C ₄ H ₄ N ₂	Pyridazine	66.5	56.0	-10.5	-22.9	-11.2	a
C ₄ H ₄ N ₂	Pyrimidine	47.0	38.0	-9.0	-12.0	-3.1	a
C ₄ H ₄ N ₂	Pyrazine	46.9	39.3	-7.6	-9.1	-2.7	a
C ₆ H ₁₄ N ₂	azo- <i>n</i> -Propane	8.6	5.8	-2.8	-6.0	4.3	p
C ₂ H ₆ N ₂ O ₂	<i>N</i> -Nitrodimethylamine	-3.2	1.3	4.5	25.5	24.9	d
C ₆ H ₆ N ₂ O ₂	<i>p</i> -Nitroaniline	16.2	10.7	-5.5	19.4	5.3	a
CH ₂ N ₂ O ₄	Dinitromethane	-13.3	-11.9	1.4	41.2	16.2	n
C ₂ H ₄ N ₂ O ₄	1,1-Dinitroethane	-24.1	-17.4	6.7	47.3	21.5	n
C ₂ H ₄ N ₂ O ₄	1,2-Dinitroethane	-22.9	-19.6	3.3	42.9	12.9	n
C ₃ H ₆ N ₂ O ₄	1,1-Dinitropropane	-25.9	-22.0	3.9	45.3	16.7	a
C ₃ H ₆ N ₂ O ₄	1,3-Dinitropropane	-31.6	-26.6	5.0	44.5	12.8	n
C ₃ H ₆ N ₂ O ₄	2,2-Dinitropropane	-27.0	-23.0	4.0	50.2	21.5	n
C ₄ H ₈ N ₂ O ₄	1,1-Dinitrobutane	-34.1	-27.2	6.9	48.9	18.1	n

TABLE 1 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AMI	
C ₄ H ₈ N ₂ O ₄	1,4-Dinitrobutane	-38.9	-32.7	6.2	45.8	11.2	n
C ₆ H ₄ N ₂ O ₄	<i>m</i> -Dinitrobenzene	11.3	9.2	-2.1	43.9	21.8	a
C ₆ H ₄ N ₂ O ₄	<i>o</i> -Dinitrobenzene	20.2	9.2	-11.0	36.4	12.9	m
C ₆ H ₄ N ₂ O ₄	<i>p</i> -Dinitrobenzene	13.3	10.1	-3.2	41.5	20.0	m
C ₇ H ₆ N ₂ O ₄	2,4-Nitrotoluene	4.7	2.0	-2.7	44.2	21.5	m
C ₇ H ₆ N ₂ O ₄	2,6-Nitrotoluene	9.6	6.4	-3.2	42.3	20.5	m
CHN ₃ O ₆	Trinitromethane	-3.2	-4.7	-1.5	61.9	28.2	q
C ₂ H ₃ N ₃ O ₆	1,1,1-Trinitroethane	-12.4	-10.0	2.4	68.8	33.5	n
C ₃ H ₅ N ₃ O ₆	1,1,1-Trinitropropane	-18.4	-8.1	10.3	76.0	36.9	n
C ₆ H ₄ N ₃ O ₆	1,3,5-Trinitrobenzene	14.9	8.0	-6.9	37.3	3.5	m
C ₇ H ₅ N ₃ O ₆	2,4,6-Trinitrotoluene	12.9	3.3	-9.6	61.8	28.4	a
C ₃ H ₅ N ₃ O ₉	Glycerol trinitrate	-64.7	-76.6	-11.9	56.3	-6.5	a
CH ₂ N ₄	1-H Tetrazole	79.9	86.3	6.3	-26.1	29.7	a
CN ₄ O ₈	Tetranitromethane	18.5	6.4	-12.1	76.5	34.6	n
C ₅ H ₈ N ₄ O ₁₂	Pentaerythritol tetranitrate	-92.5	-98.2	-5.7	102.9	-2.8	a
CS	Carbon sulfide	67.0	97.3	30.3	37.5		b
CH ₄ S	Thiomethanol	-5.4	-5.5	-0.1	-1.9		a
C ₂ H ₄ S	Thiirane	19.7	28.8	9.1	-0.9		a
C ₂ H ₆ S	Thioethanol	-11.0	-8.7	2.3	-2.4		a
C ₂ H ₆ S	Dimethyl thioether	-8.9	-11.0	-2.1	-8.1		a
C ₃ H ₆ S	Thietane	14.6	7.5	-7.1	-19.7		a
C ₃ H ₈ S	Isopropanthiol	-18.1	-13.3	4.8	1.9		b
C ₃ H ₈ S	1-Propanthiol	-16.2	-14.1	2.1	-1.9		a
C ₄ H ₄ S	Thiophene	27.6	30.7	3.1	-1.1		a
C ₄ H ₈ S	Tetrahydrothiophene	-8.1	-10.4	-2.3	-16.0		a
C ₄ H ₁₀ S	Butanethiol	-21.1	-19.5	1.6	-1.8		b
C ₆ H ₆ S	Thiophenol	26.9	27.7	0.8	-3.5		a
C ₆ H ₁₂ S	Cyclohexanethiol	-23.0	-20.6	2.4	-2.7		c
CSO	Carbon oxysulfide	-33.8	-23.8	10.1	11.0		a
C ₂ H ₄ SO	Thiolacetic acid	-43.5	-38.9	4.6	2.1		o
CHNS	Hydrogen isothiocyanate	30.0	39.5	9.5	13.4		b
C ₂ H ₃ NS	Methyl isothiocyanate	27.1	36.1	9.0	9.8		k
C ₂ H ₃ NS	Methyl thiocyanate	38.3	28.3	-10.0	-15.2		k
CS ₂	Carbon disulfide	28.0	36.9	8.9	8.9		b
C ₂ H ₆ S ₂	Ethanedithiol-1,2	-2.2	1.2	3.4	-4.1		b
C ₂ H ₆ S ₂	2,3-Dithiabutane	-5.6	-4.8	0.8	-9.2		a
C ₂ N ₂ S ₂	S2(CN)2	82.3	78.5	-3.8	-11.7		a
C ₂ H ₆ S ₃	2,3,4-Trithiapentane	0.0	-6.9	-6.9	-13.2		r
C ₃ H ₄ S ₃	1,3-Dithiolan-2-thione	22.7	40.4	17.7	-11.3		b
CH ₃ F	Fluoromethane	-56.8	-53.8	3.0	-4.1	-4.2	s
C ₂ HF	Fluoroacetylene	30.0	18.1	-11.9	-14.3	-14.8	b
C ₂ H ₃ F	Fluoroethylene	-32.5	-28.6	3.9	-2.0	-1.5	t
C ₂ H ₅ F	Fluoroethane	-62.9	-60.2	2.7	-2.2	-3.4	a
C ₃ H ₇ F	2-Fluoropropane	-69.4	-66.8	2.6	2.8	-0.4	a
C ₆ H ₅ F	Fluorobenzene	-27.8	-20.2	7.5	2.5	4.4	a
C ₂ H ₃ OF	Acetyl fluoride	-106.4	-98.7	7.7	9.9	7.6	a

TABLE 1 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AMI	
C ₇ H ₅ O ₂ F	<i>p</i> -Fluorobenzoic acid	−118.4	−108.9	9.5	5.3	6.4	a
CNF	Cyanogen fluoride	8.6	6.5	−2.1	−10.9	−13.0	b
CH ₂ F ₂	Difluoromethane	−108.1	−103.8	4.4	−3.6	−8.0	a
C ₂ F ₂	Difluoroacetylene	5.0	−11.6	−16.6	−26.0	−24.6	b
C ₂ H ₂ F ₂	<i>gem</i> -Difluoroethylene	−80.5	−73.0	7.5	−3.1	−2.2	a
C ₂ H ₄ F ₂	1,1-Difluoroethane	−118.8	−111.9	6.9	5.4	0.2	a
C ₆ H ₄ F ₂	<i>o</i> -Difluorobenzene	−70.3	−63.1	7.2	−0.3	3.9	a
C ₆ H ₄ F ₂	<i>m</i> -Difluorobenzene	−74.0	−63.3	10.7	3.1	6.1	a
C ₆ H ₄ F ₂	<i>p</i> -Difluorobenzene	−73.3	−63.3	10.0	2.3	5.3	a
COF ₂	Carbonyl fluoride	−152.7	−141.6	11.1	14.1	6.4	a
CHF ₃	Trifluoromethane	−166.3	−162.0	4.3	2.5	−6.2	a
C ₂ HF ₃	Trifluoroethylene	−117.3	−121.5	−4.2	−13.8	−13.3	a
C ₂ H ₃ F ₃	1,1,1-Trifluoroethane	−178.0	−172.3	5.7	13.6	5.4	a
C ₇ H ₅ F ₃	Trifluoromethylbenzene	−143.2	−134.9	8.3	15.7	8.8	a
C ₂ HO ₂ F ₃	Trifluoroacetic acid	−255.0	−244.0	11.0	16.9	12.3	a
C ₂ NF ₃	Trifluoroacetonitrile	−118.4	−115.1	3.3	5.2	−1.1	b
CF ₄	Carbon tetrafluoride	−223.3	−225.1	−1.8	9.1	−2.4	a
C ₂ F ₄	Tetrafluoroethylene	−157.9	−168.2	−10.3	−17.0	−16.9	a
COF ₄	Trifluoromethyl hypofluorite	−182.8	−187.3	−4.5	19.5	5.1	b
C ₆ HF ₅	Pentafluorobenzene	−192.5	−188.6	3.9	−9.2	0.5	a
C ₂ F ₆	Hexafluoroethane	−321.2	−317.8	3.4	21.6	8.0	b
C ₆ F ₆	Hexafluorobenzene	−228.5	−229.3	−0.8	−14.9	−2.6	a
C ₃ OF ₆	Perfluoroacetone	−325.2	−340.0	−14.8	3.3	−6.4	u
C ₄ F ₈	Perfluorocyclobutane	−369.5	−379.2	−9.7	5.8	2.3	a
CH ₃ Cl	Methyl chloride	−20.0	−14.7	5.3	−2.5	1.0	b
C ₂ HCl	Chloroacetylene	51.1	46.6	−4.5	1.5	−3.3	b
C ₂ H ₃ Cl	Chloroethylene	8.6	9.7	1.1	−3.7	−2.7	b
C ₂ H ₅ Cl	Chloroethane	−26.8	−22.1	4.7	−2.0	0.6	v
C ₇ H ₅ OCl	Benzoyl chloride	−26.1	−18.4	7.7	2.7	10.4	a
CNCl	Cyanogen chloride	31.6	31.6	0.0	1.7	−7.0	b
CH ₂ FCl	Fluorochloromethane	−62.6	−57.5	5.0	−5.4	−2.7	b
COFCl	Carbonyl fluoride chloride	−102.0	−93.6	8.4	9.8	10.0	b
CHF ₂ Cl	Difluorochloromethane	−115.6	−109.7	5.9	1.2	1.4	a
CF ₃ Cl	Trifluorochloromethane	−169.2	−169.3	−0.1	9.6	6.6	b
CH ₂ Cl ₂	Dichloromethane	−23.0	−17.1	5.8	−5.1	−2.9	a
C ₂ H ₂ Cl ₂	<i>gem</i> -Dichloroethylene	0.6	4.0	3.4	−3.2	−3.9	b
C ₂ H ₂ Cl ₂	<i>cis</i> -Dichloroethylene	1.0	4.0	3.0	−3.6	−4.3	b
C ₂ H ₂ Cl ₂	<i>trans</i> -Dichloroethylene	1.2	3.6	2.4	−4.9	−4.6	b
C ₂ H ₄ Cl ₂	1,1-Dichloroethane	−30.9	−26.5	4.4	−1.6	−0.2	v
C ₂ H ₄ Cl ₂	1,2-Dichloroethane	−31.0	−24.7	6.3	−5.4	−2.8	v
C ₆ H ₄ Cl ₂	<i>o</i> -Dichlorobenzene	7.1	11.1	4.0	1.5	2.1	a
C ₆ H ₄ Cl ₂	<i>m</i> -Dichlorobenzene	6.1	10.2	4.1	0.5	2.1	a
C ₆ H ₄ Cl ₂	<i>p</i> -Dichlorobenzene	5.3	10.1	4.8	1.1	2.7	a
COCl ₂	Carbonyl chloride	−52.6	−49.1	3.5	0.0	5.3	b
CHFCl ₂	Fluorodichloromethane	−67.7	−62.0	5.7	−1.5	2.5	l
CF ₂ Cl ₂	Difluorodichloromethane	−117.5	−116.1	1.4	7.3	10.5	b

TABLE 1 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
CHCl ₃	Chloroform	-24.7	-20.9	3.8	-4.3	-4.3	l
C ₂ HCl ₃	Trichloroethylene	-2.0	-2.3	-0.3	-4.4	-6.4	b
C ₂ H ₃ Cl ₃	1,1,1-Trichloroethane	-35.5	-31.9	3.6	4.0	3.6	a
CFCl ₃	Fluorotrichloromethane	-69.0	-67.3	1.7	3.8	8.1	b
CCl ₄	Carbon tetrachloride	-22.9	-26.0	-3.1	-2.6	-5.2	b
C ₂ Cl ₄	Tetrachloroethylene	-2.7	-8.1	-5.4	-5.3	-9.7	a
C ₂ Cl ₆	Hexachloroethane	-34.5	-36.5	-2.0	7.1	-1.3	a
C ₆ Cl ₆	Hexachlorobenzene	-8.6	-9.1	-0.5	6.0	0.8	a
CH ₃ Br	Bromomethane	-9.1	-2.0	7.1	-1.3	2.9	a
C ₂ H ₃ Br	Bromoethylene	18.7	23.8	5.1	-2.9	-0.8	a
C ₂ H ₅ Br	Bromoethane	-15.2	-11.4	3.8	-1.8	2.1	a
C ₃ H ₅ Br	3-Bromopropene	10.9	15.3	4.4	-2.1	1.5	w
C ₃ H ₇ Br	1-Bromopropane	-20.5	-16.7	3.8	-1.5	0.6	a
C ₃ H ₇ Br	2-Bromopropane	-23.5	-20.9	2.6	2.8	5.6	x
C ₆ H ₅ Br	Bromobenzene	25.2	31.0	5.8	-1.3	1.5	a
C ₂ H ₃ OBr	Acetyl bromide	-45.6	-43.5	2.1	2.4	11.3	a
C ₇ H ₅ OBr	Benzoyl bromide	-11.6	-7.7	4.0	0.7	12.9	a
CNBr	Cyanogen bromide	43.3	53.7	10.4	-3.3	-10.8	a
CF ₃ Br	Bromotrifluoromethane	-155.1	-157.9	-2.8	8.5	10.5	b
CCl ₃ Br	Trichlorobromomethane	-9.3	-14.1	-4.8	-5.8	-5.4	a
CH ₂ Br ₂	Dibromomethane	-3.5	7.9	11.4	-1.6	2.5	y
COBr ₂	Carbonyl bromide	-20.1	-25.3	-5.2	-11.5	2.3	a
C ₂ F ₄ Br ₂	1,2-Dibromotetrafluoroethane	-189.0	-191.3	-2.3	18.6	27.8	x
CHBr ₃	Bromoform	4.4	17.5	13.1	-1.3	2.0	y
CBr ₄	Carbon tetrabromide	35.1	32.9	-2.2	-21.3	-19.2	z
CH ₃ I	Methyl iodide	3.4	9.4	6.0	-1.5	2.3	a
C ₂ H ₅ I	Iodoethane	-2.0	2.1	4.1	-2.5	0.9	a
C ₃ H ₅ I	Allyl iodide	22.8	30.2	7.4	-3.3	-0.4	a
C ₃ H ₅ I	E-1-Iodo-1-propene	22.3	25.4	3.2	-7.8	-2.6	c
C ₃ H ₅ I	Z-1-Iodo-1-propene	20.7	29.2	8.6	-5.4	-0.2	c
C ₃ H ₇ I	1-Iodopropane	-7.1	-3.0	4.2	-2.2	-0.7	a
C ₃ H ₇ I	2-Iodopropane	-9.8	-5.3	4.5	2.3	4.1	a
C ₄ H ₉ I	1-Butyl iodide	-12.0	-8.3	3.7	-2.0	-2.7	a
C ₄ H ₉ I	2-Iodo-2-methylpropane	-17.2	-12.5	4.7	10.7	8.9	c
C ₆ H ₅ I	Iodobenzene	39.4	44.7	5.3	-6.9	-1.3	c
C ₆ H ₁₁ I	Iodocyclohexane	-11.9	-11.7	0.2	-5.0	-8.1	c
C ₇ H ₇ I	<i>o</i> -Iodotoluene	31.7	38.8	7.1	-4.7	0.1	c
C ₇ H ₇ I	<i>m</i> -Iodotoluene	31.9	35.3	3.4	-7.1	-1.4	c
C ₇ H ₇ I	<i>p</i> -Iodotoluene	29.1	35.3	6.2	-4.4	1.3	a
C ₇ H ₇ I	Benzyl iodide	25.1	37.6	12.5	3.6	5.8	a
C ₂ H ₃ OI	Acetyl iodide	-30.2	-29.9	0.3	3.3	9.5	c
C ₃ H ₅ OI	1-Iodo-2-propanone	-31.2	-26.5	4.7	-1.6	0.2	c
C ₇ H ₅ OI	Benzoyl iodide	2.5	8.0	5.5	2.6	11.6	c
CNI	Cyanogen iodide	53.7	63.5	9.8	-14.1	-11.1	c
CF ₃ I	Trifluoroiodomethane	-140.5	-137.9	2.5	12.3	7.9	c
CH ₂ I ₂	Diiodomethane	27.0	33.5	6.5	-10.2	-5.5	aa

TABLE I (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₂ H ₂ I ₂	E-1,2-Diiodoethene	49.6	55.0	5.4	-14.3	-5.5	c
C ₂ H ₂ I ₂	Z-1,2-Diiodoethene	49.6	60.5	11.0	-14.5	-6.1	c
C ₂ H ₄ I ₂	1,2-Diiodoethane	16.0	23.3	7.4	-4.4	-0.2	c
C ₃ H ₆ I ₂	1,2-Diiodopropane	8.5	20.8	12.3	-1.2	1.2	a
C ₄ H ₈ I ₂	1,2-Diiodobutane	2.7	16.1	13.4	3.7	3.5	a
C ₆ H ₄ I ₂	<i>o</i> -Diiodobenzene	60.2	73.8	13.7	-15.4	-6.1	c
COI ₂	Carbonyl iodide	9.6	-1.5	-11.1	-15.1	-3.0	z
CHI ₃	Iodoform	50.4	60.6	10.2	-18.4	-12.6	y
CI ₄	Carbon tetraiodide	108.2	102.7	-5.5	-61.3	-54.0	z
C ₃ H ₉ Al	Trimethylaluminum	-20.9	-5.7	15.2	-19.2		a
CH ₅ Si	Methylsilyl	30.5	23.3	-7.2	-11.5	-21.5	bb
CH ₆ Si	Methylsilane	-7.8	-3.6	4.2	-5.8	-3.0	c
C ₂ H ₆ Si	Vinylsilane	-1.9	19.7	21.6	8.2	13.3	v
C ₂ H ₇ Si	Dimethylsilyl	14.3	3.9	-10.4	-13.6	-21.8	bb
C ₂ H ₈ Si	Ethylsilane	-15.0	-10.2	4.8	-6.7	-1.5	cc
C ₂ H ₈ Si	Dimethylsilane	-20.0	-20.8	-0.8	-9.2	-5.6	c
C ₃ H ₉ Si	Trimethylsilyl	-0.8	-14.9	-14.1	-16.9	-22.1	bb
C ₃ H ₁₀ Si	Trimethylsilane	-37.4	-37.3	0.1	-6.9	-1.9	c
C ₄ H ₁₂ Si	Diethylsilane	-43.6	-32.6	11.0	-0.5	7.3	dd
C ₄ H ₁₂ Si	Tetramethylsilane	-55.7	-53.7	2.0	-3.4	3.6	ee
C ₅ H ₁₂ Si	1,1-Dimethylsilacyclobutane	-33.7	-35.6	-1.9	-14.7	-3.5	c
C ₆ H ₁₆ Si	Triethylsilane	-39.5	-55.4	-15.9	-24.5	-15.2	dd
C ₈ H ₂₀ Si	Tetraethylsilane	-64.4	-77.9	-13.5	-17.8	-7.4	dd
C ₃ H ₁₀ SiO	Trimethylsilicon hydroxide	-119.4	-115.4	4.0	-2.5	8.9	a
C ₂ H ₇ SiCl	Chlorodimethylsilane	-69.9	-63.7	6.2	-3.1	-0.1	dd
C ₃ H ₉ SiCl	Chlorotrimethylsilane	-84.6	-81.6	3.0	-2.8	-0.2	a
CH ₄ SiCl ₂	Dichloromethylsilane	-96.0	-88.9	7.1	-1.4	-2.5	a
C ₂ H ₆ SiCl ₂	Dichlorodimethylsilane	-109.5	-108.1	1.4	-1.8	-5.8	c
CH ₃ SiCl ₃	Trichloromethylsilane	-131.2	-132.9	-1.7	0.6	-12.4	c
C ₃ H ₉ SiBr	Trimethylbromosilane	-70.0	-68.5	1.5	7.7	3.6	a
C ₆ H ₁₈ Si ₂	Hexamethyldisilane	-85.8	-83.2	2.7	12.1	19.7	c
C ₆ H ₁₈ Si ₂ O	Hexamethyldisiloxane	-185.8	-182.8	3.0	-8.8	18.1	a
C ₆ H ₁₉ Si ₂ N	Hexamethyldisilazane	-113.9	-120.8	-6.9	-9.7	-4.1	a
CHP	Methinophosphine	35.8	46.5	10.7	6.4	11.6	b
CH ₃ P	Methylphosphine	-7.0	-9.5	-2.5	-7.7	5.8	ff
C ₂ H ₇ P	Dimethylphosphine	-15.0	-19.6	-4.6	-17.1	3.4	ff
C ₂ H ₇ P	Ethylphosphine	-12.0	-11.7	0.3	-9.1	8.1	ff
C ₃ H ₉ P	Trimethylphosphine	-22.5	-29.8	-7.3	-25.7	0.9	a
C ₄ H ₁₁ P	Diethylphosphine	-25.0	-23.3	1.7	-20.0	6.7	ff
C ₆ H ₁₅ P	Triethylphosphine	-11.8	-36.7	-24.9	-53.0	-18.2	a

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TABLE 2
COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF FORMATION FOR ORGANIC RADICALS

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AMI	
CH	Methylidyne	142.4	146.8	4.4	1.2	2.6	a
CH ₂	Methylene, triplet	92.3	75.6	-16.7	-15.0	-11.5	b
CH ₃	Methyl radical	34.8	29.8	-5.0	-9.0	-3.5	b
C ₂	Carbon, dimer, triplet	200.2	230.3	30.1	32.2	16.1	c
C ₂ H ₃	Vinyl	59.6	63.3	3.7	4.2	5.2	d
C ₂ H ₄	Methylmethylene	90.3	88.6	-1.7	-1.9	-2.6	e
C ₂ H ₅	Ethyl radical	25.0	17.3	-7.7	-12.2	-6.9	f
C ₃	Carbon, trimer	196.0	206.6	10.6	24.3	16.4	b
C ₃ H ₅	Allyl	40.0	39.6	-0.4	-4.6	-1.4	d
C ₃ H ₇	<i>i</i> -Propyl radical	16.8	5.5	-11.3	-15.4	-10.0	f
C ₄	Carbon, tetramer, triplet	232.0	265.9	33.9	44.0	47.9	b
C ₄ H ₉	Isobutyl	4.5	-5.9	-10.4	-11.7	-7.4	f
CHO	HCO	10.4	-9.3	-19.7	-10.8	-11.4	b
CH ₂ O	Hydroxymethylene (trans)	27.2	16.4	-10.8	-13.7	-10.5	e
CH ₃ O	Methoxy	-0.5	-6.8	-6.3	0.3	-3.2	f
C ₂ H ₂ O	HCCOH	36.0	23.2	-12.8	-16.7	-11.5	e
CN	Cyanide	104.0	128.0	24.0	25.3	10.4	b
CH ₄ N	CH ₃ - NH	37.0	27.3	-9.7	-4.3	-2.9	f
CF	Fluoromethylidyne	61.0	54.0	-7.0	-22.4	-23.0	b
COF	COF	-42.3	-55.0	-12.7	-7.7	-13.6	c
CHOF	HCOF	-90.0	-88.8	1.2	1.2	-2.9	b
CF ₂	Difluoromethylene	-45.0	-49.1	-4.1	-20.2	-23.0	g
CF ₃	Trifluoromethyl	-112.4	-132.1	-19.7	-24.7	-30.4	b
C ₂ H ₂ F ₃	CF ₃ CH ₂	-123.6	-131.2	-7.6	-6.0	-7.8	h
CCl	Chloromethylidyne	111.3	105.3	-6.1	-3.9	-10.2	c
CHCl	Chloromethylene	80.0	83.2	3.2	0.9	-2.3	b
COCl	COCl	-15.0	-16.1	-1.1	-0.6	-0.4	b
CCl ₂	Dichloromethylene	57.0	57.5	0.5	0.6	-8.5	b
CCl ₃	Trichloromethyl	21.0	1.6	-19.4	-20.5	-25.7	c
CBr	Bromomethylidyne	125.9	138.4	12.5	1.6	0.9	c
CBr ₂	Dibromomethylene	84.3	104.9	20.6	7.8	5.7	c
CBr ₃	Tribromomethyl	64.7	64.2	-0.5	-35.8	-37.8	c
CI	Iodomethylidyne	144.8	145.5	0.7	7.1	6.2	c
COI	COI	63.5	-2.9	-66.4	-62.5	-58.8	c
CI ₂	Diiodomethylene	120.4	121.6	1.2	-15.5	1.2	c
CI ₃	Triiodomethyl	117.3	105.7	-11.6	-68.0	-52.7	c
CP	Carbon phosphide	107.5	119.6	12.1	22.1	23.6	b

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TABLE 3

COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF FORMATION FOR ORGANIC IONS

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
CH ₃	Methyl (+)	261.0	256.5	-4.5	-17.1	-8.6	a
C ₂ H ₃	Vinyl (+)	266.0	263.9	-2.1	-0.3	-4.5	b
C ₂ H ₄	Ethylene (+)	257.0	248.7	-8.3	-18.7	-13.1	c
C ₂ H ₅	Ethyl (+) (classical)	216.0	222.5	6.5	3.7	0.8	d
C ₂ H ₅	Ethyl (+) (non-classical)	216.0	232.1	16.1	18.7	10.3	d
C ₃ H ₃	Propynyl (+)	281.0	275.3	-5.7	-15.6	-7.3	c
C ₃ H ₃	Cyclopropenyl (+)	257.0	269.8	12.8	15.5	19.4	c
C ₃ H ₅	Allyl (+)	226.0	232.7	6.7	-4.6	0.2	c
C ₃ H ₅	Propenyl (+)	237.0	238.2	1.2	3.1	-3.3	c
C ₃ H ₅	Cyclopropyl (+)	235.0	261.8	26.8	23.2	25.6	c
C ₃ H ₇	Propyl (+)	208.0	214.4	6.4	4.4	-0.2	c
C ₃ H ₇	2-Propyl (+)	192.0	197.3	5.3	8.7	-0.1	d
C ₄ H ₇	2-Butenyl (+)	200.0	212.6	12.6	7.0	6.3	c
C ₄ H ₇	Cyclobutyl (+)	213.0	225.6	12.6	8.4	13.2	c
C ₄ H ₉	<i>n</i> -Butyl (+)	201.0	208.0	7.0	5.8	-1.1	c
C ₄ H ₉	1-Methyl propyl (+)	183.0	190.8	7.8	11.0	1.0	c
C ₄ H ₉	Isobutyl (+)	176.0	178.7	2.7	12.0	-1.2	c
C ₅ H ₅	Cyclopentadienyl (-)	21.3	15.9	-5.4	-2.4	3.9	e
C ₅ H ₉	Cyclopentyl (+)	188.0	193.5	5.5	6.2	-2.1	f
C ₅ H ₁₁	1-Pentyl (+)	194.0	202.4	8.4	7.9	-1.2	c
C ₅ H ₁₁	2-Pentyl (+)	173.0	184.6	11.6	15.5	3.4	c
C ₅ H ₁₁	2-Ethylisopropyl (+)	156.0	171.9	15.9	25.6	10.5	c
C ₅ H ₁₁	Neopentyl (+)	188.0	171.8	-16.2	-6.4	-21.5	g
C ₆ H ₁₁	1-Methylcyclopentyl (+)	165.0	174.5	9.5	13.6	2.4	c
C ₆ H ₁₁	Cyclohexyl (+)	177.0	186.1	9.1	9.9	-2.8	f
C ₇ H ₇	Benzyl (+)	216.0	227.4	11.4	2.0	6.1	h
C ₇ H ₇	Tropylium (+)	209.0	221.0	12.0	-1.3	1.4	i
C ₇ H ₁₁	2-Norbornyl (+)	182.0	208.5	26.5	31.1	21.0	c
CHO	HCO (+)	199.0	176.9	-22.1	-14.1	-11.5	j
CH ₃ O	CH ₂ OH (+)	168.0	166.3	-1.7	-12.4	-6.7	c
CH ₃ O	Methoxy (-)	-36.0	-37.9	-1.9	-3.7	-2.5	e
C ₂ H ₅ O	Ethoxy (-)	-47.5	-44.8	2.8	2.2	2.0	e
C ₆ H ₅ O	Phenoxy (-)	-40.5	-44.1	-3.6	-1.7	-0.5	e
CHO ₂	HCOO (-)	-106.6	-110.9	-4.3	5.0	-2.8	e
C ₂ H ₃ O ₂	CH ₃ COO (-)	-122.5	-119.7	2.8	12.5	7.1	e
CH ₄ N	CH ₂ -NH ₂ (+)	178.0	185.3	7.3	8.8	-1.7	k
CH ₄ N	CH ₃ NH (-)	30.5	21.7	-8.8	-7.0	2.6	e
C ₂ H ₆ N	Me ₂ N (-)	24.7	7.8	-16.9	-16.2	-2.3	e
CH ₂ F	Fluoromethyl (+)	200.3	200.3	0.0	-17.5	-19.9	l
CH ₃ F	Trifluoromethane (+)	233.3	228.2	-5.1	-10.1	-29.3	l
C ₂ H ₄ F	CH ₃ CHF (+)	166.0	172.9	6.9	-1.3	-8.9	m
CHF ₂	Diffuoromethyl (+)	142.4	145.5	3.1	-10.0	-20.5	l
CH ₂ F ₂	Diffuoromethane (+)	185.2	180.4	-4.8	-6.8	-33.6	l
C ₂ H ₃ F ₂	CH ₃ CF ₂ (+)	107.0	122.2	15.2	9.6	-1.7	m
CF ₃	Trifluoromethyl (-)	-163.4	-178.8	-15.4	-15.4	-15.4	n
CF ₃	Trifluoromethyl (+)	99.3	99.6	0.3	1.6	-17.2	l
CHF ₃	Trifluoromethane (+)	151.9	149.4	-2.5	6.8	-30.7	l
C ₂ H ₂ F ₃	CF ₃ CH ₂ (+)	114.0	122.3	8.3	7.2	0.4	m
C ₂ H ₂ F ₃	CH ₂ F.CF ₂ (+)	81.0	92.7	11.7	1.4	-11.9	m

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TABLE 4
COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF FORMATION FOR NORMAL VALENT INORGANIC MOLECULES

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
H ₂	Hydrogen	0.0	-13.4	-13.4	0.7	-5.2	a
HO	Hydroxyl radical	9.5	3.0	-6.5	-9.0	-8.6	b
H ₂ O	Water	-57.8	-53.4	4.4	-3.1	-1.4	c
O ₂	Oxygen (singlet)	22.0	18.4	-3.6	-9.9	-21.3	d
O ₂	Oxygen (triplet)	0.0	-4.2	-4.2	-15.3	-27.0	a
H ₂ O ₂	Hydrogen peroxide	-32.5	-40.8	-8.3	-5.7	-2.8	c
O ₃	Ozone	34.1	51.1	17.0	14.4	3.7	c
H ₂ N	Amidogen	45.5	35.4	-10.1	-8.5	-7.1	c
H ₃ N	Ammonia	-11.0	-3.1	7.9	4.6	3.7	c
NO	Nitrogen oxide	21.6	14.8	-6.8	-21.7	-20.4	c
NO ₂	Nitrogen dioxide	7.9	-1.0	-8.9	-12.5	-22.9	c
HNO ₂	Nitrous acid, trans	-18.8	-14.9	3.9	-21.9	-20.6	c
NO ₃	Nitrate radical	17.0	22.9	5.9	27.9	16.2	c
HNO ₃	Nitric acid	-32.1	-38.0	-5.9	14.6	-5.4	c
N ₂	Nitrogen	0.0	17.6	17.6	8.3	11.2	a
H ₂ N ₂	Diazene	36.0	37.8	1.8	-4.1	-4.5	e
H ₄ N ₂	Hydrazine	22.8	20.6	-2.1	-8.6	-9.1	c
N ₂ O	Nitrous oxide	19.6	25.4	5.8	11.4	8.9	c
N ₂ O ₃	Dinitrogen trioxide	19.8	23.7	3.9	-6.1	2.1	c
N ₂ O ₄	Dinitrogen tetroxide	2.2	8.3	6.2	27.8	22.9	c
N ₂ O ₅	Dinitrogen pentoxide	2.7	-19.0	-21.7	31.5	3.0	c
N ₃	Azide	99.0	106.0	7.0	3.4	8.4	b
HN ₃	Hydrazoic acid	70.3	75.3	5.0	2.8	5.5	f
HS	Hydrogen sulfide	33.3	38.2	4.9	4.0		c
H ₂ S	Hydrogen sulfide	-4.9	-0.9	4.0	8.7		c
SO	Sulfur monoxide (triplet)	1.2	-13.6	-14.8	3.0		c
S ₂	Sulfur dimer	30.8	28.7	-2.1	4.0		c
H ₂ S ₂	Hydrogen disulfide	3.7	8.6	4.9	2.8		f
S ₄	Sulfur tetramer	34.8	55.2	20.4	11.0		c
H ₂ S ₃	Hydrogen trisulfide	7.3	26.4	19.1	1.1		f
H ₂ S ₄	Hydrogen tetrasulfide	10.6	-0.3	-10.9	0.0		f
H ₂ S ₅	Hydrogen pentasulfide	13.8	2.0	-11.9	66.2		f
S ₈	S ₈	24.0	18.2	-5.8	-0.7		c
HF	Hydrogen fluoride	-65.1	-62.8	2.4	5.4	-9.1	c
OF	FO	26.1	21.2	-4.9	-4.4	-3.5	g
HOF	Hypofluorous acid	-23.5	-29.2	-5.7	4.9	0.9	h
NOF	Nitrosyl fluoride	-15.7	-3.3	12.4	-9.1	-10.8	c
SF	SF	-4.1	-11.6	-7.5	4.8		c
F ₂	Fluorine	0.0	-21.7	-21.7	7.3	-22.5	a
OF ₂	Difluorine oxide	5.9	-4.8	-10.7	12.3	4.6	c
NF ₂	NF ₂	10.1	11.9	1.8	-24.9	-16.5	c
N ₂ F ₂	cis-Difluorodiazene	16.4	28.0	11.6	-18.6	4.4	c
N ₂ F ₂	trans-Difluorodiazene	19.4	29.2	9.8	-17.0	11.9	c
SF ₂	Sulfur difluoride	-70.9	-91.9	-21.0	18.0		c

TABLE 4 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
S ₂ F ₂	FSSF	-80.4	-73.8	6.6	39.1		c
S ₂ F ₂	SSF ₂	-95.9	-56.1	39.8	111.4		c
NF ₃	Nitrogen trifluoride	-31.6	-24.4	7.2	-2.6	-8.4	c
H ₄ F ₄	Hydrogen fluoride tetramer	-282.9	-280.2	2.7	38.6	-30.2	c
N ₂ F ₄	Tetrafluorohydrazine	-2.0	-0.5	1.5	-17.7	7.8	c
HCl	Hydrogen chloride	-22.1	-20.5	1.6	6.8	-2.5	c
HOCl	Hypochlorous acid	-17.8	-34.3	-16.5	2.1	-4.0	c
NOCl	Nitrosyl chloride	12.4	4.5	-7.9	-16.6	-7.7	c
SCl	SCl	41.8	28.6	-13.2	-25.3		i
FCl	Chlorine fluoride	-12.1	-21.7	-9.6	20.3	1.6	c
F ₃ Cl	Chlorine trifluoride	-38.0	-22.1	15.9	116.7	58.2	c
F ₅ Cl	Chlorine pentafluoride	-54.0	-54.0	0.0	258.8	144.5	c
Cl ₂	Chlorine	0.0	-11.6	-11.6	-10.7	-14.2	a
OCl ₂	Chlorine monoxide	25.0	-16.2	-41.2	6.3	-5.5	c
SCl ₂	Sulfur dichloride	-4.2	-10.9	-6.7	-19.7		c
S ₂ Cl ₂	ClSSCl	-4.0	-7.7	-3.7	-16.8		c
HBr	Hydrogen bromide	-8.7	5.3	14.0	12.4	-1.8	c
HOBr	Hypobromous acid	-20.0	-33.9	-13.9	-2.7	-4.7	j
NOBr	Nitrosyl bromide	19.6	6.6	-13.0	-17.8	1.7	c
SBr	SBr	56.1	48.3	-7.8	-26.7		i
FBr	Bromine fluoride	-14.0	-21.3	-7.3	8.2	6.8	c
ClBr	Bromine chloride	3.5	-3.2	-6.7	-13.0	-14.1	c
Br ₂	Bromine	7.4	4.9	-2.5	-9.1	-12.7	c
SBr ₂	Sulfur dibromide	48.0	24.9	-23.1	-48.2		i
S ₂ Br ₂	S ₂ Br ₂	25.1	21.8	-3.3	-23.6		i
HI	Hydrogen iodide	6.3	28.8	22.5	9.4	1.6	c
NOI	Nitrosyl iodide	26.8	18.2	-8.6	-5.9	5.5	c
SI	SI	73.1	58.0	-15.1	-26.4		i
FI	Iodine fluoride	-22.6	-8.0	14.6	13.4	13.5	c
ClI	Iodine chloride	4.6	10.8	6.2	-11.4	-9.2	k
BrI	Iodine bromide	9.8	15.6	5.9	-2.5	-3.8	c
I ₂	Iodine	14.9	20.7	5.8	6.3	4.9	c
SI ₂	Sulfur diiodide	81.9	51.6	-30.3	-52.4		i
S ₂ I ₂	S ₂ I ₂	59.0	46.3	-12.7	-26.7		i
HAi	AlH	62.0	70.1	8.1	-16.0		c
AlO	AlO	16.0	-7.8	-23.9	-17.8		c
HAiO	Al-O-H	-43.0	-33.4	9.6	-18.1		c
HAiO	H-Al=O	-8.0	2.2	10.2	-13.7		c
AlO ₂	AlO ₂	-20.6	-37.4	-16.8	6.2		c
HAiO ₂	AlO ₂ H	-110.0	-105.1	4.9	16.2		c
AlN	Aluminum nitride	125.0	75.5	-49.5	15.9		c
AlF	Aluminum fluoride	-63.5	-50.1	13.4	-20.1		c
AlOF	AlFO	-139.0	-124.7	14.3	25.4		c
AlF ₂	AlF ₂	-166.0	-162.7	3.3	-5.1		c
AlOF ₂	AlF ₂ O	-265.0	-208.5	56.5	62.5		c
AlF ₃	Aluminum trifluoride	-289.0	-291.5	-2.5	-2.3		c

TABLE 4 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
AlCl	Aluminum chloride	-12.3	-5.5	6.8	-15.5		c
AlOCl	AlClO	-83.2	-72.4	10.8	14.5		c
AlFCl	AlClF	-117.0	-116.0	1.0	-7.7		c
AlF ₂ Cl	AlClF ₂	-238.8	-234.6	4.2	-2.8		c
AlCl ₂	Aluminum dichloride	-67.0	-68.2	-1.2	-7.6		c
AlFCl ₂	AlCl ₂ F	-189.0	-178.0	11.0	-2.4		c
AlCl ₃	Aluminum trichloride	-139.7	-122.1	17.6	-0.6		c
AlBr ₃	Aluminum tribromide	-98.1	-85.8	12.3	37.8		c
AlI	AlI	16.2	49.3	33.1	15.0		c
AlI ₃	Aluminum triiodide	-46.2	-39.9	6.3	57.8		c
Al ₂	Al ₂	116.4	79.6	-36.8	14.9		c
Al ₂ O	Al ₂ O	-34.7	-28.6	6.1	-37.0		c
Al ₂ O ₂	Al ₂ O ₂	-94.3	-87.6	6.8	-13.5		c
Al ₂ F ₆	Al ₂ F ₆	-629.5	-631.4	-1.9	-2.1		c
Al ₂ Cl ₆	Al ₂ Cl ₆	-309.7	-311.2	-1.5	14.4		c
Al ₂ Br ₆	Al ₂ Br ₆	-224.0	-224.9	-0.9	91.4		c
Al ₂ I ₆	Al ₂ I ₆	-117.0	-117.4	-0.4	124.4		c
HSi	SiH	86.3	94.6	8.3	3.9	3.5	l
H ₂ Si	Silylene (singlet)	61.1	72.8	11.7	3.2	6.7	m
H ₂ Si	Silylene (triplet)	6.5	-2.9	-9.4	-2.7	-30.7	n
H ₃ Si	Silyl	46.4	42.9	-3.5	-9.5	-20.1	o
H ₄ Si	Silane	8.2	12.5	4.3	-7.0	-4.1	c
SiO	Silicon monoxide	-23.9	-26.0	-2.1	1.3	21.8	i
SiO ₂	Silicon dioxide	-73.0	-88.9	-15.9	50.1	5.5	c
SiF	Silicon fluoride	1.7	-20.9	-22.6	-30.5	-27.8	l
H ₃ SiF	Fluorosilane	-90.0	-77.4	12.6	-6.4	4.2	p
SiOF	SiOF	-136.1	-107.5	28.6	56.1	30.1	i
SiF ₂	Silicon difluoride	-141.2	-154.9	-13.7	-23.7	-13.4	q
H ₂ SiF ₂	Difluorosilane	-189.0	-175.2	13.8	-3.5	7.5	q
SiOF ₂	SiOF ₂	-231.0	-229.4	1.6	42.4	10.3	c
SiF ₃	Trifluorosilyl	-245.0	-260.3	-15.3	-3.9	-22.8	o
HSiF ₃	Trifluorosilane	-287.0	-280.2	6.8	1.9	6.1	c
SiF ₄	Silicon tetrafluoride	-386.0	-390.6	-4.6	15.6	4.0	q
SiCl	Silicon chloride	45.3	29.8	-15.5	-15.6	-18.0	l
H ₃ SiCl	Chlorosilane	-32.4	-27.6	4.8	-11.5	-5.3	q
SiOCl	SiOCl	-86.7	-59.0	27.7	44.2	28.6	i
SiCl ₂	Silicon dichloride	-40.6	-49.4	-8.8	-5.7	-6.1	q
H ₂ SiCl ₂	Dichlorosilane	-75.3	-69.5	5.8	-8.2	-5.4	q
SiOCl ₂	SiOCl ₂	-167.7	-121.2	46.5	73.6	49.4	i
SiCl ₃	Trichlorosilyl	-76.0	-94.8	-18.8	-13.5	-40.0	o
HSiCl ₃	Trichlorosilane	-119.3	-112.7	6.6	1.4	-5.8	q
SiCl ₄	Silicon tetrachloride	-158.4	-156.4	2.0	10.8	-12.5	c
SiBr	Silicon bromide	50.0	41.0	-9.0	7.8	-3.0	l
H ₃ SiBr	Bromosilane	-15.3	-16.0	-0.7	-2.7	-5.8	r
SiOBr	SiOBr	-71.4	-47.1	24.3	42.8	31.1	i
SiBr ₂	Silicon dibromide	-9.6	-27.4	-17.8	20.8	3.6	q

TABLE 4 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
H ₂ SiBr ₂	Dibromosilane	-43.2	-47.2	-4.0	11.2	-2.6	q
SiOBr ₂	SiOBr ₂	-137.4	-94.1	43.3	86.0	60.0	i
SiBr ₃	Silicon tribromide	-56.1	-60.8	-4.7	41.1	-9.6	i
SiBr ₄	Silicon tetrabromide	-99.3	-107.9	-8.6	48.9	4.8	l
SiI	Silicon iodide	76.4	71.0	-5.4	15.5	4.1	i
H ₃ SiI	Iodosilane	-0.5	0.9	1.4	11.5	5.4	q
SiOI	SiOI	-53.3	-47.9	5.4	37.7	43.3	i
SiI ₂	Silicon diiodide	22.0	24.0	2.0	60.1	35.5	q
H ₂ SiI ₂	Diiodosilane	-9.1	-12.4	-3.3	32.1	14.1	c
SiOI ₂	SiOI ₂	-99.4	-50.2	49.2	89.7	80.7	i
SiI ₃	Silicon triiodide	0.5	4.7	4.2	44.9	11.9	i
HSiI ₃	Triiodosilane	-17.8	-9.0	8.8	51.9	21.7	q
SiI ₄	Silicon tetraiodide	-26.4	-14.2	12.2	68.8	28.0	c
Si ₂	Silicon dimer	140.9	135.7	-5.2	74.4	-1.4	i
H ₆ Si ₂	Disilane	17.1	17.9	0.8	5.3	-0.9	s
Si ₂ Cl ₆	Hexachlorodisilane	-243.5	-229.7	13.8	30.8	1.9	s
Si ₂ Br ₆	Hexabromodisilane	-182.8	-164.7	18.1	116.9	38.9	i
Si ₃	Silicon trimer	152.2	152.8	0.6	15.0	32.7	i
H ₈ Si ₃	Si ₃ H ₈	28.9	21.7	-7.2	2.9	-4.3	l
HP	Phosphinidene	60.6	73.4	12.8	27.9	15.1	c
H ₃ P	Phosphine	1.3	0.2	-1.1	2.6	8.9	c
H ₂ P	Phosphino	30.1	29.3	-0.8	1.3	4.1	c
PO	Phosphorus oxide	-2.9	-19.5	-16.6	-18.1	-13.6	i
NP	Phosphorus nitride	25.0	32.9	7.9	8.9	7.5	c
PF	Phosphorus fluoride	-20.8	-20.4	0.4	10.9	-15.3	i
POF	POF	-111.8	-124.0	-12.2	-2.4	0.5	i
PF ₂	Phosphorus difluoride	-119.0	-144.4	-25.4	-19.0	-14.2	i
PF ₃	Phosphorus trifluoride	-229.1	-252.2	-23.1	-0.2	0.2	c
PCl	Phosphorus chloride	25.6	28.9	3.3	10.8	-4.3	i
POCl	POCl	-64.7	-76.4	-11.7	-10.1	-0.4	i
PCl ₂	Phosphorus dichloride	-21.3	-40.1	-18.8	-28.1	-26.3	i
PCl ₃	Phosphorus trichloride	-69.0	-88.5	-19.5	-27.4	-20.0	c
PBr	Phosphorus bromide	43.0	34.9	-8.1	-13.6	-15.4	k
POBr	POBr	-50.2	-59.9	-9.7	-3.7	10.6	i
PBr ₂	Phosphorus dibromide	6.7	0.4	-6.3	-16.0	-11.1	i
PBr ₃	Phosphorus tribromide	-34.9	-28.2	6.7	-3.2	11.6	c
PI	PI (triplet)	54.6	51.0	-3.6	-3.1	-2.5	i
POI	POI	-33.4	-43.6	-10.2	8.8	17.7	i
PI ₂	Phosphorus diiodide	41.3	36.6	-4.7	-4.8	-6.3	i
POI ₂	POI ₂	-40.1	-35.2	4.9	19.5	33.0	i
PI ₃	Phosphorus triiodide	25.1	31.3	6.2	-0.3	-0.7	i
P ₂	Phosphorus dimer	42.8	32.0	-10.8	-1.7	-18.2	i
H ₄ P ₂	P ₂ H ₄	5.0	-3.7	-8.7	-7.9	1.6	l
P ₄	Phosphorus tetramer	31.1	42.9	11.8	5.1	19.3	i
P ₄ O ₆	Phosphorus trioxide	-529.2	-511.0	18.2	8.1		c

References to Table 4

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TABLE 5
COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF FORMATION FOR HYPERVALENT
MOLECULES

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₂ H ₆ SO	Dimethyl sulfoxide	-36.1	-38.8	-2.7	40.0		a
C ₄ H ₁₀ SO	Diethyl sulfoxide	-49.1	-46.6	2.5	41.5		a
SO ₂	Sulfur dioxide	-71.0	-50.8	20.2	75.4		b
C ₂ H ₆ SO ₂	Dimethyl sulfone	-89.1	-76.3	12.8	142.8		a
C ₄ H ₁₀ SO ₂	Diethyl sulfone	-102.5	-80.8	21.7	143.1		a
SO ₃	Sulfur trioxide	-94.6	-104.8	-10.2	153.1		b
C ₂ H ₆ SO ₃	Dimethyl sulfite	-115.5	-130.0	-14.5	50.4		a
H ₂ SO ₄	Sulfuric acid	-175.7	-181.4	-5.8	172.2		b
C ₂ H ₆ SO ₄	Dimethyl sulfate	-164.1	-172.1	-8.0	158.6		a
O ₂ F	Fluorine dioxide	3.0	12.9	9.9	21.1	6.0	b
NO ₂ F	Fluorine nitrite	-26.0	-25.6	0.4	26.7	4.7	b
NO ₃ F	Fluorine nitrate	2.5	-6.1	-8.6	25.5	11.2	b
SOF	SOF	-63.3	-74.4	-11.1	35.0		c
SO ₂ F	SO ₂ F	-113.2	-102.5	10.7	127.2		c
SOF ₂	Thionyl fluoride	-130.0	-138.2	-8.2	84.3		b
SO ₂ F ₂	Sulfuryl fluoride	-181.3	-184.3	-3.0	203.3		b
NOF ₃	F ₃ NO	-39.0	-26.6	12.4	61.8	24.4	b
SF ₃	Sulfur trifluoride	-130.0	-134.3	-4.3	89.9		c
SOF ₃	SOF ₃	-185.1	-176.5	8.6	180.2		c
SF ₄	Sulfur tetrafluoride	-182.4	-185.3	-2.9	135.9		b
SOF ₄	SOF ₄	-235.5	-236.3	-0.8	269.1		c
SF ₅	Sulfur pentafluoride	-217.1	-232.5	-15.4	208.2		b
SF ₅	Sulfur pentafluoride (-)	-291.0	-303.0	-12.0	159.4		d
SF ₆	Sulfur hexafluoride	-291.4	-304.6	-13.2	320.7		b
O ₂ Cl	Chlorine dioxide	25.0	1.5	-23.5	111.0	80.9	b
NO ₂ Cl	Nitryl chloride	2.9	-13.0	-15.9	14.4	11.7	b
SOCl	SOCl	-17.4	-31.1	-13.7	1.5		c
SO ₂ Cl	SO ₂ Cl	-66.4	-57.3	9.1	92.3		c
O ₃ FCl	Perchloryl fluoride	-5.1	14.6	19.7	328.4	251.6	b
SOCl ₂	Thionyl chloride	-50.8	-47.6	3.2	28.6		e
SO ₂ Cl ₂	Sulfuryl chloride	-86.2	-62.3	23.9	79.9		b
SCl ₃	Sulfur trichloride	8.8	-19.1	-27.9	-41.3		c
SOCl ₃	SOCl ₃	-47.5	-46.5	1.0	49.9		c
SCl ₄	Sulfur tetrachloride	-0.7	-19.8	-19.1	-32.6		c
SOCl ₄	SOCl ₄	-55.7	-59.3	-3.6	22.7		c
SCl ₅	Sulfur pentachloride	-8.6	9.2	17.8	4.3		c
SCl ₆	Sulfur hexachloride	-19.8	10.3	30.1	138.1		c
OBr	BrO	30.1	20.8	-9.3	5.3	5.6	f
SOBr	SOBr	-4.3	-16.2	-11.9	2.2		c
SO ₂ Br	SO ₂ Br	-52.8	-42.9	9.9	89.5		c
F ₃ Br	Bromine trifluoride	-61.1	-47.1	14.0	84.0	82.6	b
F ₅ Br	Bromine pentafluoride	-102.5	-75.8	26.7	207.4	183.7	b
SOBr ₂	Thionyl bromide	-11.5	-18.6	-7.1	16.1		c
SO ₂ Br ₂	Sulfuryl bromide	-59.5	-46.2	13.3	127.9		c

TABLE 5 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
SBr ₃	Sulfur tribromide	50.2	16.4	-33.8	-51.3		c
SOBr ₃	SOBr ₃	-8.6	-10.0	-1.4	41.4		c
SBr ₄	Sulfur tetrabromide	53.0	18.8	-34.2	-42.9		c
SOBr ₄	SOBr ₄	-3.3	-20.7	-17.4	26.6		c
SBr ₅	Sulfur pentabromide	55.9	44.0	-11.9	23.5		c
SBr ₆	Sulfur hexabromide	58.8	78.1	19.3	107.6		c
OI	IO	41.8	31.0	-10.9	4.8	-4.9	f
SOI	SOI	12.7	-0.4	-13.1	7.0		c
SO ₂ I	SO ₂ I	-34.9	-32.0	2.9	64.5		c
F ₅ I	Iodine pentafluoride	-200.8	-202.9	-2.1	298.8	267.9	b
F ₇ I	Iodine heptafluoride	-229.7	-225.4	4.3	334.9	274.1	b
SOI ₂	Thionyl iodide	21.5	11.1	-10.4	26.6		c
SO ₂ I ₂	Sulfuryl iodide	-26.0	-30.0	-4.0	51.7		c
SI ₃	Sulfur triiodide	100.3	54.7	-45.6	-60.0		c
SOI ₃	SOI ₃	40.4	23.8	-16.6	1.7		c
SI ₄	Sulfur tetraiodide	120.2	83.8	-36.4	-38.0		c
SOI ₄	SOI ₄	60.0	27.6	-32.4	-17.0		c
SI ₅	Sulfur pentaiodide	130.9	129.6	-1.3	-1.0		c
SI ₆	Sulfur hexaiodide	158.9	167.0	8.1	48.7		c
C ₄ H ₁₂ SiF	SiMe ₄ F (-) C3v symmetry	-147.5	-122.4	25.1	33.5	23.5	d
SiF ₅	SiF ₅ (-)	-507.1	-504.4	2.7	17.7	3.6	d
SiF ₄ Cl	SiF ₄ Cl (-)	-465.3	-465.2	0.1	17.5	8.0	d
SiCl ₅	SiCl ₅ (-)	-237.2	-254.6	-17.4	-19.3	-30.4	d
C ₃ H ₉ PO	Trimethylphosphine oxide	-102.2	-82.7	19.5	59.3	0.7	a
PO ₂	Phosphorus dioxide	-71.0	-76.7	-5.7	24.0	13.2	c
CH ₃ PO ₃	Methylphosphonic acid	-240.5	-213.3	27.2	25.2	31.0	a
C ₂ H ₇ PO ₃	Ethylphosphonic acid	-239.4	-218.5	20.9	19.9	26.0	a
C ₃ H ₉ PO ₃	Trimethyl phosphite	-168.3	-192.2	-23.9	-38.0	-17.3	a
C ₆ H ₁₅ PO ₃	Triethyl phosphite	-195.9	-208.5	-12.6	-27.5	-11.2	a
C ₆ H ₁₅ PO ₄	Triethyl phosphate	-284.5	-252.9	31.6	75.0	8.3	a
C ₂ H ₆ PO ₂ F	Methyl methylphosphonofluoridate	-197.3	-207.6	-10.3	51.4	-20.9	g
C ₃ H ₈ PO ₂ F	Ethyl methylphosphonofluoridate	-205.8	-212.3	-6.5	53.9	-18.7	g
C ₄ H ₁₀ PO ₂ F	<i>n</i> -Propyl methylphosphonofluoridate	-210.2	-217.4	-7.2	53.9	-21.0	g
C ₄ H ₁₀ PO ₂ F	<i>i</i> -Propyl methylphosphonofluoridate	-214.6	-216.7	-2.1	60.8	-15.1	g
C ₃ H ₁₂ PO ₂ F	<i>s</i> -Butyl methylphosphonofluoridate	-220.1	-221.2	-1.1	63.2	-15.5	g
C ₃ H ₁₂ PO ₂ F	<i>i</i> -Propyl ethylphosphonofluoridate	-219.8	-217.5	2.2	59.4	-12.1	g
C ₅ H ₁₂ PO ₂ F	<i>n</i> -Butyl methylphosphonofluoridate	-215.1	-222.9	-7.8	53.8	-22.9	g
C ₆ H ₁₄ PO ₂ F	Neopentyl methylphosphonofluoridate	-224.2	-226.6	-2.4	70.4	-13.7	g
POF ₂	POF ₂	-213.6	-188.9	24.7	61.7	39.4	c
CH ₃ POF ₂	Methylphosphonodifluoride	-233.2	-225.3	7.9	86.1	5.6	g
POF ₃	Phosphorus oxyfluoride	-289.5	-297.7	-8.2	90.0	-3.3	h
PF ₄	Phosphorus tetrafluoride (-)	-325.0	-332.1	-7.1	22.8	26.2	d
PF ₄	Phosphorus tetrafluoride	-287.9	-303.9	-16.0	53.3	6.8	c
PF ₅	Phosphorus pentafluoride	-381.1	-386.9	-5.8	132.3	1.8	b
PF ₆	Phosphorus hexafluoride (-)	-522.0	-508.5	13.5	152.4	17.6	d
POCl ₂	POCl ₂	-109.9	-94.8	15.1	33.9	24.8	c

TABLE 5 (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
CH ₃ POCl ₂	Methylphosphonodichloride	−124.1	−128.9	−4.8	48.7	9.3	g
POCl ₃	Phosphorus oxychloride	−132.8	−140.2	−7.4	53.2	14.9	h
PSCl ₃	Phosphorus thiochloride	−91.0	−60.2	30.8	62.6		b
PCl ₄	Phosphorus tetrachloride	−80.5	−102.8	−22.3	−22.7	−29.5	c
PCl ₅	Phosphorus pentachloride	−89.6	−111.6	−22.0	47.7	17.8	h
POBr ₂	POBr ₂	−78.3	−50.8	27.5	26.4	56.5	c
POBr ₃	Phosphorus oxybromide	−97.0	−80.2	16.8	68.3	68.0	b
PSBr ₃	Phosphorus thiobromide	−67.2	−7.8	59.4	85.7		b
PBr ₄	Phosphorus tetrabromide	−17.4	−17.4	0.0	−11.9	−8.5	c
PBr ₅	Phosphorus pentabromide	−11.0	−27.1	−16.1	42.8	103.9	c
POI ₃	Phosphorus oxyiodide	−39.7	−8.3	31.4	71.3	75.9	c
PI ₄	Phosphorus tetraiodide	60.2	44.7	−15.5	−36.1	−33.7	c
PI ₅	Phosphorus pentaiodide	97.7	88.5	−9.2	−16.0	−42.1	c
P ₄ O ₁₀	Phosphorus pentoxide	−694.1	−712.6	−18.5	262.4	−6.8	b

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TABLE 6
COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF FORMATION FOR INORGANIC IONS

Empirical formula	Chemical name	Heat of formation		Difference			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
H	Hydrogen (+)	365.7	353.6	-12.1	-39.0	-50.8	a
HO	Hydroxide (-)	-33.2	-17.5	15.7	27.4	19.1	b
H ₃ O	Hydronium (+)	138.9	159.1	20.2	-4.7	4.6	c
H ₄ N	Ammonium (+)	155.0	153.4	-1.6	9.6	-4.4	d
NO	NO (+)	237.0	238.2	1.2	-6.4	-8.8	c
NO ₂	Nitrogen dioxide (+)	233.0	208.4	-24.6	7.6	-11.9	e
NO ₃	Nitrate anion	-74.7	-93.3	-18.6	7.7	-14.2	f
S	S (-)	16.8	20.7	3.9	29.8		c
HS	HS (-)	-17.1	-15.9	1.2	24.0		g
F	Fluoride (-)	-61.0	-31.2	29.8	43.9	64.4	c
NF ₂	NF ₂ (-)	-29.5	-31.0	-1.5	-14.1	4.3	h
Cl	Chloride (-)	-55.9	-51.2	4.7	1.2	18.2	c
HFCl	Hydrogen chloride fluoride (-)	-142.0	-137.0	5.0	15.8	15.9	i
HCl ₂	Hydrogen dichloride (-)	-142.0	-111.0	31.0	47.2	47.6	i
Br	Bromide (-)	-52.3	-56.2	-3.9	14.8	31.9	c
HBr	HBr (+)	261.1	274.7	13.6	16.8	-12.3	j
ClBr	Bromine chloride (+)	261.0	247.6	-13.4	4.8	-14.6	f
Br ₂	Bromine (+)	253.5	263.0	9.5	12.5	-7.7	j
I	Iodide (-)	-46.5	-64.6	-18.1	40.1	44.3	c
Al	Al (+)	218.1	279.8	61.7	-24.2		c
AlO	AlO (+)	237.3	202.4	-34.9	-14.2		c
AlO	AlO (-)	-64.4	-50.9	13.5	8.6		c
HAIO	AlOH (+)	130.0	129.3	-0.7	59.2		c
HAIO	AlOH (-)	-55.0	-105.7	-50.7	13.9		c
AlO ₂	AlO ₂ (-)	-116.0	-117.1	-1.1	25.5		c
AlF	AlF (+)	165.4	160.4	-5.0	-50.6		c
AlF ₂	AlF ₂ (+)	22.0	29.0	7.0	-7.8		c
AlF ₂	AlF ₂ (-)	-217.0	-229.6	-12.6	7.4		c
AlOF ₂	AlF ₂ O (-)	-311.6	-286.0	25.6	53.7		c
AlF ₄	AlF ₄ (-)	-476.0	-469.2	6.8	35.4		c
AlCl	Aluminum chloride (+)	206.0	198.7	-7.3	-31.2		c
AlFCl	Aluminum chloride fluoride (+)	66.0	74.9	8.9	-2.5		c
AlCl ₂	AlCl ₂ (+)	115.0	124.3	9.3	3.9		c
AlCl ₂	AlCl ₂ (-)	-115.0	-145.0	-30.0	-15.6		c
Al ₂ O	Al ₂ O (+)	155.9	168.4	12.6	-46.8		c
Al ₂ O ₂	Al ₂ O ₂ (+)	126.0	107.3	-18.7	-47.1		c
H ₃ Si	Silyl (-)	14.0	-2.8	-16.8	32.5	-15.8	k
H ₃ Si	Silyl (+)	234.1	223.3	-10.8	-43.3	-11.2	k

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TABLE 7
STATISTICAL ANALYSIS OF DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED HEATS OF FORMATION

Type of compounds	Number of compounds	Average difference						Root mean square		
		Signed			Unsigned					
		PM3	MNDO	AM1	PM3	MNDO	AM1	PM3	MNDO	AM1
Hydrogen	456	6.2	12.8	7.3	1.5	14.9	−0.1	8.3	24.2	10.4
Carbon	459	6.2	12.8	7.9	1.2	3.5	−0.3	8.7	23.1	11.5
Nitrogen	117	6.5	18.8	9.6	0.6	10.0	13.3	8.3	27.0	12.5
Oxygen	234	9.0	32.4	14.4	−0.1	26.8	4.5	12.9	56.4	25.2
Fluorine	133	8.6	44.4	22.7	0.7	37.4	6.2	11.2	84.2	49.5
Silicon	78	10.1	22.4	14.5	1.9	13.0	3.6	14.2	32.9	20.8
Phosphorus	70	12.4	37.7	19.5	−0.8	25.0	6.4	16.1	55.6	29.1
Sulfur	101	12.0	50.3	23.4	−1.4	36.9	−10.4	16.2	79.8	34.0
Chlorine	93	9.6	24.6	18.8	−0.1	15.1	2.6	13.4	54.1	37.8
Bromine	67	11.4	27.8	23.4	1.5	16.4	6.2	15.5	46.5	39.9
Iodine	73	10.7	29.2	25.7	−0.3	10.9	4.2	15.8	60.7	53.5
Set of compounds used in Refs. 2 and 4	138	4.4	6.2	5.5	0.0	−1.4	0.7	6.3	9.1	7.3
Compounds of C, H, N, and O, only	276	5.5	11.2	7.5	0.4	3.8	1.4	7.9	18.5	10.5
Nitro compounds	29	5.2	39.6	15.7	2.5	38.1	14.5	6.2	44.1	18.5
Organophosphorus-V compounds	15	10.9	53.9	15.5	3.6	50.2	−4.7	14.3	56.7	17.3
Normal valent compounds	607	7.3	13.1	9.6	0.5	3.1	−0.2	11.2	24.3	14.8
Hypervalent	106	13.6	75.8	37.7	−0.8	67.2	8.9	17.3	104.5	62.3
All compounds	713	8.2	22.5	13.8	0.3	13.8	1.2	11.6	46.2	27.6

TABLE 8
BARRIERS TO ROTATION AND INVERSION

Molecule	Barrier			
	Exp.	PM3	MNDO	AM1
Ethylene	65.0	35.90	38.83	45.01 ^a
Ethylene	65.0	65.31	62.48	65.93 ^b
Ethane	2.9	1.43	1.01	1.25
Methylamine	2.0	1.10	1.07	1.27
Methanol	1.1	0.90	0.74	1.04
HO-OH (cis)	7.0	7.27	6.90	7.01
HO-OH (trans)	1.1	0.00	0.00	0.10
Formamide	- 20	21.00	19.00	17.00 ^c
Formamide	- 20	1.40	3.29	10.11 ^d
<i>n</i> -Butane (gauche)	0.8	0.53	0.58	0.71
<i>n</i> -Butane (eclipsed)	4 - 6	4.00	3.23	3.28
Nitrobenzene		1.64	1.78	3.48 ^e
Ammonia (inversion)	6	9.98	11.58	4.24

^a Barrier calculated with minimal configuration interaction. The transition state for the rotation of the C = C bond involves two electronic states. When both states are used, the 'reaction' has a well-defined transition state.

^b Barrier calculated without configuration interaction. Using only one configuration results in an intersystem crossing. The D2d geometry does not correspond to a stationary point.

^c Barrier calculated with molecular mechanics correction. The MM correction can be invoked by the keyword MMOK.

^d Barrier calculated without molecular mechanics correction. The correction can be omitted by using the keyword NOMM.

^e For PM3 and AM1 the minimum energy configuration of nitrobenzene is with the NO₂ coplanar with the aromatic ring. For MNDO the NO₂ is perpendicular to the aromatic ring. This is characteristic of most sp²-hybridized groups attached to otherwise unsubstituted benzene rings.

TABLE 9
INTERMOLECULAR INTERACTION ENERGIES (kcal/mol)

Molecular pair	Heat of association		
	PM3	MNDO	AM1
H ₂ - N ₂	0.0	0.0	0.0
NH ₃ - H ₂	0.0	0.0	0.0
CO ₂ - CO ₂	0.0	0.0	0.0
O ₂ - O ₂	0.0	0.0	0.0
H ₂ - CO ₂	0.0	0.0	0.0
NH ₃ - CO ₂	-0.5	-0.4	-1.8
CH ₄ - CH ₄	-0.9	0.0	-0.4
H ₂ O - H ₂	-0.9	0.0	-1.1
H ₂ O - CO ₂	-0.9	-0.8	-2.7
NH ₃ - NH ₃	-0.9	-0.8	-2.4
CH ₂ O - CH ₂ O	-1.0	-0.8	-2.4
H ₂ O - NH ₃	-1.1	-0.5	-2.7
H ₂ O - CH ₄	-1.2	0.0	-1.2
CH ₃ OH - H ₂ O	-1.5	-0.7	-2.7
CH ₂ O - H ₂ O	-1.6	-0.7	-3.7
H ₂ O - CH ₂ O	-1.6	-1.0	-4.0
H ₂ O - C ₅ H ₅ N	-1.7	-1.1	-3.1
H ₂ O - O ₃	-1.8	-1.1	-6.8
H ₂ O - CH ₃ OH	-1.9	-0.9	-4.8
NH ₂ COOH - NH ₂ COOH	-1.9	-3.3	-9.0
HCOOH - CH ₄	-2.3	0.1	-0.8
C ₆ H ₆ - C ₆ H ₆	-3.8	0.0	-0.4
NH ₂ CHO - NH ₂ CHO	-4.7	-2.1	-8.1
H ₂ O - HCOOH	-5.3	-1.0	-7.4
HCOOH - NH ₃	-5.3	-0.9	-4.1
HCOOH - HCOOH	-8.6	-1.7	-6.4

TABLE 10
COMPARISON OF EXPERIMENTAL AND CALCULATED MOLECULAR GEOMETRIES FOR ORGANIC MOLECULES

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
CH ₂	Methylene, singlet	CH	1.110	1.092	-0.018	-0.019	-0.007	a
		HCH	102.4	103.7	1.3	8.7	8.1	
CH ₂	Methylene, triplet	CH	1.029	1.064	0.035	0.024	0.034	a
		HCH	144.7	144.7	0.0	4.9	3.6	
CH ₄	Methane	CH	1.094	1.087	-0.007	0.010	0.018	b
C ₂	Carbon, dimer	CC	1.242	1.189	-0.053	-0.073	-0.078	a
C ₂ H ₂	Acetylene	CC	1.203	1.190	-0.013	-0.008	-0.008	b
		CH	1.060	1.064	0.004	-0.009	0.001	
C ₂ H ₄	Ethylene	CC	1.339	1.322	-0.017	-0.004	-0.013	b
		CH	1.086	1.086	0.000	0.003	0.012	
		HCC	121.2	123.1	1.9	2.0	1.5	
C ₂ H ₆	Ethane	CC	1.536	1.504	-0.032	-0.015	-0.036	b
		CH	1.091	1.098	0.007	0.018	0.026	
		HCC	110.9	111.6	0.7	0.3	-0.2	
C ₃ H ₄	Allene	CC	1.308	1.297	-0.011	-0.002	-0.010	c
		CH	1.087	1.086	-0.001	0.003	0.013	
		HCC	120.9	122.3	1.4	2.0	1.4	
C ₃ H ₄	Cyclopropene	C2C3	1.509	1.484	-0.025	0.003	-0.020	d
		C1C2	1.296	1.314	0.018	0.032	0.022	
		C1H	1.072	1.073	0.001	-0.010	-0.003	
		HC1C2	149.9	151.5	1.6	1.7	2.0	
C ₃ H ₄	Propyne	C2C1	1.206	1.191	-0.015	-0.009	-0.009	e
		C1H	1.056	1.064	0.008	-0.005	0.004	
		C3C3	1.459	1.433	-0.026	-0.014	-0.032	
		C3H	1.105	1.098	-0.007	0.006	0.016	
		HCC	111.0	110.7	-0.3	0.0	-0.5	
C ₃ H ₆	Cyclopropane	CC	1.510	1.499	-0.011	0.016	-0.009	f
		CH	1.089	1.095	0.006	0.007	0.015	
C ₃ H ₆	Propene	C = C	1.336	1.328	-0.008	0.004	-0.005	g
		C - C	1.501	1.480	-0.021	-0.005	-0.025	
		CCC	124.3	123.4	-0.9	2.6	0.0	
		C3H	1.085	1.098	0.013	0.024	0.033	
		HC3C2	111.2	112.9	1.7	1.8	0.7	
		C2H	1.090	1.097	0.007	0.006	0.013	
		HC2C1	119.0	120.8	1.8	0.3	1.9	
		HC1	1.091	1.087	-0.004	-0.002	0.007	
		HC1C2	121.5	122.7	1.2	0.8	0.8	
C ₃ H ₈	Propane	CC	1.526	1.512	-0.014	0.004	-0.019	g
		CCC	112.4	111.7	-0.7	3.0	-0.6	
		C2H	1.115	1.108	-0.007	0.000	0.007	
		HC2C1	109.5	109.9	0.4	-0.7	0.0	
		C1H	1.096	1.097	0.001	0.014	0.021	
		HC1C2	111.8	111.4	-0.4	-1.5	-1.4	

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
C ₄ H ₂	Diacetylene	C1C2	1.205	1.193	-0.012	-0.006	-0.006	h
		C2C3	1.376	1.371	-0.005	-0.008	-0.020	
		CH	1.046	1.065	0.019	0.004	0.014	
C ₄ H ₄	CH ₂ =C=C=CH ₂	CH	1.083	1.087	0.004	0.007	0.017	i
		C1C2	1.318	1.301	-0.017	-0.007	-0.016	
		C2C3	1.283	1.267	-0.016	-0.013	-0.017	
C ₄ H ₄	Vinylacetylene	C3C4	1.341	1.332	-0.009	0.004	-0.005	j
		C2C3	1.431	1.414	-0.017	-0.014	-0.026	
		C2C3C4	123.1	122.5	-0.6	2.3	1.0	
C ₄ H ₆	Bicyclobutane	C1C2	1.208	1.193	-0.015	-0.010	-0.010	k
		C1C2	1.498	1.507	0.009	0.029	0.012	
		C1C3	1.497	1.481	-0.016	0.039	-0.002	
C ₄ H ₆	2-Butyne	C2C3C1C4	121.7	120.0	-1.7	0.9	0.3	j
		C1H	1.071	1.083	0.012	0.003	0.008	
		C2H	1.093	1.095	0.002	0.005	0.012	
C ₄ H ₆	1,3-Butadiene	C2C3	1.213	1.193	-0.020	-0.013	-0.015	j
		C1C2	1.467	1.432	-0.035	-0.023	-0.042	
		CH	1.115	1.098	-0.017	-0.004	0.006	
C ₄ H ₆	1,3-Butadiene	HCC	110.7	110.7	0.0	0.3	-0.1	l
		C1C2	1.344	1.331	-0.013	0.000	-0.009	
		C2C3	1.467	1.456	-0.011	-0.002	-0.016	
C ₄ H ₈	1-Butene	CCC	122.9	122.3	-0.6	2.8	0.5	m
		C2C3	1.347	1.328	-0.019	-0.006	-0.016	
		C1C2	1.508	1.489	-0.019	-0.003	-0.024	
C ₄ H ₈	Cyclobutane	CCC	123.8	122.6	-1.2	1.6	-0.4	n
		CC	1.548	1.542	-0.006	0.001	-0.005	
		C1C2C4C3	153.0	180.0	27.0	27.0	27.0	
C ₄ H ₈	Isobutene	CH	1.105	1.100	-0.005	0.000	0.005	o
		C1C2	1.330	1.333	0.003	0.018	0.006	
		C2C3	1.507	1.487	-0.020	0.002	-0.023	
C ₄ H ₁₀	<i>n</i> -Butane	C1C2C3	122.4	122.1	-0.3	-0.5	0.0	e
		C1C2	1.533	1.512	-0.021	-0.002	-0.026	
		C2C3	1.533	1.521	-0.012	0.007	-0.019	
C ₄ H ₁₀	Isobutane	CCC	112.8	111.6	-1.2	2.0	-1.2	p
		CC	1.525	1.520	-0.005	0.016	-0.011	
		C=C	1.339	1.328	-0.011	0.001	-0.008	
C ₅ H ₈	1,4-Pentadiene C1	C-C	1.511	1.489	-0.022	-0.005	-0.027	q
		C-C=C	115.5	123.1	7.6	11.1	8.4	
		C-C-C	113.1	114.4	1.3	-0.5	1.2	
C ₅ H ₈	1,4-Pentadiene C2	C1-C2-C3-C4	-116.9	-127.5	-10.6	9.6	-13.8	q
		C2-C3-C4-C5	-4.3	14.2	18.5	110.0	16.2	
		C=C	1.339	1.328	-0.011	0.001	-0.008	
C ₅ H ₈	1,4-Pentadiene C2	C-C	1.511	1.490	-0.021	-0.005	-0.025	q
		C-C=C	115.5	123.1	7.6	11.2	8.3	
		C-C-C	108.9	110.8	1.9	3.8	2.9	
C ₅ H ₈	1,4-Pentadiene C2	C1-C2-C3-C4	-122.2	-129.3	-7.1	15.1	-11.9	q

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
C ₅ H ₈	1,4-Pentadiene Cs	C = C	1.339	1.328	-0.011	0.001	-0.008	q
		C - C	1.511	1.490	-0.021	-0.005	-0.025	
		C - C = C	115.5	123.0	7.5	11.1	8.3	
		C - C - C	108.9	111.1	2.2	3.7	3.0	
		C1-C2-C3-C4	-128.6	-132.2	-3.6	22.1	-5.3	
C ₅ H ₁₂	Neopentane	CC	1.539	1.527	-0.012	0.015	-0.018	f
		CH	1.120	1.098	-0.022	-0.011	-0.004	
		HCC	110.0	111.3	1.3	1.7	0.3	
C ₆ H ₆	Benzene	CC	1.399	1.391	-0.008	0.008	-0.004	r
		CH	1.084	1.095	0.011	0.006	0.016	
C ₆ H ₆	Fulvene	C3C4	1.476	1.471	-0.005	0.000	0.000	s
		C2C3	1.355	1.355	0.000	0.011	0.008	
		C1C2	1.470	1.478	0.008	0.021	0.013	
		C1C6	1.349	1.331	-0.018	-0.004	-0.017	
C ₆ H ₁₀	Cyclohexene	C1C2	1.335	1.334	-0.001	0.011	0.002	t
		C2C3	1.504	1.487	-0.017	0.000	-0.021	
		C3C4	1.515	1.521	0.006	0.026	0.002	
		C4C5	1.550	1.519	-0.031	-0.011	-0.036	
		C5C4C2C1	21.8	27.8	6.0	-0.8	5.4	
C ₆ H ₁₂	Cyclohexane	CC	1.536	1.521	-0.015	0.002	-0.021	u
		CCC	111.4	111.0	-0.4	2.7	-0.1	
		CCCC	54.9	56.0	9.7	0.0	8.9	
		CH	1.104	1.107	-0.014	-0.007	0.000	
		CH ⁺	1.121	1.108	-0.013	-0.007	0.001	
CO	Carbon monoxide	CO	1.128	1.135	0.007	0.035	0.043	v
CH ₂ O	Formaldehyde	CO	1.208	1.202	-0.006	0.008	0.019	w
		CH	1.116	1.091	-0.025	-0.010	-0.006	
		HCO	121.8	121.8	0.0	1.7	0.4	
CH ₄ O	Methanol	CO	1.425	1.395	-0.030	-0.034	-0.015	x
		CH	1.094	1.097	0.003	0.025	0.025	
		HCO	108.5	112.2	3.7	3.8	2.4	
		OH	0.945	0.949	0.004	0.002	0.019	
		COH	107.0	107.5	0.5	4.6	0.2	
C ₂ H ₂ O	Ketene	CO	1.161	1.175	0.014	0.023	0.032	y
		CC	1.314	1.308	-0.006	0.005	-0.007	
		CH	1.083	1.084	0.001	0.002	0.012	
		HCC	118.7	122.0	3.3	3.0	2.7	
C ₂ H ₆ O	Dimethyl ether	CC	1.410	1.406	-0.004	-0.014	0.007	z
		COC	111.3	114.1	2.8	8.7	1.6	
C ₃ H ₄ O	Acrolein	C3C2	1.335	1.330	-0.005	0.008	-0.001	aa
		C2C1	1.478	1.479	0.001	0.007	-0.010	
		CCC	121.0	123.6	2.6	6.3	2.2	
		CO	1.208	1.211	0.003	0.016	0.026	
		OCC	124.0	124.0	0.0	1.5	0.0	

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
C ₄ H ₄ O	Furan	CO	1.362	1.378	0.016	0.005	0.033	bb
		CCO	106.6	106.9	0.3	1.0	0.0	
		C3C2	1.361	1.373	0.012	0.029	0.019	
		CCC	110.7	110.2	-0.5	-0.4	-0.6	
CO ₂	Carbon dioxide	CO	1.162	1.181	0.019	0.024	0.027	b
CH ₂ O ₂	Formic acid	C = O	1.202	1.211	0.009	0.025	0.028	cc
		C - O	1.343	1.344	0.001	0.011	0.014	
		OCO	124.9	117.1	-7.8	-4.3	-7.3	
		OH	0.972	0.953	-0.019	-0.023	-0.001	
		HOC	106.3	111.6	5.3	9.9	4.3	
		CH	1.097	1.095	-0.002	0.008	0.006	
		HC - O	124.1	130.4	6.3	2.7	6.0	
C ₂ H ₂ O ₂	<i>trans</i> -Glyoxal	CO	1.207	1.207	0.000	0.013	0.022	aa
		CC	1.525	1.526	0.001	0.004	-0.017	
		CCO	121.2	120.5	-0.7	0.8	-0.2	
C ₆ H ₄ O ₂	<i>p</i> -Benzoquinone	C1C2	1.477	1.487	0.010	0.024	0.002	dd
		C2C3	1.322	1.335	0.013	0.027	0.016	
		CCC	121.1	121.6	0.5	1.0	0.8	
		CO	1.222	1.217	-0.005	0.004	0.014	
CN	Cyanide (+)	CN	1.290	1.355	0.065	-0.149	-0.164	a
CN	Cyanide	CN	1.175	1.157	-0.018	-0.022	-0.027	a
CHN	Hydrogen cyanide	CN	1.154	1.156	0.002	0.006	0.006	ee
		CH	1.063	1.070	0.007	-0.008	0.006	
CH ₅ N	Methylamine	CN	1.474	1.469	-0.005	-0.014	-0.042	ff
		NH	1.011	0.999	-0.012	-0.003	-0.011	
		HNC	112.0	109.8	-2.2	-2.2	-0.7	
		HNH	105.9	108.7	2.8	-0.4	3.1	
C ₂ H ₃ N	Acetonitrile	CC	1.458	1.440	-0.018	-0.006	-0.019	gg
		CH	1.104	1.098	-0.006	0.006	0.016	
		HCC	109.5	110.4	0.9	1.1	0.6	
		CN	1.157	1.159	0.002	0.005	0.006	
C ₂ H ₃ N	Methyl isocyanide	CN -	1.424	1.433	0.009	0.000	-0.029	gg
		CH	1.101	1.097	-0.004	0.014	0.024	
		HCN	109.1	109.7	0.6	1.1	1.0	
		-CN	1.166	1.181	0.015	0.025	0.015	
C ₃ H ₉ N	Trimethylamine	CN	1.451	1.480	0.029	0.013	-0.006	hh
		CNC	110.9	112.3	1.4	5.1	2.1	
C ₄ H ₅ N	Pyrrole	CN	1.370	1.397	0.027	0.028	0.022	i
		CNC	107.7	109.7	2.0	2.0	1.1	
		C3C2	1.382	1.390	0.008	0.013	0.020	
		CCC	109.8	107.0	-2.8	-2.4	-1.4	
		C4C3	1.417	1.390	-0.027	-0.022	-0.015	
CHNO	Hydrogen isocyanate	NH	0.987	0.985	-0.002	0.011	-0.002	a
		CN	1.207	1.251	0.044	0.042	0.025	
		CNH	128.1	123.7	-4.4	-7.9	-0.9	
		CO	1.171	1.181	0.010	0.014	0.031	
		OCN	180.0	168.7	-11.3	-12.5	-13.3	

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
CH ₃ NO	Formamide	CN	1.376	1.413	0.037	0.033	-0.009	ii
		NH	1.002	0.994	-0.008	-0.002	-0.016	
		CH	1.102	1.102	0.000	0.006	0.012	
		CO	1.193	1.217	0.024	0.032	0.050	
		OCN	123.8	118.5	-5.3	-2.7	-1.9	
C ₂ N ₂	Cyanogen	CN	1.154	1.159	0.005	0.008	0.008	b
		CC	1.389	1.382	-0.007	-0.011	-0.005	
C ₂ H ₆ N ₂	Dimethyldiazene	NN	1.254	1.228	-0.026	-0.032	-0.030	b
		CN	1.474	1.467	-0.007	0.000	-0.022	
		CNN	111.9	119.3	7.4	5.0	7.9	
C ₄ H ₄ N ₂	Pyrimidine	C4C5	1.393	1.396	0.003	0.016	0.015	kk
		N3C4	1.350	1.354	0.004	0.003	0.000	
		N3C4C5	121.2	120.7	-0.5	0.1	1.1	
		C2N3	1.328	1.357	0.029	0.029	0.033	
		C2H	1.082	1.098	0.016	0.016	0.028	
		C5H	1.087	1.094	0.007	0.000	0.008	
		C6H	1.079	1.096	0.017	0.016	0.026	
		CN	1.338	1.358	0.020	0.019	0.026	
C ₃ H ₃ N ₃	s-Triazine	NCN	126.8	121.6	-5.2	-3.4	-1.1	ll
CS	Carbon sulfide	CS	1.534	1.447	-0.087	-0.050		mm
CH ₂ S	Thioformaldehyde	CS	1.611	1.539	-0.072	-0.074		ii
		CH	1.093	1.095	0.002	-0.001	0.006	
		HCS	121.6	126.1	4.5	2.4	1.6	
CH ₄ S	Thiomethanol	CS	1.818	1.801	-0.017	-0.101		nn
		SH	1.329	1.306	-0.023	-0.027	-0.009	
		HSC	100.3	100.0	-0.3	2.1	1.0	
		HCSH	180.0	179.9	-0.1	-0.2	-0.1	
C ₂ H ₆ S	Dimethyl thioether	CS	1.802	1.802	0.000	-0.079		oo
		CSC	98.9	102.1	3.2	9.4	3.8	
		HCS	106.6	110.4	3.8	3.1	2.2	
		H'CS	106.6	106.0	-0.6	-0.6	-0.6	
C ₄ H ₄ S	Thiophene	CS	1.714	1.725	0.011	-0.035		pp
		CCS	92.2	91.4	-0.8	1.4	2.0	
		C3C2	1.370	1.366	-0.004	0.004	-0.003	
		CCC	111.5	112.1	0.6	0.4	-0.4	
CSO	Carbon oxysulfide	CO	1.159	1.176	0.017	0.022		qq
		CS	1.559	1.504	-0.055	-0.049	-0.065	
C ₂ H ₃ NS	Methyl isothiocyanate	CS	1.597	1.498	-0.099	-0.088		rr
		C=N	1.192	1.231	0.039	0.027	0.025	
		C-N	1.479	1.440	-0.039	-0.042	-0.072	
		C-N=C	141.6	139.4	-2.2	-0.3	-1.0	
C ₂ N ₂ S	Sulfur dicyanide	CN	1.157	1.164	0.007	0.007		ss
		CS	1.701	1.664	-0.037	-0.071	-0.067	
		NCS	170.0	176.5	6.5	7.0	7.4	
		CSC	98.4	101.5	3.1	5.1	3.4	
CS ₂	Carbon disulfide	CS	1.553	1.481	-0.072	-0.061		oo

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
C ₂ H ₆ S ₂	2,3-Dithiabutane	CS	1.810	1.804	-0.006	-0.085		tt
		SS	2.038	2.021	-0.017	-0.103	-0.108	
		CSS	102.8	109.2	6.4	5.2	3.4	
		CSSC	84.7	88.0	3.3	19.8	10.0	
		SSC	102.8	109.2	6.4	5.1	3.4	
CF	Fluoromethyldiyne	CF	1.266	1.259	-0.007	-0.003	-0.007	a
CHF	Fluoromethylene	CH	1.121	1.100	-0.021	-0.001	0.006	a
		CF	1.314	1.284	-0.030	-0.029	-0.023	
		FCH	101.6	105.6	4.0	9.5	9.0	
CH ₃ F	Fluoromethane	CH	1.098	1.092	-0.006	0.020	0.023	uu
		CF	1.382	1.351	-0.031	-0.035	-0.007	
		FCH	108.5	108.6	0.1	2.1	1.0	
C ₂ H ₃ F	Fluoroethylene	CC	1.333	1.333	0.000	0.018	0.007	vv
		CH(g)	1.076	1.093	0.017	0.023	0.028	
		CCH(g)	127.7	126.2	-1.5	-4.7	-3.8	
		CH(t)	1.085	1.085	0.000	0.002	0.011	
		CCH(t)	123.9	121.2	-2.7	-3.0	-3.1	
		CH(c)	1.090	1.086	-0.004	-0.003	0.006	
		CCH(c)	121.4	123.8	2.4	3.1	1.6	
		CF	1.348	1.338	-0.010	-0.024	0.003	
		FCC	121.0	122.0	1.0	2.3	2.2	
		C1C2	1.301	1.310	0.009	0.019	0.012	ww
		C1H	1.083	1.094	0.011	0.016	0.022	
C ₃ H ₃ F	Fluoroallene	HC1C2	124.3	124.8	0.5	-1.4	-1.4	
		C1F	1.360	1.340	-0.020	-0.035	-0.008	
		FC1C2	121.9	122.2	0.3	1.0	1.8	
		C2C3	1.309	1.294	-0.015	-0.006	-0.014	
		C3H	1.086	1.087	0.001	0.005	0.015	
		HC3C2	120.8	122.3	1.5	2.1	1.5	
CNF	Cyanogen fluoride	CN	1.159	1.159	0.000	0.001	0.006	xx
		CF	1.262	1.297	0.035	0.011	0.045	
CF ₂	Difluoromethylene	CF	1.300	1.298	-0.002	0.004	0.012	a
		FCF	104.9	106.3	1.4	3.4	1.1	
COF ₂	Carbonyl difluoride	CO	1.174	1.199	0.025	0.045	0.046	a
		CF	1.312	1.322	0.010	0.004	0.016	
		FCO	126.0	124.6	-1.4	-1.9	-1.5	
CSF ₂	Thiocarbonyl difluoride	CS	1.589	1.600	0.011	-0.014		oo
		CF	1.315	1.338	0.023	0.006	0.027	
		FCS	126.5	128.9	2.4	-0.5	1.1	
CHF ₃	Trifluoromethane	CH	1.098	1.110	0.012	0.038	0.032	a
		CF	1.333	1.346	0.013	0.020	0.035	
		FCH	110.3	113.1	2.8	1.2	2.7	
C ₂ NF ₃	Trifluoroacetonitrile	CC	1.461	1.487	0.026	0.037	0.025	a
		CF	1.335	1.350	0.015	0.020	0.036	
		CCF	111.4	113.4	2.0	0.5	2.1	
		CN	1.153	1.155	0.002	0.006	0.006	

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
CF ₄	Carbon tetrafluoride	CF	1.321	1.337	0.016	0.026	0.037	yy
C ₂ F ₄	Tetrafluoroethylene	CC	1.311	1.355	0.044	0.070	0.057	vv
		CF	1.319	1.326	0.007	-0.001	0.021	
		FCC	123.8	125.1	1.3	0.4	1.6	
C ₂ F ₆	Hexafluoroethane	CC	1.560	1.608	0.048	0.114	0.061	a
		CF	1.320	1.341	0.021	0.026	0.043	
		FCC	109.5	111.4	1.9	1.2	2.6	
CHCl	Chloromethylene	CH	1.120	1.100	-0.020	-0.020	-0.010	a
		CCl	1.689	1.554	-0.135	0.050	-0.042	
		CiCH	103.4	115.5	12.1	6.0	7.7	
CH ₃ Cl	Chloromethane	CCl	1.781	1.764	-0.017	0.014	-0.040	a
		CH	1.096	1.094	-0.002	0.006	0.016	
		HCCl	110.9	109.9	-1.0	-2.8	-2.6	
CHF ₂ Cl	Chlorodifluoromethane	CH	1.090	1.108	0.018	0.036	0.037	zz
		CCl	1.740	1.822	0.082	0.099	0.069	
		CiCH	107.0	109.9	2.9	-2.2	-1.8	
		CF	1.350	1.346	-0.004	-0.008	0.019	
		FCCl	110.5	110.1	-0.4	-0.4	1.9	
		FCCiH	120.0	122.6	2.6	1.0	2.0	
CH ₂ Cl ₂	Dichloromethane	CCl	1.772	1.758	-0.014	0.014	-0.031	yy
		CiCCl	111.8	107.9	-3.9	-0.6	1.2	
		CH	1.103	1.102	-0.001	0.000	0.010	
COCl ₂	Carbonyl chloride	CO	1.166	1.198	0.032	0.034	0.056	a
		CCl	1.746	1.737	-0.009	0.014	-0.027	
		CiCO	124.4	124.2	-0.2	-0.5	-1.1	
CF ₂ Cl ₂	Dichlorodifluoro- methane	CCl	1.770	1.808	0.038	0.055	0.037	a
		CiCCl	108.5	106.6	-1.9	-1.7	-1.8	
		CF	1.330	1.345	0.015	0.007	0.040	
		FCCl	109.8	111.4	1.6	0.8	2.1	
CHCl ₃	Chloroform	CCl	1.782	1.753	-0.029	0.000	-0.034	yy
		CiCH	107.5	110.4	2.9	1.1	0.2	
CFCl ₃	Trichlorofluoromethane	CF	1.330	1.349	0.019	-0.003	0.046	a
		CCl	1.760	1.779	0.019	0.046	0.026	
CCl ₄	Carbon tetrachloride	CCl	1.760	1.747	-0.013	0.022	0.000	yy
C ₂ Cl ₆	Hexachloroethane	CC	1.550	1.512	-0.038	0.016	0.007	a
		CCl	1.740	1.754	0.014	0.050	0.020	
		CiCC	109.0	110.2	1.2	2.4	0.7	
CH ₃ Br	Bromomethane	CBr	1.933	1.951	0.018	-0.055	-0.028	oo
		CH	1.086	1.090	0.004	0.016	0.024	
		HCBBr	107.7	108.4	0.7	0.8	1.1	
C ₂ H ₃ OBr	Acetyl bromide	CC	1.516	1.477	-0.039	-0.001	-0.026	oo
		CBr	1.973	1.966	-0.007	-0.086	-0.026	
		BrCC	111.0	106.3	-4.7	2.0	2.3	
		CO	1.183	1.185	0.002	0.026	0.042	
		CCO	127.1	134.3	7.2	0.2	-3.0	

TABLE 10 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
CNBr	Cyanogen bromide	BrC	1.789	1.796	0.007	-0.046	-0.029	a
		CN	1.158	1.155	-0.003	0.003	0.006	
CF ₃ Br	Trifluorobromomethane	CBr	1.909	1.960	0.051	0.029	0.134	a
		CF	1.328	1.335	0.007	0.019	0.039	
		FCBr	110.3	110.8	0.5	0.8	3.4	
CH ₂ Br ₂	Dibromomethane	CH	1.079	1.095	0.016	0.023	0.031	oo
		HCH	113.6	111.4	-2.2	-2.7	-3.3	
		CBr	1.927	1.912	-0.015	-0.059	-0.025	
		BrCH	106.5	112.5	6.0	2.0	1.7	
C ₄ O ₂ Br ₂	1,2-Dibromocyclobu- tene-3,4-dione	C = C2	1.356	1.343	-0.013	0.008	0.015	aaa
C ₂ Br ₄	Tetrabromoethylene	CC	1.362	1.450	0.088	-0.020	-0.018	oo
		CBr	1.881	1.865	-0.016	-0.060	-0.024	
		BrCC	122.4	111.9	-10.5	1.3	0.0	
CH ₃ I	Iodomethane	CH	1.084	1.093	0.009	0.020	0.025	oo
		CI	2.132	2.028	-0.104	-0.117	-0.082	
		HCH	111.2	109.9	-1.3	-2.8	-1.4	
CNI	Cyanogen iodide	CN	1.159	1.155	-0.004	0.005	0.003	a
		CI	1.994	1.908	-0.086	-0.103	-0.067	
CF ₃ I	Trifluoroiodomethane	CI	2.130	2.052	-0.078	-0.005	0.045	a
		CF	1.332	1.340	0.008	0.022	0.037	
		FCI	110.6	112.1	1.5	1.9	3.5	
CP	Carbon phosphide	CP	1.562	1.389	-0.173	-0.145	-0.029	a

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TABLE 11
COMPARISON OF EXPERIMENTAL AND CALCULATED MOLECULAR GEOMETRIES FOR INORGANIC MOLECULES

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
H ₂	Hydrogen	HH	0.741	0.699	-0.042	-0.078	-0.064	a
H ₂ O	Water	OH	0.957	0.951	-0.006	-0.014	0.004	b
		HOH	104.5	107.7	3.2	2.3	-1.0	
O ₂	Oxygen, triplet state	OO	1.216	1.169	-0.047	-0.082	-0.130	c
H ₂ O ₂	Hydrogen peroxide	OO	1.475	1.482	0.007	-0.179	-0.175	d
		OH	0.950	0.945	-0.005	0.011	0.033	
		HOO	94.8	96.5	1.7	12.2	11.2	
		HOOH	119.8	180.0	60.2	60.5	8.1	
H ₄ O ₂	Water dimer	OO	3.000	2.769	-0.231	0.905	-0.383	
H ₃ N	Ammonia	NH	1.012	0.999	-0.013	-0.005	-0.014	a
		HNH	106.7	108.1	1.4	-1.4	2.4	
NO	Nitrogen oxide	NO	1.151	1.127	-0.024	-0.028	-0.036	a
NO ₂	Nitrogen dioxide	NO	1.197	1.181	-0.016	-0.023	-0.038	a
		ONO	136.0	137.8	1.8	-2.8	0.4	
		N-O	1.460	1.339	-0.121	-0.163	-0.169	a
HNO ₂	Nitrous acid (<i>cis</i>)	N=O	1.200	1.175	-0.025	-0.031	-0.038	
		ONO	114.0	113.3	-0.7	3.1	2.6	
		OH	0.980	0.960	-0.020	-0.017	0.003	
		HON	103.0	109.9	6.9	16.7	12.5	
		N-O	1.460	1.383	-0.077	-0.148	-0.141	a
HNO ₂	Nitrous acid (<i>trans</i>)	N=O	1.200	1.167	-0.033	-0.034	-0.042	
		ONO	118.0	109.1	-8.9	-4.7	-5.2	
		OH	0.980	0.950	-0.030	-0.022	-0.005	
		HON	105.0	104.6	-0.4	5.0	2.0	
		N=O	1.206	1.203	-0.003	0.005	-0.011	a
HNO ₃	Nitric acid	O=N=O	130.0	132.7	2.7	-3.5	-1.0	
		N-O	1.405	1.410	0.005	-0.065	-0.072	
		OH	0.960	0.953	-0.007	0.002	0.022	
		NOH	102.0	109.0	7.0	12.0	7.7	
		N=O	1.206	1.203	-0.003	0.005	-0.011	a
N ₂	Nitrogen	NN	1.094	1.098	0.004	0.010	0.012	c
H ₄ N ₂	Hydrazine	NN	1.449	1.440	-0.009	-0.052	-0.071	a
		NH	1.022	1.001	-0.021	-0.001	-0.008	
		HNN	112.0	106.5	-5.5	-4.8	-4.6	
		HNNH	90.0	180.3	90.3	90.2	90.2	
		NN	1.128	1.124	-0.004	0.000	0.000	a
N ₂ O	Nitrous oxide	NO	1.184	1.197	0.013	-0.003	-0.009	
H ₂ N ₂ O ₂	NH ₂ -NO ₂	NN	1.427	1.431	0.004	-0.020	-0.060	e
		NO	1.206	1.211	0.005	0.003	-0.002	
		NH	1.005	1.000	-0.005	0.013	-0.003	
		ONO	130.1	127.2	-2.9	-6.0	-6.1	
		NN	2.080	1.409	-0.671	-0.706	-0.728	a
N ₂ O ₃	Dinitrogen trioxide	NO	1.100	1.172	0.072	0.063	0.061	
		NNO	110.0	118.2	8.2	11.0	12.8	
		NO'	1.180	1.268	0.088	0.079	0.101	
		O'NO'	134.0	150.4	16.4	14.8	13.5	
		NN	2.080	1.409	-0.671	-0.706	-0.728	a

TABLE 11 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
N ₂ O ₄	Dinitrogen tetroxide	NN	1.750	1.759	0.009	-0.135	0.068	a
		NO	1.180	1.195	0.015	0.009	-0.008	
		ONN	113.2	114.6	1.4	2.1	1.0	
N ₃	Azide	NN	1.181	1.174	-0.007	-0.007	-0.004	a
H ₂ S	Hydrogen sulfide	HS	1.328	1.290	-0.038	-0.028		a
		HSH	92.2	93.5	1.3	5.9	6.6	
SO ₂	Sulfur dioxide	SO	1.432	1.442	0.010	0.044		a
		OSO	119.5	106.1	-13.4	-12.7	-16.6	
SO ₃	Sulfur trioxide	SO	1.430	1.384	-0.046	0.061		a
H ₂ SO ₄	Sulfuric acid	S-O	1.550	1.668	0.118	0.078		a
		OH	0.970	0.947	-0.023	-0.023	-0.006	
		SOH	105.0	117.7	12.7	12.2	1.5	
		S=O	1.420	1.668	0.248	0.209	0.287	
NS	Sulfur nitride	SN	1.495	1.452	-0.043	-0.055		a
S ₂	Sulfur dimer	SS	1.889	1.857	-0.032	-0.114		a
H ₂ S ₂	H ₂ S ₂	SS	2.055	2.034	-0.021	-0.131		f
		SH	1.327	1.311	-0.016	-0.023	-0.005	
		HSS	91.3	103.2	11.9	11.2	9.9	
		HSSH	90.5	93.4	2.9	9.1	21.7	
		SS	2.057	2.048	-0.009	-0.110		
S ₆	S ₆	SSS	102.2	107.5	5.3	2.9	2.9	g
		SSSS	74.5	64.6	-9.9	-5.1	-5.0	
		SS	2.048	1.973	-0.075	-0.113		
S ₈	S ₈	SSS	107.9	116.0	8.1	0.4	0.4	h
		SSSS	98.6	87.6	-11.0	-0.2	-0.2	
		SS	2.048	1.973	-0.075	-0.113		
HF	Hydrogen fluoride	HF	0.917	0.938	0.021	0.039	-0.091	i
NOF	Nitrosyl fluoride	NF	1.520	1.367	-0.153	-0.215	-0.153	a
		NO	1.130	1.162	0.032	0.031	0.018	
		FNO	110.2	111.6	1.4	3.7	2.1	
F ₂	Fluorine	FF	1.412	1.350	-0.062	-0.146	0.015	a
H ₂ F ₂	Hydrogen fluoride dimer	HF	0.920	0.939	0.019	0.036	-0.093	a
		H'F	1.870	1.743	-0.127	1.093	0.417	
		H'FH	108.0	147.0	39.0	71.5	-18.1	
OF ₂	F ₂ O	OF	1.412	1.378	-0.034	-0.131	-0.058	a
		FOF	103.2	100.9	-2.3	5.9	-0.7	
SF ₂	Sulfur difluoride	SF	1.592	1.560	-0.032	-0.020		a
		FSF	98.2	96.5	-1.7	1.3	-1.3	
SOF ₂	Thionyl fluoride	SO	1.412	1.467	0.055	0.068		a
		SF	1.585	1.574	-0.011	0.023	0.058	
		FSO	106.8	101.0	-5.8	-3.9	-7.0	
		FSF	92.8	93.9	1.1	4.2	2.0	
SO ₂ F ₂	Sulfuryl fluoride	SF	1.530	1.547	0.017	0.080		a
		FSF	96.1	95.3	-0.8	1.7	1.1	
		SO	1.405	1.400	-0.005	0.103	0.171	
		OSO	124.0	126.4	2.4	0.8	3.5	

TABLE 11 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
S ₂ F ₂	FSSF	SF	1.635	1.584	-0.051	-0.063		a
		SS	1.888	2.008	0.120	0.078	0.060	
		FSS	108.3	112.0	3.7	-1.8	-2.1	
		FSSF	87.9	87.4	-0.5	-1.3	-0.8	
S ₂ F ₂	SSF ₂	SS	1.860	1.919	0.059	0.035		a
		SF	1.598	1.592	-0.006	0.003	0.054	
		FSS	107.5	114.5	7.0	1.4	1.3	
		FSF	92.5	90.8	-1.7	3.9	0.2	
NF ₃	Nitrogen trifluoride	NF	1.371	1.354	-0.017	-0.056	-0.011	a
		FNF	102.2	105.0	2.8	4.0	0.4	
SF ₄	Sulfur tetrafluoride	SF	1.545	1.633	0.088	0.061		a
		FSF	101.6	81.0	-20.6	-13.0	-18.6	
		SF'	1.646	1.591	-0.055	-0.005	0.022	
		FSF'	87.8	81.0	-6.8	0.9	-4.8	
SF ₆	Sulfur hexafluoride	SF	1.564	1.560	-0.004	0.091		a
HCl	Hydrogen chloride	HCl	1.275	1.268	-0.007	0.073	0.009	a
OCl	Chlorine monoxide	ClO	1.546	1.548	0.002	0.073	0.090	a
NOCl	NOCl	CIN	1.950	1.764	-0.186	-0.167	-0.219	a
		NO	1.170	1.156	-0.014	-0.033	-0.033	
		CNCl	114.0	118.9	4.9	3.5	5.4	
NO ₂ Cl	NO ₂ Cl	CIN	1.830	1.818	-0.012	-0.020	-0.059	a
		NOCl	1.210	1.197	-0.013	-0.019	-0.024	
		ClF	1.628	1.582	-0.046	0.022	0.019	a
O ₃ FCI	ClO ₃ F	ClF	1.630	1.690	0.060	0.105	0.051	a
		ClO	1.460	1.453	-0.007	0.270	0.328	
		OCIF	95.2	102.8	7.6	11.0	3.0	
F ₃ Cl	Chlorine trifluoride C _{2v}	ClF	1.598	1.671	0.073	0.101	0.085	a
		ClF'	1.698	1.671	-0.027	0.001	-0.015	
		FCIF'	87.5	120.0	32.5	32.5	32.5	
		ClCl	1.986	2.035	0.049	0.010	-0.068	a
Cl ₂	Chlorine	ClO	1.701	1.700	-0.001	-0.018	0.032	a
		ClOCl	110.8	109.2	-1.6	2.1	0.3	
		SCl	2.015	2.031	0.016	-0.043		a
SOCl ₂	Thionyl chloride	ClSCl	102.7	101.6	-1.1	3.6	3.1	j
		SO	1.443	1.479	0.036	0.026		
		SCl	2.076	2.080	0.004	-0.038	-0.102	
		ClSO	106.3	104.7	-1.6	0.3	-0.2	
S ₂ Cl ₂	ClSSCl	SCl	2.057	2.044	-0.013	-0.081		a
		SS	1.931	1.965	0.034	-0.011	-0.004	
		ClSSCl	108.2	113.1	4.9	0.0	-0.3	
		SCl	2.057	2.044	-0.013	-0.081		
HBr	Hydrogen bromide	HBr	1.415	1.471	0.056	0.025	0.006	k
NOBr	BrNO	BrN	2.140	1.888	-0.252	-0.271	-0.218	l
		NO	1.146	1.147	0.001	-0.007	-0.011	
		BrNO	114.5	120.8	6.3	4.4	8.0	
FBr	BrF	BrF	1.755	1.774	0.019	-0.029	0.022	a

TABLE 11 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
F ₃ Br	Bromine trifluoride	BrF	1.721	1.786	0.065	0.036	0.087	a
		BrF'	1.806	1.786	-0.020	-0.049	0.010	
		FBrF'	86.2	120.0	33.8	33.8	-4.8	
F ₅ Br	Bromine pentafluoride	BrF(ax)	1.680	1.755	0.075	0.086	0.134	a
		BrF(eq)	1.790	1.774	-0.016	-0.019	0.014	
ClBr	Bromine chloride	BrCl	2.136	2.176	0.040	-0.056	-0.072	a
Br ₂	Bromine	BrBr	2.283	2.443	0.160	-0.115	-0.099	a
HI	Hydrogen iodide	HI	1.609	1.677	0.068	-0.042	-0.022	k
FI	Iodine fluoride	IF	1.906	1.889	-0.017	-0.004	-0.025	a
F ₅ I	Iodine pentafluoride	IF(ax)	1.844	1.867	0.023	0.139	0.087	m
		IF(eq)	1.869	1.882	0.013	0.088	0.029	
		F(ax)IF(eq)	81.9	102.6	20.7	-3.8	-4.6	
F ₇ I	Iodine heptafluoride	IF(ax)	1.760	2.698	0.938	0.731	0.866	n
		IF(eq)	1.860	1.913	0.053	0.218	0.114	
ClI	Iodine chloride	ICl	2.327	2.192	-0.135	-0.065	-0.109	a
BrI	Iodine bromide	IBr	2.485	2.561	0.076	-0.135	-0.131	a
I ₂	Iodine	II	2.666	2.668	0.002	-0.151	-0.128	a
HAi	AlH	AlH	1.648	1.663	0.015	-0.222		a
AlO	AlO	AlO	1.618	1.533	-0.085	-0.143		a
AlF	Aluminum fluoride	AlF	1.654	1.652	-0.002	-0.094		a
AlF ₃	Aluminum trifluoride	AlF	1.630	1.644	0.014	-0.038		a
AlF ₄	AlF ₄ (-)	AlF	1.690	1.688	-0.002	-0.041		a
AlCl	Aluminum chloride	AlCl	2.130	1.947	-0.183	-0.055		a
AlCl ₃	Aluminum trichloride	AlCl	2.060	1.966	-0.094	0.005		a
AlBr	Aluminum bromide	AlBr	2.295	2.292	-0.003	-0.093		a
AlBr ₃	Aluminum tribromide	AlBr	2.270	1.875	-0.395	-0.095		a
AlI ₃	Aluminum triiodide	AlI	2.499	2.487	-0.012	-0.174		a
Al ₂	Al ₂	AlAl	2.467	2.554	0.087	-0.175		a
Al ₂ O	Al ₂ O	AlO	1.730	1.677	-0.053	-0.124		a
H ₂ Si	Silylene (singlet)	SiH	1.519	1.513	-0.006	-0.139	-0.062	o
		HSiH	92.1	94.9	2.8	5.2	8.9	
H ₄ Si	Silane	SiH	1.481	1.488	0.007	-0.105	-0.020	a
SiN	Silicon nitride	SiN	1.572	1.464	-0.108	-0.021	-0.087	a
SiF ₂	Difluorosilylene	SiF	1.591	1.575	-0.016	-0.013	0.021	a
		FSiF	101.0	95.3	-5.7	-4.1	-3.9	
HSiF ₃	Trifluorosilane	SiH	1.447	1.507	0.060	-0.072	-0.007	a
		SiF	1.562	1.590	0.028	0.031	0.047	
		FSiH	110.6	112.6	2.0	3.0	1.2	
SiF ₄	Tetrafluorosilane	SiF	1.552	1.580	0.028	0.032	0.052	a
SiCl	Chlorosilyldiyne	SiCl	2.063	1.946	-0.117	0.009	-0.077	a
SiCl ₂	Dichlorosilylene	ClSiCl	109.7	101.9	-7.8	-4.2	-5.3	p
SiCl ₄	Silicon tetrachloride	SiCl	2.017	2.041	0.024	0.063	0.022	a
H ₃ SiBr	Bromosilane	SiBr	2.210	1.901	-0.309	0.018	0.030	l
		SiH	1.481	1.491	0.010	-0.113	-0.016	
		HSiBr	107.9	108.3	0.4	-1.0	2.4	
SiBr ₄	Silicon tetrabromide	SiBr	2.150	1.796	-0.354	0.040	0.093	a

TABLE 11 (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Ref.
					PM3	MNDO	AM1	
H ₃ SiI	Iodosilane	SiI	2.437	2.012	-0.425	-0.051	-0.003	a
		SiH	1.486	1.492	0.006	-0.116	-0.020	
		HSiI	108.5	108.0	-0.5	-0.1	1.3	
SiI ₄	Silicon tetraiodide	SiI	2.430	2.467	0.037	-0.097	-0.005	a
Si ₂	Silicon dimer	SiSi	2.246	2.297	0.051	-0.259	-0.019	a
H ₆ Si ₂	Disilane	SiSi	2.331	2.396	0.065	-0.158	0.086	q
		SiH	1.492	1.487	-0.005	-0.113	-0.026	
		HSiSi	110.3	109.7	-0.6	0.9	-0.7	
H ₃ P	Phosphine	PH	1.420	1.324	-0.096	-0.080	-0.057	a
		HPH	93.8	97.1	3.3	2.3	2.7	
PO	Phosphorus oxide	PO	1.476	1.459	-0.017	-0.053	-0.039	a
PF ₃	Phosphorus trifluoride	PF	1.570	1.558	-0.012	-0.014	-0.027	a
		FPF	97.8	95.8	-2.0	1.1	0.2	
PF ₅	Phosphorus pentafluoride	PF(ax)	1.577	1.553	-0.024	0.025	-0.028	a
		PF(eq)	1.534	1.528	-0.006	0.039	0.001	
		PCl	2.039	2.064	0.025	-0.050	-0.120	a
PCl ₃	Phosphorus trichloride	CIPCl	100.3	99.7	-0.6	4.9	5.1	
PCl ₅	Phosphorus pentachloride	PCl(ax)	2.190	2.093	-0.097	-0.078	-0.115	a
		PCl(eq)	2.040	2.052	0.012	-0.007	-0.069	
PBr ₃	Phosphorus tribromide	PBR	2.220	2.150	-0.070	-0.131	-0.119	l
		BrPBr	101.0	101.3	0.3	4.7	5.8	
P ₂	Phosphorus dimer	PP	1.894	1.715	-0.179	-0.200	-0.271	a
P ₄	Phosphorus tetramer	PP	2.210	2.197	-0.013	-0.158	-0.170	a
P ₄ O ₆	Phosphorus trioxide	PO	1.650	1.708	0.058	-0.046		a
		OPO	99.0	96.5	-2.5	-3.0		

References to Table 11

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TABLE 12 UNSIGNED AVERAGE ERRORS IN BOND LENGTHS (Å)

		H	C	N	O	F	Al	Si	P	S	Cl	Br	I
	H	1											
PM3		0.042											
MNDO		0.078											
AM1		0.064											
	C	50	72										
PM3		0.009	0.017										
MNDO		0.010	0.014										
AM1		0.015	0.017										
	N	7	21	8									
PM3		0.011	0.018	0.092									
MNDO		0.139	0.022	0.120									
AM1		0.051	0.024	0.122									
	O	8	18	18	3								
PM3		0.014	0.012	0.034	0.095								
MNDO		0.014	0.021	0.085	0.389								
AM1		0.012	0.030	0.062	0.229								
	F	3	19	2	1	1							
PM3		0.056	0.015	0.085	0.034	0.062							
MNDO		0.389	0.016	0.135	0.131	0.146							
AM1		0.200	0.026	0.082	0.058	0.015							
	Al	1			2	3	1						
PM3		0.015			0.069	0.006	0.087						
MNDO		0.222			0.133	0.058	0.175						
	Si	6	1	1		3		2					
PM3		0.016	0.011	0.108		0.024		0.058					
MNDO		0.110	0.064	0.021		0.025		0.209					
AM1		0.025	0.050	0.087		0.040		0.052					
	P	1	1		2	3			2				
PM3		0.096	0.173		0.038	0.014			0.096				
MNDO		0.080	0.145		0.050	0.026			0.179				
AM1		0.057	0.029		(see text)	0.019			0.221				
	S	3	10	1	7	8				8			
PM3		0.026	0.047	0.043	0.074	0.033				0.046			
MNDO		0.026	0.063	0.055	0.084	0.043				0.087			
	Cl	1	10	2	3	4	2	2	3	3	1		
PM3		0.007	0.037	0.099	0.003	0.052	0.138	0.070	0.045	0.011	0.049		
MNDO		0.073	0.036	0.093	0.120	0.057	0.030	0.036	0.045	0.054	0.010		
AM1		0.009	0.033	0.139	0.150	0.042		0.049	0.101		0.068		
	Br	1	6	1		5	2	2	1		1	1	
PM3		0.056	0.019	0.252		0.039	0.199	0.332	0.070		0.040	0.160	
MNDO		0.025	0.056	0.271		0.044	0.094	0.029	0.131		0.056	0.115	
AM1		0.006	0.044	0.218		0.053		0.061			0.072	0.099	
	I	1	3			5	1	2			1	1	1
PM3		0.068	0.089			0.209	0.012	0.231			0.135	0.076	0.002
MNDO		0.042	0.075			0.236	0.174	0.074			0.065	0.135	0.151
AM1		0.022	0.065			0.224		0.004			0.109	0.131	0.128

TABLE 13 SIGNED AVERAGE ERRORS IN BOND LENGTHS (Å)

		H	C	N	O	F	Al	Si	P	S	Cl	Br	I
	H	1											
PM3		-0.04											
MNDO		-0.08											
AM1		-0.06											
	C	50	72										
PM3		0.00	-0.01										
MNDO		0.01	0.00										
AM1		0.01	-0.01										
	N	7	21	8									
PM3		-0.01	0.01	-0.09									
MNDO		0.14	0.00	-0.12									
AM1		0.04	-0.01	-0.10									
	O	8	18	18	3								
PM3		-0.01	0.01	0.00	-0.09								
MNDO		-0.01	0.02	0.02	0.21								
AM1		0.01	0.03	-0.01	-0.23								
	F	3	19	2	1	1							
PM3		-0.03	0.00	-0.08	-0.03	-0.06							
MNDO		0.39	0.00	-0.14	-0.13	-0.15							
AM1		0.08	0.02	-0.08	-0.06	0.01							
	Al	1			2	3	1						
PM3		0.02			-0.07	0.00	0.09						
MNDO		-0.22			-0.13	-0.06	-0.18						
	Si	6	1	1		3		2					
PM3		0.01	0.01	-0.11		0.01		0.06					
MNDO		-0.11	-0.06	-0.02		0.02		-0.21					
AM1		-0.03	-0.05	-0.09		0.04		0.03					
	P	1	1		2	3			2				
PM3		-0.10	-0.17		0.02	-0.01			-0.10				
MNDO		-0.08	-0.14		-0.05	0.02			-0.18				
AM1		-0.06	-0.03		(see text)	-0.02			-0.22				
	S	3	10	1	7	8				8			
PM3		-0.03	-0.04	-0.04	0.06	-0.01				0.01			
MNDO		-0.03	-0.06	-0.05	0.08	0.02				-0.06			
	Cl	1	10	2	3	4	2	2	3	3	1		
PM3		-0.01	-0.01	-0.10	0.00	0.01	-0.14	-0.05	-0.02	0.00	0.05		
MNDO		0.07	0.04	-0.09	0.11	0.06	-0.02	0.04	-0.05	-0.05	0.01		
AM1		0.01	0.00	-0.14	0.15	0.03		-0.03	-0.10		-0.07		
	Br	1	6	1		5	2	2	1		1	1	
PM3		0.06	0.01	-0.25		0.02	-0.20	-0.33	-0.07		0.04	0.16	
MNDO		0.02	-0.05	-0.27		0.00	-0.09	0.03	-0.13		-0.06	-0.11	
AM1		0.01	0.00	-0.22		0.05		0.06	-0.12		-0.07	-0.10	
	I	1	3			5	1	2			1	1	1
PM3		0.07	-0.09			0.20	-0.01	-0.19			-0.14	0.08	0.00
MNDO		-0.04	-0.08			0.23	-0.17	-0.07			-0.07	-0.14	-0.15
AM1		-0.02	-0.03			0.21		0.00			-0.11	-0.13	-0.13

TABLE 14
AVERAGE ERRORS IN CALCULATED GEOMETRIES

In bonds involving		No.	Average error (Å) in bond lengths			
			PM3	MNDO	AM1 ^a	
Hydrogen		83	0.005	0.015	0.006	
Carbon		211	0.002	0.002	0.002	
Nitrogen		61	0.012	0.015	0.014	
Oxygen		62	0.006	0.017	0.011	
Fluorine		57	0.011	0.023	0.017	
Aluminum		12	0.044	0.074		
Silicon		19	0.045	0.030	0.019	
Phosphorus		13	0.041	0.050	0.044	
Sulfur		40	0.007	0.010		
Chlorine		33	0.021	0.020	0.028	
Bromine		21	0.059	0.046	0.042	
Iodine		15	0.055	0.063	0.049	

Atoms				No.	Average error (degrees) in bond angles					
					PM3		MNDO		AM1	
					Unsigned	Signed	Unsigned	Signed	Unsigned	Signed
H	C	H		4	1.200	-0.550	4.775	2.025	4.100	1.750
H	C	C		19	1.342	0.826	1.658	0.468	1.342	0.237
H	C	O		3	3.333	3.333	2.733	2.733	2.933	2.933
H	C	F		3	2.300	2.300	4.267	4.267	4.233	4.233
H	C	Cl		4	4.725	4.225	3.025	0.525	3.075	0.875
H	C	Br		2	3.350	3.350	1.400	1.400	1.400	1.400
C	C	C		16	2.319	1.581	4.137	4.013	2.431	2.144
C	C	O		4	2.100	1.500	0.725	0.525	0.950	-0.950
C	C	F		5	1.300	1.300	1.080	1.080	2.060	2.060
C	C	Br		2	7.600	-7.600	1.650	1.650	1.150	1.150
N	C	O		2	8.300	-8.300	7.600	-7.600	7.600	-7.600
F	C	Cl		2	1.000	0.600	0.600	0.200	2.000	2.000
Cl	C	Cl		2	2.900	-2.900	1.150	-1.150	1.500	-0.300
H	N	H		2	2.100	2.100	0.900	-0.900	2.750	2.750
H	N	C		2	3.300	-3.300	5.050	-5.050	0.800	-0.800
C	N	C		3	1.867	0.400	2.467	2.267	1.400	0.733
N	N	O		3	8.667	8.667	9.300	9.300	9.100	9.100
O	N	O		5	3.400	-1.600	4.020	-2.780	3.060	-1.860
H	O	C		2	2.900	2.900	7.250	7.250	2.250	2.250
H	O	N		3	4.767	4.500	11.233	11.233	7.400	7.400
C	O	C		2	1.550	1.550	4.850	4.850	0.800	0.800
C	S	C		2	1.950	1.150	3.250	3.250		
C	S	S		2	6.400	6.400	5.150	5.150		
O	S	O		2	7.900	-5.500	6.750	-5.950		
F	S	F		6	5.450	-5.083	4.167	-0.167		
F	S	S		2	5.350	5.350	1.600	-0.200		
S	S	S		2	6.700	6.700	1.650	1.650		

^a AM1 results are for systems which do not include aluminum or sulfur.

TABLE 15
COMPARISON OF EXPERIMENTAL AND CALCULATED DIPOLE MOMENTS

Empirical formula	Chemical name	Dipole moment		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₃ H ₄	Cyclopropene	0.45	0.39	−0.06	0.03	−0.09	a
C ₃ H ₄	Propyne	0.78	0.36	−0.42	−0.66	−0.38	a
C ₃ H ₆	Propene	0.37	0.23	−0.14	−0.33	−0.14	a
C ₃ H ₈	Propane	0.08	0.01	−0.07	−0.08	−0.08	a
C ₄ H ₆	Bicyclobutane	0.68	0.43	−0.25	−0.27	−0.26	a
C ₄ H ₆	Cyclobutene	0.13	0.15	0.02	−0.05	0.04	a
C ₅ H ₆	Cyclopentadiene	0.42	0.53	0.11	−0.24	0.11	a
C ₅ H ₈	Cyclopentene	0.20	0.15	−0.05	−0.15	−0.03	a
C ₆ H ₆	Fulvene	0.42	0.66	0.24	0.27	0.27	b
C ₇ H ₈	Toluene	0.36	0.26	−0.10	−0.30	−0.10	a
H ₂ O	Water	1.85	1.74	−0.11	−0.07	0.01	a
CO	Carbon monoxide	0.11	0.18	0.07	0.09	−0.05	a
CH ₂ O	Formaldehyde	2.33	2.16	−0.17	−0.17	−0.01	a
CH ₄ O	Methanol	1.70	1.49	−0.21	−0.22	−0.08	a
C ₂ H ₂ O	Ketene	1.42	1.06	−0.36	−0.38	−0.07	a
C ₂ H ₄ O	Acetaldehyde	2.69	2.54	−0.15	−0.31	0.00	a
C ₂ H ₄ O	Ethylene oxide	1.89	1.77	−0.12	0.03	0.02	a
C ₂ H ₆ O	Ethanol	1.69	1.45	−0.24	−0.29	−0.14	a
C ₂ H ₆ O	Dimethyl ether	1.30	1.25	−0.05	−0.03	0.13	a
C ₃ H ₂ O	Propynal	2.47	2.62	0.15	0.38	0.35	a
C ₃ H ₄ O	Acrolein	3.12	2.36	−0.76	−0.66	−0.59	a
C ₃ H ₆ O	Acetone	2.88	2.78	−0.10	−0.37	0.04	a
C ₄ H ₄ O	Furan	0.66	0.22	−0.44	−0.24	−0.17	a
C ₄ H ₁₀ O	Diethyl ether	1.15	1.33	0.18	0.21	0.30	a
C ₆ H ₆ O	Phenol	1.45	1.14	−0.31	−0.29	−0.22	a
C ₇ H ₈ O	Anisole	1.38	1.08	−0.30	−0.31	−0.13	a
CH ₂ O ₂	Formic acid	1.41	1.51	0.10	0.08	0.07	a
C ₂ H ₄ O ₂	Acetic acid	1.74	1.83	0.09	−0.06	0.12	a
C ₂ H ₄ O ₂	Methyl formate	1.77	1.59	−0.18	−0.15	−0.26	a
C ₃ H ₆ O ₂	Propionic acid	1.75	1.81	0.06	−0.04	0.08	a
C ₃ H ₆ O ₂	Methyl acetate	1.72	1.82	0.10	0.03	0.02	a
O ₃	Ozone	0.53	1.71	1.18	0.65	0.67	a
H ₃ N	Ammonia	1.47	1.55	0.08	0.28	0.38	a
CHN	Hydrogen cyanide	2.98	2.70	−0.28	−0.48	−0.62	a
CH ₃ N	Methylamine	1.31	1.40	0.09	0.17	0.18	a
C ₂ H ₃ N	Acetonitrile	3.92	3.21	−0.71	−1.29	−1.03	a
C ₂ H ₃ N	Methyl isocyanide	3.85	3.69	−0.16	−1.68	−1.02	a
C ₂ H ₅ N	Ethyleneimine (Azirane)	1.90	1.69	−0.21	−0.15	−0.15	a
C ₂ H ₇ N	Ethylamine	1.22	1.43	0.21	0.30	0.33	a
C ₂ H ₇ N	Dimethylamine	1.03	1.27	0.24	0.14	0.20	a
C ₃ HN	CH ₃ CN	3.72	3.33	−0.39	−0.50	−0.68	a
C ₃ H ₃ N	Acrylonitrile	3.87	3.25	−0.62	−0.90	−0.87	a
C ₃ H ₉ N	Trimethylamine	0.61	1.15	0.54	0.14	0.41	a
C ₄ H ₅ N	Pyrrole	1.74	2.18	0.44	0.07	0.21	c
C ₅ H ₅ N	Pyridine	2.22	1.94	−0.28	−0.26	−0.25	d

TABLE 15 (continued)

Empirical formula	Chemical name	Dipole moment		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₆ H ₇ N	Aniline	1.53	1.30	-0.23	-0.07	0.01	a
CH ₃ NO	Formamide	3.73	3.12	-0.61	-0.62	-0.03	a
C ₂ H ₇ NO	Dimethylformamide	3.82	3.06	-0.76	-0.65	-0.27	a
HNO ₂	Nitrous acid, trans	1.86	2.08	0.22	0.42	0.45	e
HNO ₂	Nitrous acid, cis	1.42	1.27	-0.15	0.14	0.02	e
HNO ₃	Nitric acid	2.17	2.32	0.15	0.61	0.40	a
CH ₂ N ₂	Diazomethane	1.50	1.92	0.42	-0.25	-0.17	a
CH ₂ N ₂	N = N - CH ₂ -	1.59	1.87	0.28	-0.04	0.04	a
CH ₆ N ₂	Methylhydrazine	1.66	0.32	-1.34	-1.42	-0.89	f
N ₂ O	Nitrous oxide	0.17	0.26	0.09	0.59	0.47	a
CH ₃ N ₃	Methyl azide	2.17	2.28	0.11	-0.54	-0.23	a
H ₂ S	Hydrogen sulfide	0.97	1.78	0.81	0.51		g
CH ₂ S	Thioformaldehyde	1.65	2.07	0.42	0.88		h
CH ₄ S	Thiomethanol	1.52	1.95	0.43	0.01		g
C ₂ H ₆ S	Thioethanol	1.52	1.98	0.46	-0.04		g
C ₂ H ₆ S	Dimethyl thioether	1.50	1.96	0.46	0.07		h
C ₄ H ₄ S	Thiophene	0.53	0.67	0.14	0.01		g
CSO	Carbon oxysulfide	0.71	0.38	-0.33	-0.31		h
SO ₂	Sulfur dioxide	1.57	3.63	2.06	2.16		g
C ₂ H ₆ S ₂	2,3-Dithiabutane	1.98	2.57	0.59	-0.09		g
HF	Hydrogen fluoride	1.83	1.40	-0.43	0.16	-0.09	i
CH ₃ F	Fluoromethane	1.86	1.44	-0.42	-0.10	-0.24	j
C ₂ HF	Fluoroacetylene	0.70	1.11	0.41	0.88	0.36	k
C ₂ H ₃ F	Fluoroethylene	1.43	1.37	-0.06	0.27	-0.05	h
C ₂ H ₅ F	Fluoroethane	1.96	1.58	-0.38	-0.09	-0.27	h
C ₆ H ₅ F	Fluorobenzene	1.66	1.60	-0.06	0.30	-0.08	h
HO ₂ F	Hypofluorous acid	2.23	1.68	-0.55	-0.42	-0.63	l
CHOF	HCOF	2.02	2.46	0.44	0.48	0.55	h
CNF	Cyanogen fluoride	2.17	1.63	-0.54	-1.28	-0.96	k
NOF	Nitrosyl fluoride	1.81	0.26	-1.55	-1.30	-1.43	h
NO ₂ F	Fluorine nitrite	0.47	0.89	0.42	0.19	0.35	g
CH ₂ F ₂	Difluoromethane	1.96	1.81	-0.15	0.26	0.08	h
C ₂ H ₄ F ₂	1,1-Difluoroethane	2.30	2.12	-0.18	0.20	-0.03	h
C ₆ H ₄ F ₂	<i>o</i> -Difluorobenzene	2.59	2.74	0.15	0.77	0.09	m
OF ₂	Difluorine oxide	0.30	0.38	0.08	0.02	-0.19	h
COF ₂	Carbonyl fluoride	0.95	1.08	0.13	-0.14	0.33	g
N ₂ F ₂	<i>cis</i> -Difluorodiazene	0.16	0.63	0.47	-0.14	0.50	g
CHF ₃	Trifluoromethane	1.65	1.88	0.23	0.58	0.43	j
C ₂ HF ₃	Trifluoroethylene	1.30	1.49	0.19	0.52	0.13	n
C ₂ H ₃ F ₃	1,1,1-Trifluoroethane	2.32	2.40	0.08	0.55	0.27	h
C ₂ HO ₂ F ₃	Trifluoroacetic acid	2.28	1.96	-0.32	0.17	-0.42	h
NF ₃	Nitrogen trifluoride	0.24	0.26	0.02	-0.04	-0.20	h
C ₂ NF ₃	Trifluoroacetone nitrile	1.26	0.32	-0.94	-0.90	-1.23	o
COF ₄	Trifluoromethyl hypofluorite	0.33	0.28	-0.05	-0.24	0.02	p
HCl	Hydrogen chloride	1.12	1.38	0.26	0.36	0.26	q
C ₂ HCl	Chloroacetylene	0.44	0.14	-0.30	0.34	-0.17	r

TABLE 15 (continued)

Empirical formula	Chemical name	Dipole moment		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
FCI	Chlorine fluoride	0.88	1.42	0.54	0.59	0.03	s
SCl ₂	Sulfur dichloride	0.36	0.59	0.23	0.61		g
HBr	Hydrogen bromide	0.83	1.27	0.44	0.24	0.55	a
CH ₃ Br	Bromomethane	1.82	1.55	-0.27	-0.26	-0.34	a
C ₂ HBr	Bromoacetylene	0.00	0.28	0.28	0.43	0.57	r
C ₂ H ₃ Br	Bromoethylene	1.42	1.33	-0.09	-0.11	-0.12	s
C ₂ H ₅ Br	Bromoethane	2.03	1.85	-0.18	-0.37	-0.37	a
C ₃ H ₇ Br	1-Bromopropane	2.18	1.81	-0.37	-0.47	-0.48	a
C ₆ H ₅ Br	Bromobenzene	1.70	1.18	-0.52	-0.28	-0.25	a
OBBr	BrO	1.61	3.32	1.71	0.38	0.75	t
C ₂ H ₃ OBBr	Acetyl bromide	2.43	2.95	0.52	0.02	0.16	s
FBr	Bromine fluoride	1.42	2.25	0.83	0.68	0.04	s
CF ₃ Br	Bromotrifluoromethane	0.65	0.90	0.25	0.53	0.37	u
ClBr	Bromine chloride	0.52	0.06	-0.46	0.23	-0.07	v
CH ₂ Br ₂	Dibromomethane	1.43	1.45	0.02	-0.06	-0.11	s
CF ₂ Br ₂	Difluorodibromomethane	0.66	0.54	-0.12	0.17	-0.06	s
CHBr ₃	Bromoform	0.99	0.96	-0.03	-0.08	-0.08	s
HI	Hydrogen iodide	0.44	0.97	0.53	0.57	0.83	a
CH ₃ I	Methyl iodide	1.65	1.44	-0.21	-0.28	-0.30	a
C ₂ H ₅ I	Iodoethane	1.91	1.83	-0.08	-0.50	-0.41	a
C ₃ H ₇ I	1-Iodopropane	2.04	1.78	-0.26	-0.57	-0.50	a
C ₆ H ₅ I	Iodobenzene	1.70	0.81	-0.89	-0.10	-0.27	a
CF ₃ I	Trifluoroiodomethane	1.00	1.55	0.55	1.13	0.67	w
BrI	Iodine bromide	0.74	0.53	-0.21	-0.02	-0.11	v
CH ₂ I ₂	Diiodomethane	1.62	1.20	-0.42	-0.47	-0.50	a
AlF	Aluminum fluoride	1.53	3.29	1.76	-1.22		x
C ₂ H ₆ Si	Vinylsilane	0.66	0.24	-0.42	-0.12	-0.11	a
C ₂ H ₈ Si	Ethylsilane	0.81	0.37	-0.44	-0.71	-0.45	g
C ₂ H ₈ Si	Dimethylsilane	0.75	0.46	-0.29	-0.57	-0.30	a
C ₃ H ₁₀ Si	Trimethylsilane	0.52	0.37	-0.15	-0.35	-0.13	a
H ₂ SiF ₂	Difluorosilane	1.54	1.41	-0.13	0.69	0.03	a
HSiF ₃	Trifluorosilane	1.27	1.51	0.24	1.53	0.28	a
H ₂ SiCl ₂	Dichlorosilane	1.18	2.68	1.50	2.29	0.58	a
HSiCl ₃	Trichlorosilane	0.86	2.38	1.52	1.87	0.56	a
H ₂ SiBr ₂	Dibromosilane	1.43	3.09	1.66	1.90	0.38	s
C ₆ H ₁₉ Si ₂ N	Hexamethyldisilazane	0.37	0.35	-0.02	-0.10	0.24	a
H ₃ P	Phosphine	0.58	1.18	0.60	0.77	1.71	a
CH ₃ P	Methylphosphine	1.10	1.15	0.05	0.51	0.92	h
C ₂ H ₇ P	Dimethylphosphine	1.23	1.16	-0.07	0.58	0.56	h
C ₃ H ₉ P	Trimethylphosphine	1.19	1.08	-0.11	0.74	0.37	h
PF ₃	Phosphorus trifluoride	1.03	2.25	1.22	1.41	0.63	a
POF ₃	Phosphorus oxyfluoride	1.76	2.04	0.28	-0.56	0.88	a
H ₄ P ₂	P ₂ H ₄	0.92	2.19	1.27	-0.92	-0.92	y

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TABLE 16
COMPARISON OF EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS

Empirical formula	Chemical name	Ionization potential		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
H ₂	Hydrogen	15.40	16.11	0.71	0.35	−0.48	a
CH ₄	Methane	13.60	13.64	0.04	0.27	−0.29	b
C ₂ H ₂	Acetylene	11.40	11.61	0.21	−0.39	0.10	a
C ₂ H ₄	Ethylene	10.51	10.64	0.13	−0.34	0.04	a
C ₂ H ₆	Ethane	12.00	11.98	−0.02	0.70	−0.23	a
C ₃	Carbon, trimer	11.10	11.75	0.65	−0.06	0.23	a
C ₃ H ₄	Allene	10.07	10.18	0.11	−0.05	0.07	a
C ₃ H ₄	Cyclopropene	9.86	9.88	0.02	0.02	−0.04	c
C ₃ H ₄	Propyne	10.37	10.89	0.52	0.35	0.37	b
C ₃ H ₆	Cyclopropane	11.00	11.78	0.78	0.43	0.48	b
C ₃ H ₆	Propene	9.88	10.10	0.22	0.08	0.11	d
C ₃ H ₈	Propane	11.50	11.51	0.01	0.84	−0.18	e
C ₄ H ₂	Diacetylene	10.17	10.47	0.30	−0.18	0.20	a
C ₄ H ₄	CH ₂ = C = C = CH ₂	9.10	9.34	0.24	−0.09	0.24	a
C ₄ H ₆	1,2-Butadiene	9.15	9.72	0.57	0.69	0.52	a
C ₄ H ₆	1-Butyne	10.20	10.77	0.57	0.48	0.42	a
C ₄ H ₆	2-Butyne	9.60	10.34	0.74	0.87	0.57	a
C ₄ H ₆	Cyclobutene	9.43	9.82	0.39	0.34	0.29	a
C ₄ H ₆	1,3-Butadiene	9.08	9.47	0.39	0.06	0.25	b
C ₄ H ₈	1-Butene	9.70	10.03	0.33	0.24	0.23	a
C ₄ H ₈	Cyclobutane	10.70	11.02	0.32	1.11	0.29	a
C ₄ H ₁₀	<i>n</i> -Butane	11.20	11.35	0.15	1.01	−0.03	a
C ₄ H ₁₀	Isobutane	11.40	11.59	0.19	0.72	−0.11	e
C ₅ H ₆	Cyclopentadiene	8.57	9.23	0.66	0.47	0.51	a
C ₅ H ₈	Cyclopentene	9.18	9.52	0.34	0.54	0.26	a
C ₅ H ₁₀	1-Pentene	7.90	10.15	2.25	2.07	2.09	a
C ₅ H ₁₀	2-Methyl-1-butene	7.40	9.85	2.45	2.41	2.30	a
C ₅ H ₁₀	2-Methyl-2-butene	8.70	9.39	0.69	0.94	0.55	a
C ₅ H ₁₀	3-Methyl-1-butene	9.60	10.26	0.66	0.38	0.49	a
C ₅ H ₁₀	Cyclopentane	10.50	11.07	0.57	1.56	0.47	a
C ₅ H ₁₂	2-Methylbutane	10.30	11.44	1.14	1.70	0.90	a
C ₅ H ₁₂	Neopentane	11.30	12.06	0.76	0.82	0.23	e
C ₅ H ₁₂	<i>n</i> -Pentane	10.30	11.30	1.00	1.86	0.81	a
C ₆ H ₆	Benzene	9.25	9.75	0.50	0.14	0.40	a
C ₆ H ₁₀	Cyclohexene	10.30	9.59	−0.71	−0.55	−0.81	a
C ₆ H ₁₂	Cyclohexane	10.30	11.29	0.99	1.44	0.64	a
C ₇ H ₈	Cycloheptatriene	8.50	8.95	0.45	0.22	0.25	a
C ₇ H ₈	Toluene	8.82	9.44	0.62	0.46	0.51	b
C ₈ H ₁₀	Ethylbenzene	8.80	9.52	0.72	0.48	0.58	a
C ₈ H ₁₄	Bicyclo(2.2.2)-octane	9.45	10.94	1.49	1.95	1.11	a
C ₁₀ H ₈	Naphthalene	8.15	8.84	0.69	0.42	0.56	a
C ₁₀ H ₁₆	Adamantane	9.60	10.85	1.25	1.67	0.83	a
C ₁₄ H ₁₀	Anthracene	8.16	8.25	0.09	−0.11	−0.04	a
H ₂ O	Water	12.62	12.32	−0.30	−0.43	−0.16	b
H ₂ O	Water, second I.P.	14.70	14.52	−0.18	−0.23	0.25	f

TABLE 16 (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
H ₂ O	Water, third I.P.	18.50	17.58	-0.92	0.61	-0.30	f
H ₂ O	Water, fourth I.P.	32.20	36.83	4.63	7.83	4.22	f
CO	Carbon monoxide	14.01	13.03	-0.98	-0.58	-0.70	a
CH ₂ O	Formaldehyde	10.10	10.63	0.53	0.94	0.68	a
CH ₄ O	Methanol	10.96	11.14	0.18	0.46	0.17	a
C ₂ H ₂ O	Ketene	9.64	9.46	-0.18	-0.35	-0.04	a
C ₂ H ₄ O	Acetaldehyde	10.21	10.71	0.50	0.67	0.51	a
C ₂ H ₄ O	Ethylene oxide	10.57	11.34	0.77	0.92	0.76	b
C ₂ H ₆ O	Ethanol	10.60	10.90	0.30	0.70	0.28	a
C ₂ H ₆ O	Dimethyl ether	10.04	10.69	0.65	1.00	0.57	a
C ₃ H ₄ O	Acrolein	10.11	10.68	0.57	0.53	0.58	a
C ₃ H ₆ O	Acetone	9.72	10.77	1.05	1.04	0.95	a
C ₃ H ₆ O	Propanal	10.00	10.62	0.62	0.81	0.59	a
C ₄ H ₄ O	Furan	8.88	9.38	0.50	0.26	0.44	a
C ₄ H ₆ O	2-Butenal	9.90	10.50	0.60	0.49	0.57	a
C ₄ H ₈ O	Butanal	9.83	10.63	0.80	0.97	0.76	a
C ₄ H ₁₀ O	Diethyl ether	9.60	10.79	1.19	1.18	0.96	a
C ₅ H ₁₂ O	3-Pentanol	10.16	10.92	0.76	0.93	0.65	a
C ₇ H ₆ O	Benzaldehyde	9.70	10.05	0.35	0.04	0.30	a
C ₇ H ₈ O	Anisole	8.40	9.11	0.71	0.44	0.60	a
CO ₂	Carbon dioxide	13.78	12.73	-1.05	-0.99	-0.57	b
CH ₂ O ₂	Formic acid	11.51	11.56	0.05	0.23	0.31	a
C ₂ H ₂ O ₂	<i>trans</i> -Glyoxal	10.59	10.57	-0.02	0.16	0.07	a
C ₂ H ₄ O ₂	Acetic acid	10.80	11.44	0.64	0.77	0.82	a
C ₂ H ₄ O ₂	Methyl formate	11.02	11.35	0.33	0.59	0.55	g
C ₂ H ₆ O ₂	Dimethyl peroxide	10.60	10.77	0.17	0.09	0.29	a
C ₃ O ₂	Carbon suboxide	10.60	10.22	-0.38	-0.53	-0.10	a
C ₃ H ₄ O ₂	β -Propiolactone	10.60	9.96	-0.64	-0.73	-0.54	a
C ₃ H ₆ O ₂	Propionic acid	10.50	11.34	0.84	1.00	0.99	a
C ₃ H ₆ O ₂	Methyl acetate	10.60	11.27	0.67	0.86	0.80	a
C ₅ H ₈ O ₂	Acetylacetone	8.38	10.89	2.51	2.40	2.36	a
C ₇ H ₆ O ₂	Benzoic acid	9.80	10.13	0.33	-0.03	0.28	a
O ₃	Ozone	12.75	12.69	-0.06	-0.05	0.35	h
C ₄ H ₂ O ₃	Maleic anhydride	10.84	11.71	0.87	0.86	1.18	a
C ₂ H ₂ O ₄	Oxalic acid	11.20	11.67	0.47	0.59	0.76	a
H ₃ N	Ammonia	10.85	9.70	-1.15	0.34	-0.43	b
CHN	Hydrogen cyanide	13.60	12.60	-1.00	-0.19	0.08	b
CH ₅ N	Methylamine	9.60	9.40	-0.20	0.96	0.15	a
C ₂ H ₃ N	Acetonitrile	12.21	12.33	0.12	0.58	0.25	a
C ₂ H ₃ N	Methyl isocyanide	11.32	11.70	0.38	0.92	0.67	a
C ₂ H ₃ N	Ethyleneimine (Azirane)	9.90	9.92	0.02	0.78	0.41	a
C ₂ H ₇ N	Ethylamine	9.50	9.50	0.00	1.01	0.39	a
C ₂ H ₇ N	Dimethylamine	8.93	9.22	0.29	1.11	0.46	i
C ₃ HN	CH ₃ CN	11.75	11.58	-0.17	-0.40	-0.10	a
C ₃ H ₃ N	Acrylonitrile	10.91	10.89	-0.02	-0.30	-0.05	a
C ₃ H ₅ N	Ethyl cyanide	11.90	12.01	0.11	0.69	0.09	a

TABLE 16 (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₃ H ₉ N	Trimethylamine	8.54	9.07	0.53	1.05	0.58	i
C ₄ H ₅ N	Pyrrole	8.21	8.93	0.72	0.35	0.45	a
C ₅ H ₅ N	Pyridine	9.67	10.10	0.43	0.02	0.26	a
C ₆ H ₇ N	Aniline	7.70	8.61	0.91	1.05	0.82	a
C ₇ H ₅ N	Phenyl cyanide	9.70	10.10	0.40	0.11	0.32	a
CHNO	Hydrogen isocyanate	11.60	10.59	-1.01	-0.50	-0.36	a
CH ₃ NO ₂	Nitromethane	11.30	12.17	0.87	0.24	0.68	a
CH ₃ NO ₂	Methyl nitrite	11.00	10.64	-0.36	0.42	0.19	a
C ₃ H ₇ NO ₂	Alanine	8.10	9.88	1.78	2.71	2.27	a
C ₆ H ₅ NO ₂	Nitrobenzene	9.90	10.60	0.70	0.41	0.66	a
N ₂	Nitrogen	15.60	13.80	-1.80	-0.73	-1.28	a
CH ₂ N ₂	Diazomethane	9.00	9.22	0.22	-0.33	-0.18	a
CH ₆ N ₂	Methylhydrazine	9.30	8.92	-0.38	0.36	-0.34	a
C ₂ N ₂	Cyanogen	13.36	12.87	-0.49	-0.16	-0.05	a
C ₄ H ₄ N ₂	Pyridazine	9.30	9.94	0.64	1.19	1.37	a
C ₄ H ₄ N ₂	Pyrimidine	9.73	10.29	0.56	0.65	0.85	a
C ₄ H ₄ N ₂	Pyrazine	9.90	10.16	0.26	0.12	0.35	a
N ₂ O ₄	Dinitrogen tetroxide	11.40	11.61	0.21	0.65	-0.19	a
N ₂ O ₅	Dinitrogen pentoxide	12.30	12.38	0.08	0.88	1.32	a
CH ₃ N ₃	Methyl azide	9.81	9.96	0.15	0.10	-0.22	a
HS	Hydrogen sulfide	10.40	9.79	-0.61	-0.55		j
H ₂ S	Hydrogen sulfide	10.43	9.63	-0.80	-0.44		k
CS	Carbon sulfide	11.30	10.60	-0.70	-0.21		a
CH ₂ S	Thioformaldehyde	9.34	9.06	-0.28	0.64		l
CH ₄ S	Thiomethanol	9.44	9.21	-0.23	0.33		k
C ₂ H ₂ S	Thioketene, H ₂ CCS	8.89	8.81	-0.08	0.34		m
C ₂ H ₄ S	Thiirane	8.87	9.23	0.36	0.79		k
C ₂ H ₆ S	Thioethanol	9.21	9.19	-0.02	0.52		n
C ₂ H ₆ S	Dimethyl thioether	8.65	8.88	0.23	0.93		k
C ₃ H ₆ S	Thietane	8.65	8.95	0.30	0.88		o
C ₃ H ₈ S	Isopropanthiol	9.14	9.22	0.08	0.57		a
C ₃ H ₈ S	1-Propanthiol	9.19	9.19	0.00	0.54		a
C ₄ H ₄ S	Thiophene	8.95	9.54	0.59	0.55		k
C ₄ H ₈ S	Tetrahydrothiophene	8.60	8.79	0.19	0.85		a
C ₄ H ₁₀ S	Butanethiol	9.15	9.19	0.04	0.58		a
C ₆ H ₆ S	Thiophenol	8.47	8.78	0.31	0.36		o
CSO	Carbon oxysulfide	11.20	10.71	-0.49	-0.69		a
C ₂ H ₄ SO	Thiolacetic acid	9.70	10.05	0.35	0.83		a
C ₂ H ₆ SO	Dimethyl sulfoxide	9.01	9.35	0.34	0.79		a
SO ₂	Sulfur dioxide	12.30	10.55	-1.75	-0.44		k
SO ₃	Sulfur trioxide	11.00	12.91	1.91	2.16		k
CHNS	Hydrogen isothiocyanate	9.94	9.38	-0.56	-0.23		a
C ₂ H ₃ NS	Methyl isothiocyanate	9.37	9.17	-0.20	0.09		a
C ₂ H ₃ NS	Methyl thiocyanate	9.96	9.68	-0.28	0.33		a
H ₂ S ₂	Hydrogen disulfide	10.01	9.86	-0.15	0.21		p
CS ₂	Carbon disulfide	10.08	9.83	-0.25	-0.42		k

TABLE 16 (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₂ H ₆ S ₂	Ethanedithiol-1,2	9.30	9.32	0.02	0.54		o
C ₂ H ₆ S ₂	2,3-Dithiabutane	8.71	9.40	0.69	1.07		k
C ₂ N ₂ S ₂	S ₂ (CN) ₂	11.05	10.56	-0.49	-0.07		a
C ₃ H ₄ S ₃	1,3-Dithiolan-2-thione	8.40	9.25	0.85	1.05		a
S ₈	S ₈	9.04	9.09	0.05	1.51		k
HF	Hydrogen fluoride	16.06	16.14	0.08	-1.24	-1.97	q
CH ₃ F	Fluoromethane	13.31	12.92	-0.39	-0.26	-1.21	r
C ₂ HF	Fluoroacetylene	11.30	11.56	0.26	-0.24	-0.15	a
C ₂ H ₃ F	Fluoroethylene	10.58	10.60	0.02	-0.41	-0.34	a
C ₂ H ₅ F	Fluoroethane	12.43	12.07	-0.36	0.18	-0.85	a
C ₃ H ₇ F	2-Fluoropropane	11.08	12.10	1.02	1.25	0.44	a
C ₆ H ₅ F	Fluorobenzene	9.19	9.81	0.62	0.28	0.35	a
C ₇ H ₅ O ₂ F	<i>p</i> -Fluorobenzoic acid	9.90	10.16	0.26	-0.07	0.05	a
NOF	Nitrosyl fluoride	12.94	11.54	-1.40	-0.01	-0.42	s
NO ₂ F	Fluorine nitrite	13.51	13.37	-0.14	-0.52	-0.12	s
SF	SF	10.00	9.75	-0.25	0.13		a
CH ₂ F ₂	Difluoromethane	13.17	12.86	-0.31	-0.08	-1.15	r
C ₂ F ₂	Difluoroacetylene	11.20	11.54	0.34	-0.03	-0.27	a
C ₂ H ₂ F ₂	<i>gem</i> -Difluoroethylene	10.72	10.54	-0.18	-0.54	-0.73	a
C ₂ H ₄ F ₂	1,1-Difluoroethane	12.80	12.82	0.02	-0.07	-0.87	a
C ₆ H ₄ F ₂	<i>o</i> -Difluorobenzene	9.68	9.98	0.30	0.01	-0.05	a
C ₆ H ₄ F ₂	<i>m</i> -Difluorobenzene	9.68	10.02	0.34	0.05	0.04	a
C ₆ H ₄ F ₂	<i>p</i> -Difluorobenzene	9.30	9.87	0.57	0.26	0.19	a
OF ₂	Difluorine oxide	13.26	13.47	0.21	0.26	-0.36	t
N ₂ F ₂	<i>trans</i> -Difluorodiazene	13.40	11.91	-1.49	-0.40	-1.15	t
SF ₂	Sulfur difluoride	10.20	9.81	-0.39	0.54		a
CSF ₂	Thiocarbonyl difluoride	10.46	10.37	-0.09	0.68		a
SOF ₂	Thionyl fluoride	12.58	11.03	-1.55	-0.13		a
SO ₂ F ₂	Sulfuryl fluoride	13.04	13.10	0.06	0.71		a
S ₂ F ₂	FSSF	10.68	10.47	-0.21	0.47		a
CHF ₃	Trifluoromethane	14.80	14.36	-0.44	-0.23	-1.49	a
C ₂ HF ₃	Trifluoroethylene	10.54	10.68	0.14	-0.08	-0.45	a
C ₂ H ₃ F ₃	1,1,1-Trifluoroethane	13.80	14.38	0.58	0.21	-0.68	a
C ₇ H ₅ F ₃	Trifluoromethylbenzene	9.68	10.34	0.66	0.39	0.57	a
C ₂ HO ₂ F ₃	Trifluoroacetic acid	12.00	12.47	0.47	0.73	0.49	a
NF ₃	Nitrogen trifluoride	13.73	12.24	-1.49	0.20	-0.55	a
CF ₄	Carbon tetrafluoride	16.23	16.79	0.56	0.58	-0.91	a
C ₂ F ₄	Tetrafluoroethylene	10.50	10.84	0.34	0.42	-0.22	a
COF ₄	Trifluoromethyl hypofluorite	13.60	14.18	0.58	0.63	0.07	a
N ₂ F ₄	Tetrafluorohydrazine	12.00	12.46	0.46	1.04	0.47	a
SF ₄	Sulfur tetrafluoride	12.05	10.41	-1.64	0.66		a
C ₆ HF ₅	Pentafluorobenzene	9.75	10.55	0.80	0.65	0.32	a
C ₂ F ₆	Hexafluoroethane	14.60	14.48	-0.12	-0.10	-1.37	a
C ₆ F ₆	Hexafluorobenzene	10.90	10.85	-0.05	-0.13	-0.53	a
C ₃ OF ₆	Perfluoroacetone	12.10	12.71	0.61	0.90	0.24	a
SF ₆	Sulfur hexafluoride	15.70	16.39	0.69	0.68		a

TABLE 16 (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
HCl	Hydrogen chloride	12.75	11.06	-1.69	0.25	-0.42	q
CH ₃ Cl	Methyl chloride	11.30	10.48	-0.82	0.94	0.04	a
C ₆ H ₅ Cl	Chlorobenzene	9.08	9.39	0.31	0.54	0.48	u
C ₇ H ₅ OCl	Benzoyl chloride	9.90	10.29	0.39	0.12	0.34	a
NOCl	Nitrosyl chloride	10.90	10.59	-0.31	1.07	0.66	a
NO ₂ Cl	Nitryl chloride	11.40	12.42	1.02	1.61	1.54	a
FCI	Chlorine fluoride	12.02	11.13	-0.89	1.35	0.37	v
CH ₂ FCI	Fluorochloromethane	11.74	10.85	-0.89	0.80	-0.16	a
SO ₂ FCI	SO ₂ ClF	12.61	12.43	-0.18	0.76		a
CHF ₂ Cl	Difluorochloromethane	12.60	11.36	-1.24	0.63	-0.32	a
CF ₃ Cl	Trifluorochloromethane	10.30	11.88	1.58	3.83	2.94	a
CH ₂ Cl ₂	Dichloromethane	11.30	10.58	-0.72	1.19	0.09	a
COCl ₂	Carbonyl chloride	11.84	11.23	-0.61	0.86	0.53	a
SCl ₂	Sulfur dichloride	9.70	9.60	-0.10	1.00		a
SOCl ₂	Thionyl chloride	11.10	10.65	-0.45	1.24		a
SO ₂ Cl ₂	Sulfuryl chloride	12.40	10.55	-1.85	-0.55		a
S ₂ Cl ₂	CISSCl	9.40	9.96	0.56	1.67		a
CHFCI ₂	Fluorodichloromethane	12.00	10.99	-1.01	0.96	0.03	a
CF ₂ Cl ₂	Difluorodichloromethane	12.30	11.33	-0.97	1.06	0.21	a
CHCl ₃	Chloroform	11.48	10.84	-0.64	1.43	0.29	a
CFCl ₃	Fluorotrichloromethane	11.90	11.16	-0.74	1.39	0.55	a
C ₂ Cl ₆	Hexachloroethane	11.20	10.84	-0.36	1.88	0.98	a
HBr	Hydrogen bromide	11.71	12.13	0.42	0.39	-0.25	q
CH ₃ Br	Bromomethane	10.53	11.01	0.48	1.03	0.27	a
C ₂ H ₃ Br	Bromoethylene	9.90	10.44	0.54	0.35	0.25	a
C ₂ H ₅ Br	Bromoethane	10.28	10.91	0.63	1.20	0.41	a
C ₃ H ₇ Br	1-Bromopropane	10.18	10.93	0.75	1.29	0.51	a
C ₆ H ₅ Br	Bromobenzene	9.25	9.81	0.56	0.30	0.35	a
C ₂ H ₃ OBr	Acetyl bromide	10.55	11.20	0.65	0.88	0.63	w
CF ₃ Br	Bromotrifluoromethane	12.10	12.23	0.13	1.15	0.23	a
Br ₂	Bromine	10.70	11.24	0.54	0.96	0.24	a
CH ₂ Br ₂	Dibromomethane	10.50	10.59	0.09	1.20	0.46	a
CF ₂ Br ₂	Difluorodibromomethane	11.18	11.17	-0.01	1.10	0.13	a
C ₂ F ₄ Br ₂	1,2-Dibromotetrafluoroethane	14.44	12.00	-2.44	-1.65	-2.53	a
CHBr ₃	Bromoform	10.50	10.84	0.34	1.37	0.57	a
CBr ₄	Carbon tetrabromide	10.30	11.22	0.92	1.73	0.92	a
HI	Hydrogen iodide	10.39	9.97	-0.42	0.82	0.52	x
CH ₃ I	Methyl iodide	9.50	9.47	-0.03	1.35	1.01	a
C ₂ H ₅ I	Iodoethane	9.34	9.44	0.10	1.48	1.09	a
C ₃ H ₇ I	1-Iodopropane	9.27	9.45	0.18	1.53	1.16	a
C ₃ H ₇ I	2-Iodopropane	9.40	9.43	0.03	1.39	1.00	a
C ₄ H ₉ I	1-Butyl iodide	9.20	9.45	0.25	1.60	1.23	a
C ₆ H ₅ I	Iodobenzene	8.70	9.05	0.35	0.85	0.95	a
C ₆ H ₁₁ I	Iodocyclohexane	8.91	9.42	0.51	1.86	1.47	a
C ₇ H ₇ I	<i>o</i> -Iodotoluene	8.53	9.02	0.49	0.98	0.99	a
C ₇ H ₇ I	<i>m</i> -Iodotoluene	8.55	9.01	0.46	0.96	0.97	a

TABLE 16 (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Ref.
		Exp.	Calc.	PM3	MNDO	AM1	
C ₇ H ₇ I	<i>p</i> -Iodotoluene	8.38	8.94	0.56	1.07	1.03	a
C ₇ H ₇ I	Benzyl iodide	8.91	9.35	0.44	0.55	0.60	a
CF ₃ I	Trifluoroiodomethane	10.45	10.28	-0.17	2.03	1.52	a
ClI	Iodine chloride	10.10	9.74	-0.36	1.48	1.02	y
BrI	Iodine bromide	9.85	9.84	-0.01	1.43	0.99	y
I ₂	Iodine	9.34	9.53	0.19	1.53	1.33	z
I ₂	Iodine, second I.P.	11.03	10.27	-0.76	1.66	1.45	z
I ₂	Iodine, third I.P.	12.95	12.53	-0.42	0.40	0.25	z
CH ₂ I ₂	Diiodomethane	9.46	8.98	-0.48	1.41	1.10	a
C ₂ I ₂	Diiodoacetylene	9.03	8.64	-0.39	1.55	1.47	aa
C ₂ H ₄ I ₂	1,2-Diiodoethane	9.50	9.66	0.16	1.52	1.21	a
C ₃ H ₉ Al	Trimethylaluminum	9.76	10.12	0.36	0.92		bb
C ₂ H ₆ Si	Vinylsilane	10.40	10.01	-0.39	-0.17	-0.01	a
C ₂ H ₈ Si	Ethylsilane	10.95	10.64	-0.31	0.19	0.12	k
C ₂ H ₈ Si	Dimethylsilane	11.20	10.65	-0.55	0.27	-0.03	a
C ₃ H ₁₀ Si	Trimethylsilane	10.80	10.51	-0.29	0.60	0.15	a
C ₄ H ₁₂ Si	Tetramethylsilane	10.40	10.42	0.02	0.94	0.52	a
C ₃ H ₉ SiF	Fluorotrimethylsilane	11.00	10.47	-0.53	0.49	0.06	a
H ₂ SiF ₂	Diffuorosilane	12.85	10.82	-2.03	-0.63	-1.24	cc
SiF ₄	Silicon tetrafluoride	15.81	15.19	-0.62	0.02	-1.09	dd
H ₂ SiCl ₂	Dichlorosilane	11.70	10.27	-1.43	0.82	-0.14	cc
C ₂ H ₆ SiCl ₂	Dichlorodimethylsilane	10.79	10.27	-0.52	1.43	0.70	a
SiCl ₄	Silicon tetrachloride	11.79	11.23	-0.56	2.02	1.19	w
C ₆ H ₁₉ Si ₂ N	Hexamethyldisilazane	8.66	8.38	-0.28	1.03	0.83	ee
H ₃ P	Phosphine	9.98	8.67	-1.31	1.36	0.44	x
CP	Carbon phosphide	10.50	10.90	0.40	1.06	1.08	a
CHP	Methinophosphine	10.79	10.74	-0.05	0.44	0.43	a
CH ₃ P	Methylphosphine	9.72	8.66	-1.06	1.07	0.10	a
C ₂ H ₇ P	Dimethylphosphine	9.10	8.68	-0.42	1.14	0.21	a
C ₃ H ₉ P	Trimethylphosphine	8.60	8.81	0.21	1.25	0.30	k
C ₃ H ₉ PO ₃	Trimethyl phosphite	9.22	9.69	0.47	1.69	0.79	a
PF ₃	Phosphorus trifluoride	9.71	10.70	0.99	3.42	0.72	x
POF ₃	Phosphorus oxyfluoride	12.77	12.05	-0.72	0.40	-0.04	a
PCl ₃	Phosphorus trichloride	10.50	10.42	-0.08	1.67	0.13	a
POCl ₃	Phosphorus oxychloride	11.85	12.29	0.44	0.93	1.27	a
PCl ₅	Phosphorus pentachloride	10.80	11.86	1.06	1.49	1.90	a
PBr ₃	Phosphorus tribromide	10.00	10.84	0.84	1.44	0.60	a
PI ₃	Phosphorus triiodide	9.15	9.97	0.82	1.29	1.27	a
P ₂	Phosphorus dimer	10.62	8.91	-1.71	0.82	0.84	a
P ₄	Phosphorus tetramer	9.54	10.17	0.63	1.96	2.14	a

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