

# QUANTUM CHEMICAL MODELS

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## INTRODUCTION

The fundamental underpinnings of theoretical chemistry were uncovered in a relatively short period at the beginning of the present century. Rutherford's discovery of the nucleus in 1910 completed the identification of the constituent subparticles of atoms and molecules and was followed shortly thereafter by the Bohr treatment of electronic orbits in atoms, the "old quantum theory". The relation between the positive nuclear charge, atomic number and position of an atom in the periodic table was uncovered by 1913. It proved difficult to extend Bohr's orbits to a polyatomic situation and the next advance had to await the development of the wave theory of matter and the associated quantum mechanics in the early 1920s. By 1926, Heisenberg had developed matrix mechanics and Schrödinger had proposed the basic non-relativistic wave equation governing the motion of nuclei and electrons in molecules. The latter,

$$H\Psi = E\Psi \quad (1)$$

is a differential eigenvalue equation for the energy  $E$  and wavefunction  $\Psi$  of a particular state.  $H$  is the Hamiltonian operator and  $\Psi$  depends on cartesian and spin coordinates of the component particles. The only further restrictions are the permutational symmetry requirements for  $\Psi$  (antisymmetry for fermions such as electrons and symmetry for bosons). A relativistic generalization of this equation was proposed a short time later by Dirac.

The Schrödinger equation is easily solved for the hydrogen atom and found to give results identical to the earlier treatment of Bohr. With inclusion of relativistic corrections via the Dirac equation, almost perfect agreement was found with experimental spectroscopic data. However, exact solution for any other system was not found possible, leading to a famous remark by Dirac in 1929:

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved"

This was a cry both of triumph and of despair. It marked the end of the process of fundamental discovery in chemistry but left a colossal mathe-

mathematical task of implementation. In retrospect, the implied finality of the claim seems excessively bold. In 1929, there had only been one preliminary approximate quantum mechanical calculation on the hydrogen molecule by Heitler and London, leading to a value of the bond energy of only about 70% of the experimental value. Nevertheless, the physicists were highly confident and most moved on to study the internal structure of the nucleus during the 1930s. In fact, their boldness was apparently justified, for no significant failure of the full Schrödinger-Dirac treatment has ever been demonstrated.

This was the challenge presented to the early quantum chemists by 1930. Given the hopelessness of exact solution, how would it be possible to develop approximate mathematical procedures that could (a) assist the qualitative interpretation of chemical phenomena; and (b) provide predictive capability. Attempts to approach this problem by a model approach is the topic addressed here.

## FEATURES OF THEORETICAL MODELS

A theoretical model for any complex process is an *approximate but well-defined* mathematical procedure of simulation. When applied to chemistry, the task is to use input information about the number and character of component particles (nuclei and electrons) to derive information and understanding of resultant molecular behavior. Five stages may be distinguished in the development and use of such a model:

### *Target*

A target accuracy must be selected. A model is not likely to be of much value unless it is able to provide clear distinction between possible different modes of molecular behavior. As the model becomes quantitative, the target should be that data is reproduced and predicted within experimental accuracy. For energies, such as heats of formation or ionization potentials, a global accuracy of 1 kcal/mole would be appropriate.

### *Formulation*

The approximate mathematical procedure must be precisely formulated. This should be *general and continuous* as far as possible. Thus, particular procedures for particular molecules or particular symmetries should be avoided. If this can be done, the procedure becomes a *full theoretical model chemistry*, which can be explored in detail as far as available resources permit.

### *Implementation*

The formulated method has to be implemented in a form, which permits its application in reasonable times and at reasonable cost. In recent times, this stage involves the development of efficient and easily used computer programs. It is closely comparable to the stage of building equipment in an experimental investigation.

*Verification*

The next step is to test the model against known chemical facts to determine whether the target has been achieved. If quantitative accuracy is being sought, this can be done by various statistical criteria such as the root-mean-square difference between the results of the theoretical model and experimental data. In selecting such a data-set, it is important to make it as broad as possible, while limiting it to experimental facts known to be of high quality. If the results of such a comparison do meet the target requirements, the model may be said to be *validated*.

*Prediction*

Finally, if the model has been properly validated according to some such criterion, it may be applied to chemical problems to which the answer is unknown or in dispute. If the experimental data-set is sufficiently broad, there is a reasonable expectation that the results will be accurate to something like the target accuracy. This stage, of course, is the one of most interest to the larger chemical community.

One further aspect of theoretical models is the introduction of empirical parameterization. Models which utilize only the fundamental constants of physics are generally termed *ab initio*; if some parameters are introduced which are determined by fitting to some experimental data, the methods are *semi-empirical*. Clearly, there is a wide range of possible empiricism, as will be noted in subsequent parts of this article.

## HARTREE-FOCK MODELS

During the 1930s, most work was of a qualitative nature, treating the electrons as moving in independent *molecular orbitals*. However, the foundations of the orbital theory of many-electron systems was laid by Hartree, Fock and Slater. If the  $2n$  electrons in a closed-shell molecule are assigned to a set of  $n$  molecular orbitals  $\psi_i$  ( $i = 1, \dots, n$ ), the corresponding many-electron wavefunction can be written

$$\Psi = (n!)^{-1/2} \det[(\psi_1\alpha)(\psi_1\beta)(\psi_2\alpha)\dots] \quad (2)$$

Here the  $\psi_i$  are taken to be orthonormal and  $\alpha$  and  $\beta$  are spin functions. This single-configuration wavefunction is usually described as a *Slater determinant*.

If the molecular orbitals  $\psi_i$  are varied to minimize the energy, calculated as the expectation value of the full Hamiltonian  $H$ ,

$$E = \langle \Psi | H | \Psi \rangle \quad (3)$$

then the energy  $E$  is fully defined and, according to the variational principle, is an upper bound for the exact Schrödinger energy from the full wave equation (1). This procedure leads to a set of coupled differential equations for the  $\psi_i$ , as first derived by Fock. The method is known as *Hartree-Fock* theory, early applications having been made (to atoms) by Hartree.

Following the break due to World-War II, work on quantum chemistry resumed in a number of countries. In Cambridge, Lennard-Jones and his group (of which I became a member in 1948) reexamined the Hartree-Fock equations with a view to transforming the orbitals  $\psi_i$  into localized or equivalent orbitals, representing bonding and lone electron pairs, concepts widely used in the qualitative description of molecular structure. However, the coupled 3-dimensional differential equations appeared intractable and little progress was made towards their solution.

A major advance occurred in 1951 with the publication from Chicago of the Roothaan equations [1]. (Actually, these had been circulated in a report some time earlier.) Roothaan considered molecular orbitals that were restricted to be linear combinations of a set of prescribed 3-dimensional 1-electron functions  $\chi_\mu$  ( $\mu = 1, 2, \dots, N, N > n$ ). Thus

$$\psi_i = \sum_{\mu=1}^N c_{\mu i} \chi_\mu \quad (4)$$

Variation of the total energy (3) was then carried out with respect to the coefficients  $c_{\mu i}$ . This leads to a set of *algebraic* equations which can be written in matrix form (using real functions and atomic units throughout),

$$\text{FC} = \text{SCE} \quad (5)$$

where

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)/2] \quad (6)$$

$$H_{\mu\nu} = \int \chi_\mu H \chi_\nu d\tau \quad (7)$$

$$S_{\mu\nu} = \int \chi_\mu \chi_\nu d\tau \quad (8)$$

$$E_{ij} = \epsilon_i \delta_{ij} \quad (9)$$

$$P_{\mu\nu} = 2 \sum_i^n c_{\mu i} c_{\nu i} \quad (10)$$

$$(\mu\nu|\lambda\sigma) = \int \int \chi_\mu(1) \chi_\nu(1) (1/r_{12}) \chi_\lambda(2) \chi_\sigma(2) d\tau_1 d\tau_2 \quad (11)$$

In these and subsequent equations, we follow a useful practice of using roman suffixes for molecular orbitals  $\psi$  and greek for the expansion functions  $\chi$ .  $H$  is the core Hamiltonian, describing motion of a single electron moving in the bare field of the nuclei. The eigenvalues  $\epsilon_i$  are the one-electron *Fock energies*, the lowest  $n$  corresponding to the occupied molecular orbitals 1, 2, ...,  $n$ .

These nonlinear equations provide a complete mathematical model if the prescribed functions  $\chi_\mu$  are uniquely specified by the nuclear positions. They

are often referred to as *self consistent field* (SCF) equations. In the earliest versions of molecular orbital theory, the  $\chi_\mu$  were chosen to be the atomic orbitals of the component atoms, in which case the theory was described as LCAOSCF for 'linear combination of atomic orbitals'. More generally, the set  $\{\chi_\mu\}$  is referred to as the *basis set*. Normal practice is to choose basis functions which are centered at the nuclei and depend only on the atomic number (positive charge) of that nucleus.

The Roothaan-type of equations can be extended to electron configurations in which some orbitals are doubly occupied and some singly. Another extension is one in which electrons of  $\alpha$ -spin and  $\beta$ -spin are assigned to *different* molecular orbitals  $\psi^\alpha$  and  $\psi^\beta$ . This is usually referred to as a *spin-unrestricted* configuration. There will be two sets of coefficients  $c_{\mu i}^\alpha$  and  $c_{\mu i}^\beta$ . The corresponding generalization of the Roothaan equations was published by the author and Nesbet in 1954 [2]. These are usually denoted as Unrestricted Hartree-Fock or UHF, and the option of double and single occupation as Restricted Open Hartree-Fock or ROHF.

The introduction of basis set expansions played a major role in the development of quantum chemistry. It changed the mathematical task from the numerical solution of coupled differential equations (following the atomic work of Hartree) to the double challenge of evaluation of the 3- or 6-dimensional integrals (7),(8) and (11), followed by solution of the algebraic SCF equations (5). If analytic integration were possible, the model could become *precise* in the sense that good arithmetic correctness would be possible, even though the underlying approximations (use of a single configuration determinant and a finite basis) might still be unsatisfactory.

During the 1950s, integral evaluation was regarded as the main barrier to progress. The best choice of basis functions for LCAOSCF theory appeared to be Slater-type atomic orbitals (STO), which have exponential radial parts by analogy to the hydrogen atom. The one- and two-electron integrals (7),(8) and (11) can then be evaluated analytically in the two-center case. However, great difficulties were encountered for the three- and four-center cases. It was common to describe this impasse as "the nightmare of the integrals".

There were two responses to the integral difficulties. One was to make approximations for the more difficult integrals and to introduce parameters for others, with values obtained by empirical fits to experimental data. This practice became known as *semi-empirical*. The alternative of proceeding without approximation or empirical parameterization was, at the time, necessarily limited to very small molecules and became known as the *ab initio* approach. The most widely used semi-empirical methods were based on the zero-differential-overlap approximation, in which products of different atomic orbitals  $\chi_\mu\chi_\nu$  are neglected in most integrals. This approximation, when applied to the  $\pi$ -electrons of conjugated organic molecules, became known as the Pariser-Parr-Pople (PPP) theory [3-5]. It was later generalized to the treatment of all valence electrons in the CNDO and INDO theories [6] (1964-6) and then pursued at a more empirical level by the group of M.J.S.Dewar. The CNDO/INDO methods were genuine chemical models in the sense that they

could be used to study many molecules, vary structure to determine equilibrium geometries and generate potential surfaces. However, they were limited by uncertainty over the consequences of the massive integral approximations and the large number of empirical parameters.

Within the *ab initio* community, a truly major development was the introduction of gaussian-type basis functions. In 1950, S.F. Boys [7], working in Cambridge, had demonstrated that all integrals in SCF theory could be evaluated analytically if the radial parts had the form  $P(x,y,z)\exp(-r^2)$ , where  $P(x,y,z)$  is any polynomial in the cartesian coordinates  $x,y,z$ . Initially, this appeared to be of limited value, since single gaussian functions were poor approximations to atomic orbitals, but it was clear that prospects would improve if larger numbers of basis functions could be handled. For several years, there was competition between proponents of Slater-type and gaussian-type basis sets.

The 1950s also saw the introduction of computers into quantum chemistry. By the time of the 1959 meeting, there were already several groups developing *ab initio* programs, using both Slater and gaussian bases. Early codes for 2-center integrals with Slater basis functions were developed in Chicago and used by Ransil in the first full LCAOSCF treatment of diatomic hydrides. At the same meeting, Boys presented several prescient papers describing simple SCF calculations using gaussians. During the early 1960s, other general purpose programs were developed, notably the gaussian packages POLYATOM and IBMOL, leading to a number of individual computations of molecular orbitals at the LCAO or minimal basis level.

My own research group began *ab initio* work in 1968 with the development of the GAUSSIAN program. At that time, the relative cost of *ab initio* LCAOSCF and CNDO computations on small organic molecules was over 1000. The original intention was to use full *ab initio* results to test various integral approximations that were less severe than the use of zero differential overlap. However, in the course of developing the program, Warren Hehre and I were able to generate a new integral algorithm that improved efficiency for highly contracted gaussian basis sets by more than two orders of magnitude [8]. This was based on a method of axis rotation inside inner loops, thereby limiting the number of arithmetic operations in the innermost sections of the program. Using a procedure of least-squares fitting Slater-type basis functions by a fixed contraction of  $K$  gaussians, we were able to reproduce the results of earlier full Slater results on a series of small molecules. The choice  $K=3$  proved adequate and led to the STO-3G basis and the general theoretical model HF/STO-3G. This was published in 1969 [9] and the code was made generally available as GAUSSIAN70 shortly thereafter.

Investigation of the minimal HF/STO-3G model quickly showed major failures. Comparison of some isomeric species (e.g. propene and cyclopropane) showed too much stability for single bonds, relative to multiple bonds. This can be traced to the failure of the minimal basis to describe *anisotropic* atoms. In acetylene, for example, the carbon  $2p\sigma$  atomic orbitals should be much tighter than  $2p\pi$ ; this effect cannot be properly simulated by the

isotropic structure implied by a minimal basis with identical  $2p$  functions in all three directions. This difficulty can be overcome by using two basis functions per valence atomic orbital instead of one. Such a basis is 6-31G, which has a single contracted 6-gaussian basis function for the inner shell, a set of inner 3-contracted and a set of outer uncontracted gaussians for the valence shell of each atom. This is an example of a *split-valence* basis. Another similar commonly used type of basis set is *double-zeta*, in which there are two basis functions per atomic orbital for *all* atomic shells.

There are several notable failures for split-valence bases. In the first place, such bases tend to favor structures of high symmetry. For example, the ammonia molecule  $NH_3$  is predicted to have a trigonal structure which is too close to planarity. This deficiency can reasonably be attributed to the fact that, in a planar structure, the lone pair of electrons are assigned to a nitrogen orbital that is pure p-type, which cannot mix with higher angular momentum d-type functions, whereas, in a non-planar structure, the lone-pair orbital is a *sp* mixture, for which further stabilization by d-mixing is possible. A second deficiency in Hartree-Fock studies at the split-valence level is an exaggeration of polarity, as measured by electric dipole moments. This can also be attributed to restriction of lone-pair orbitals to pure p-type. The  $3p\pi$  lone-pair orbitals in  $HCl$ , for example, will probably be polarized towards hydrogen if mixing with  $d\pi$  basis is allowed, thereby reducing the predicted dipole moment.

Considerable improvement is found in Hartree-Fock models if a single set of uncontracted d-functions are added on each heavy (non-hydrogen) atom. Such a basis is 6-31G\*, or 6-31G(d) [10,11]. If a single set of uncontracted p-functions is added on each hydrogen, the basis is denoted by 6-31G\*\* or 6-31G(d,p). These additional basis functions are termed *polarization* functions. The full model with the 6-31G\* basis is then described as HF/6-31G\*. Other important basis set extensions are the introduction of higher polarization functions (as in 6-31G(2df,p) which contains two sets of d-functions and a set of f-functions on heavy atoms and a single set of p-functions on hydrogen) and the use of diffuse functions, which are particularly important for anions and electronic states. The latter are denoted by a '+' as in 6-31+G(d).

The Hartree-Fock model HF/6-31G\* has proved quite effective in the description of molecular conformations. Its overall performance in this and other regards has been documented elsewhere [12]. It is notably successful in giving differences of different isomeric forms of organic molecules, where no major changes of bond lengths are involved. Rotational potentials about single bonds were successfully explored using this level of theory [13]. A particular example is the anomeric effect in carbohydrate chemistry, which was not properly understood until the interaction of rotational potentials about geminal C-O single bonds was investigated using HF/6-31G\* theory [14].

## CORRELATED MODELS

The major fault implicit in all Hartree-Fock models is neglect of electron correlation between the motions of electrons of antiparallel spin ( $\alpha\beta$  correlation). In the very early days of quantum chemistry, it was recognized that neglect of correlation led to severe underestimation of bond dissociation energies. This may be understood qualitatively by considering the process of complete homolytic dissociation of a bond in which one electron ends up on one center and one on the other. If the motion of the two electrons is uncorrelated, there will be a finite possibility of both electrons ending up on the same center.

Neglect of  $\alpha\beta$  electron correlation is implicit in the use of a single-determinant wavefunction; improved wavefunctions necessarily involve the use of many determinants. Most practical correlation procedures start with the Hartree-Fock determinant and form linear combinations with other determinants. It is particularly convenient to form additional determinants from the unoccupied or virtual molecular orbitals, which are the higher eigenfunctions of the Fock operator. If a finite basis is used, with  $2n$  electrons and  $N$  cartesian basis functions, there will be  $N-n$  virtual orbitals, which may be occupied by  $\alpha$  or  $\beta$  electrons.

At this point, it is convenient to change the notation somewhat and use *spinorbital basis functions* which are products of the cartesian basis functions and the  $\alpha$  or  $\beta$  spin functions.  $N$  is now the size of this spinorbital basis (twice the number of cartesian basis functions) and  $n$  is the total number of electrons. This notation enables us to use a common notation for both spin-restricted and spin-unrestricted cases. If labels  $i, j, k, \dots$  are used for occupied spinorbitals and labels  $a, b, c, \dots$  for virtual, then single-determinant functions using Fock orbitals may be classified as unsubstituted (i.e. Hartree-Fock)  $\Psi_0$ , singly substituted  $\Psi_i^a$ , doubly substituted  $\Psi_{ij}^{ab}$  and so forth. A general multi-determinant wavefunction can then be written

$$\Psi = a_0 \Psi_0 + \sum_{ia} a_i^a \Psi_i^a + \sum_{ijab} a_{ij}^{ab} \Psi_{ij}^{ab} + \dots \quad (12)$$

The  $a$ -coefficients can be determined by variation to minimize the calculated energy. This is the method of *configuration interaction* (CI). If only singles are mixed in, no energy lowering follows, since the occupied orbitals are already optimized. The simplest effective form of CI allows for doubles only in (12). This is usually denoted by CID. If singles are also included, the method is CISD. These configuration interaction techniques were first implemented as iterative schemes around 1970 and are still often used in practical computations. If all possible substitutions are included in the expansion (a large but finite set if a finite basis set is used), the method is described as full configuration or FCI. The FCI procedure, although desirable in principle, is usually too costly to apply except for very small systems.

Although CID and CISD are well-defined models, given a standard basis set, they suffer some serious disadvantages. These have to do with *size-con-*



*sistency*. If a method such as CID is applied to a pair of completely separated systems, the resulting energy is *not* the sum of the energies obtained by applying the same theory to the systems separately. If CID is applied to two separated helium atoms, for example, the wavefunction does not allow for *simultaneous* excitation of pairs in each atom, this being strictly a quadruple excitation. This failure of CID and CISD models is likely to lead to poor descriptions of large molecules and interacting systems.

A second general method of incorporating electron correlation is to treat its effects by perturbation theory. Suppose we define a perturbed Hamiltonian as

$$H(\lambda) = F_0 + \lambda\{H - F_0\} \quad (13)$$

where  $F_0$  is the Fock Hamiltonian (for which the single determinants in (12) are exact eigenfunctions), then  $\Psi_0$  is the appropriate wavefunction if  $\lambda = 0$  and the exact (FCI)  $\Psi$  is obtained if  $\lambda = 1$ . The perturbation procedure used is to expand the computed energy in powers of  $\lambda$ ,

$$E(\lambda) = E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \dots \quad (14)$$

cut the series off at some level and then put  $\lambda = 1$ . This perturbation method was first introduced by Moeller and Plesset [15] and is often denoted by MPn if terminated at order n. The MP1 energy ( $E_0 + E_1$ ) is identical to the Hartree-Fock value. MP2 is the simplest practical perturbative procedure for electron correlation and incorporates only effects of double substitutions. At third order, MP3 also involves only double substitutions. At the fourth order level, MP4 includes a description of the (indirect) effects of singles, the leading contributions of triples and some treatment of certain quadruple substitutions.

Moeller-Plesset theory is size-consistent if the computations are carried out completely at any given order. Difficulties are that the terms become algebraically complicated at higher orders and also are increasingly costly to apply. In fact, Hartree-Fock theory (with no integral approximations) scales as  $N^4$ , MP2 as  $N^5$ , MP3 as  $N^6$  and MP4 as  $N^7$ . The triple contributions in the MP4 energy are the most expensive and generally limit the applicability of Moeller-Plesset theory to this level. The MP2, MP3 and MP4 models were implemented by several groups in the 1970s and incorporated into the GAUSSIAN program [16,17].

A third general approach to correlation theory is the use of *coupled cluster* methods, originally introduced into quantum chemistry by Cizek [18]. If the configuration interaction CID wavefunction is written in the form

$$\Psi = (1 + T_2)\Psi_0 \quad (15)$$

where  $T_2$  is an operator specifying all double substitutions, with undetermined coefficients, then the corresponding coupled-cluster function (CCD) is

$$\Psi = \exp(T_2)\Psi_0 \quad (16)$$

The CCD coefficients are determined, not by the variational method, but by requiring zero projection of  $(H - E)\Psi$  onto  $\Psi_0$  and all  $\Psi_{ij}^{ab}$ . This method was first implemented in 1978 [19–21]. Single substitutions are incorporated by using the operator  $\exp(T_1 + T_2)$  instead of  $\exp(T_1)$ . This then defines a CCSD model [22,23].

Unlike CISD, the CCSD method is size-consistent. The cost is of order  $N^6$ , as for CISD. Being non-variational, the resulting total energy is no longer an upper bound for the exact result, but it is generally thought that the achievement of size-consistency is a matter of greater importance. Another, slightly simpler, method is *quadratic configuration* denoted QCISD. This is also size-consistent and can be regarded as an approximation intermediate between CISD and CCSD.

The QCISD and CCSD methods take no account of the effects of triple substitutions, known to be important by studies at the MP4 level. A useful way to take account of triples is to carry out an iterative QCISD or CCSD computation and then do a single computation of the effects of triples, using the single and double amplitudes already found. These are the QCISD(T) and CCSD(T) methods [24,25]. A third related method is the Brueckner-doubles method, BD(T) [26], which alters the underlying occupied orbitals so that there is no singles mixing. All three of these methods are superior to MP4 in that, when the energy is expanded in a Moeller-Plesset series, complete agreement with a FCI expansion is obtained up to fourth order and many other terms at higher order are also included [27]. In fact, the QCISD, CCSD and BD methods have the further advantage of being completely correct for composite two-electron systems such as a set of isolated helium atoms.

The cost of QCISD(T) or CCSD(T) scales as iterative  $N^6$ , followed by a single computation at  $N^7$ . They represent the most sophisticated correlation methods that are simple enough to be incorporated into general theoretical models at the present time.

## GENERAL ENERGY MODELS

In recent years, progress has been made in developing models which reproduce chemical energies to an accuracy approaching that achieved in good experimental work. The description of model features in the two previous sections indicates that two main features are involved, basis set and level of correlation. The options available are usefully summarized in a two-dimensional *model chart* as shown in Figure 1. The various correlation methods are displayed horizontally in order of increasing sophistication from left to right. Basis sets are displayed vertically, becoming more flexible from top to bottom. At the far right, full configuration interaction (FCI) represents complete solution *within the finite space defined by the basis*. At the bottom of the table, we have (in principle but not in practice), the results of applying a complete basis set. At the bottom right, application of a complete basis set with full con-

figuration interaction corresponds to full solution of the non-relativistic Schrödinger equation.

Basis	HF	MP2	MP3	MP4	QCI	FCI
STO-3G						
6-31G						
6-31G(d)						
6-31+G(d)						
6-311+G(d)						
6-311+G(2df)						
$\infty$						S-eqn

Figure 1. General Model Table. (QCI refers to QCISD(T)).

Each empty box in this chart represents a well-defined size-consistent theoretical model as specified in Section 2. Clearly, we may test each level to find how far we have to proceed from top-left to bottom-right for acceptable agreement between theory and experiment. Eventually, adequate performance will be achieved, if the underlying assumptions of quantum mechanics are correct.

In practice, full models usually have to make some compromises to achieve a wide range of applicability. If the prediction of energies is most important, a common practice is to carry out a geometry optimization (to an equilibrium structure, for example) at some lower level of theory and then make a final, more expensive, computation at a higher level. A useful notation for this type of composite model is "model-1//model-2", meaning single-point calculations using model-1 at geometrical structures determined by model-2.

To illustrate these ideas, we give a partial description of the G3 model for molecular energies, recently published [28]. This is a refinement of previous energy models G1 and G2 which have been under development for more than a decade [29,30]. The main computational steps are summarized in Figure 2.

Basis	HF	MP2	MP4	QCI
6-31G(d)	freq	opt-1	2	3
6-31+G(d)		4	5	
6-31G(2df,p)		6	7	
G3large		8		?

Figure 2. G3 Model Table. (QCI refers to QCISD(T)).

In addition to the standard type of basis sets already described, a large basis (G3large), which permits a flexible description of the whole space with inner shells, is added. This basis is so large that only MP2 computations are reasonably possible. Geometrical structures in the G3 model are determined at the MP2/6-31G(d) level [31]. This is followed by a sequence of single-point calculations which aim to estimate the results of a potential QCI/G3 large energy, by assuming that effects of some of the improvement steps can be treated additively. The actual formula used is:

$$\rho = 2 + (3 - 2) + (5 - 2) + (7 - 2) + (8 - 1) - (4 - 1) - (6 - 1) \quad (17)$$

Earlier studies [32] had indicated that this kind of additivity was reasonably accurate. (It should be noted that all correlation computations except the full MP2/G3 large are carried out in the "frozen core" approximation, only interactions between valence electrons being treated).

An important contribution to total molecular energies is the zero-point vibrational energy. This is estimated in G3 theory by using harmonic frequencies calculated at the HF/6-31G(d) level and then empirically scaled by a factor 0.8929 (HF theory being known to systemically overestimate the magnitudes of frequencies [33]). In addition, a small correction is added for the spin-orbit splitting in isolated atoms, obtained from experimental data [34].

The computations as described up to this level give a reasonable account of significant energy differences, such as dissociation energies and ionization potentials. However, there is a significant systematic error, all binding energies being slightly too low. This can be reasonably interpreted as being due mostly to the limitation in the basis sets being used. An accurate description of the wavefunction cusp at the point where electrons of opposite spin come to the same point in space requires basis sets involving high angular momentum. Another reason is that, in molecules, the symmetry is lower than in atoms and again neglect of the effects of higher angular momentum basis functions will favor atomic energies relative to molecular.

These difficulties can be partly overcome by adding a *small* empirical correction, depending on the number of electrons and distinguishing between atoms and molecules. The theory therefore becomes semi-empirical or, perhaps "slightly empirical" since the parameters are small and their origin is partly understood. This higher-level correction (HLC) is  $-An_{\beta} - B(n_{\alpha} - n_{\beta})$  for molecules and  $-Cn_{\beta} - D(n_{\alpha} - n_{\beta})$  for atoms (including atomic ions).  $n_{\alpha}$  and  $n_{\beta}$  are the numbers of  $\alpha$  and  $\beta$  electrons, respectively, with  $n_{\alpha} \geq n_{\beta}$ . This completes the specification of a total G3 energy for any atom or molecule.

The parameters  $A, B, C, D$  are determined as part of the validation process. This is carried out using a large set of 299 experimental energy differences, involving molecules up to the size of benzene (42 electrons). These data include 148 heats of formation, derived from heats of atomization, 85 ionization potentials, 58 electron affinities and 8 proton affinities. All of these experimental results are believed known to an accuracy of 1 kcal/mole or better. Values of  $A, B, C, D$  are obtained by minimization of the mean absolute

deviation between theory and experiment. These are (in millihartrees) 6.386, 2.977, 6.219 and 1.185. The resulting mean deviation is 1.02 kcal/mole, close to the target accuracy. The corresponding root-mean-square deviation, which lays more emphasis on the poorer levels of agreement, is 1.45 kcal/mole. However, nearly 88 % of the G3 deviations fall in the range,  $-2.0$  to  $+2.0$  kcal/mole. These results are significantly better than the prior G1 and G2 models, which use a smaller database of experimental facts.

The poorest results are worthy of note. Largest absolute deviations are 4.9 kcal/mole ( $C_2F_4$ ) for heats of formation, 7.0 kcal/mole ( $B_2F_4$ ) for ionization potentials, 4.2 kcal/mole ( $NH$ ) for electron affinities and 1.8 kcal/mole ( $PH_3$  and  $SH_2$ ) for proton affinities.

## CONCLUSIONS

The current status of *ab initio* quantum chemical models is that some success has been achieved in approaching experimental accuracy in predictive power. The target of 1 kcal/mole is not far away for small molecules containing up to about fifty electrons. However, the G3 model has a number of remaining deficiencies that merit further attack.

1. The use of an empirical correction, which depends only on the number of electrons, is undesirable. One consequence is that the model becomes discontinuous in some manner. For example, if a bond is broken, the electron count of paired versus unpaired electrons has to change at some point, thereby providing a discontinuity in the potential surface. The same criticism can be applied to the use of different parameters for atoms and molecules. Some form of extrapolation is probably necessary, but it would be much better if this could be carried out in a continuous and differentiable manner.
2. The G3 model is based on MP2/6-31G(d) geometries, which are known to show considerable errors [31]. Some of the failures of the final energies can be attributed to this; clearly a method which would reproduce known bond lengths and angles more accurately would be preferable.
3. No account is taken of relativity in the G3 model. The total energy of a molecule is known to depend significantly on relativistic corrections, particularly for inner-shell electrons. However, considerable cancellation of errors occurs in processes such as bond dissociation. Nevertheless, some inclusion of relativistic contributions to chemical processes is clearly desirable.
4. The applicability of the G3 model to large systems is presently limited by the very expensive treatment of the triples terms, where computational cost scales as the seventh power of the size of the system. The magnitude of these terms is small, but not insignificant. A simpler treatment of three-electron effects would be desirable.

Finally, some brief comment should be made about theoretical models based on density functional theory (DFT). Such methods do not handle the two-electron interactions explicitly but rather allow for them using properties

of the one- electron density. This leads to lower cost and therefore a wider range of applicability. Recent forms of DFT have also introduced a considerable amount of empirical parameterization, sometimes using the same set of experimental data. At the present time, the principal limitation of DFT models is that there is no clear route for convergence of methods to the correct answer, comparable to the *ab initio* chart shown in Figure 1. Interaction between these two groups of theoretical chemists is a hopeful direction for future progress.

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