Translated from *Uspekhi Khimii*, 43,491-518 (1974) U.D.C. 541.20;541.63

Non-empirical Calculations of the Geometry and Conformations of Polyatomic Molecules

V.G.Dashevskii

Non-empirical methods for the calculation of the geometry, barriers to internal rotation, and conformation energies of polyatomic molecules are discussed. It is shown that the geometry can be predicted with adequate accuracy by calculations with "moderate" basis sets. Reliable estimations of barriers to internal rotation and of conformational energies require in general considerably larger basis sets. Several procedures for combining quantum-mechanical integrals are considered and the "nature" of the barriers is analysed from this standpoint.
The bibliography includes 174 references.

CONTENTS

I. Basis sets employed in *ab initio* calculations 184
II. Calculations of the equilibrium geometry of polyatomic molecules 187
III. Barriers to internal rotation and conformational energies 189
IV, The nature of the barriers to internal rotation 193
V. Calculations with localised orbitals 195
VI. Concluding remarks 196

I. BASIS SETS EMPLOYED IN *AB INITIO* CALCULATIONS

The previous review[1] dealt with the self-consistent field approximation and the Roothaan equations of the LCAO-MO method, on which modern calculations of the electronic structures of molecules are based, were discussed. These equations will serve as our starting point. However, in the analysis of non-empirical *ab initio* calculations one should note certain factors which are less important in semiempirical theories.

In the Hartree–Fock approximation for a molecule with a closed electronic shell, the wave function Ψ is represented by the antisymmetrised products of the spin-orbitals (SMO) Ψ_i or the Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \ldots \psi_{N/2}\bar{\psi}_{N/2}| \qquad (1)$$

where N is the number of electrons.

There are of course no conditions under which function (1) can be an exact wave function of the molecule whatever are the exact individual SMO; also the energy defined by this function differs from the true total energy. The difference between the Hartree–Fock energy and the energy corresponding to the exact wave function has come to be called the correlation energy. As a rule, the correlation energy of a molecule is greater than the sum of the correlation energies of its constituent atoms[2,3].

The exact wave function can be approached only by going outside the framework of the single-configuration approximation (one Slater determinant is usually termed a configuration). Thus in the configuration interaction method the molecular wave function is assumed to be

$$\Psi = C_1\Psi_1 + C_2\Psi_2 + \ldots, \qquad (2)$$

where Ψ_i is one of the configurations defined as the antisymmetrised product of the spin-orbitals. The coefficients C_i can be found by the variational method[4,5], but this procedure is extremely laborious, since series (2) converges slowly. For this reason, the exact wave functions are usually sought only for atoms and diatomic molecules. On the other hand, when considering polyatomic molecules the treatment is as a rule confined to the Hartree–Fock approximation.

The second assumption usually made in quantum-mechanical calculations on molecules involves the representation of the molecular orbitals, i.e. the spatial component of the spin-orbitals Ψ_i, by a linear combination of atomic orbitals (LCAO):

$$\varphi_i = \sum_{\nu=1}^{m} c_{i\nu}\varphi_\nu \qquad (3)$$

where φ_ν are the atomic orbitals (AO) the set of which is termed the basis set.

The LCAO approximation imparts to the wave function of the molecule a specific analytical form and in addition the Hartree–Fock formulation presupposes that the best molecular orbitals of the Slater determinant are found. However, it has been shown for other examples[5-7] that, when the basis set is sufficiently large (and also flexible), then the LCAO procedure can yield the Hartree–Fock energy to within about 0.5%. The minimum energy attainable by increasing the basis set has come to be called the Hartree–Fock limit, although in fact this is more correctly the limit of the LCAO-MO approximation and not at all the Hartree–Fock energy of the molecule.

All the calculations discussed below are based on the above two approximations. The LCAO-MO approximation for molecular properties such as geometry and conformational energies, expressed in terms of the Roothaan equation, is quite acceptable. It is shown below that, for a sufficiently large number of atomic orbitals in Eqn.(3), these properties can be calculated with "chemical" accuracy, i.e. with an accuracy characteristic of experimental determinations. The procedures used to go outside the framework of the above approximations are only briefly discussed at the end of the review and the possible limits of the errors are indicated.

We shall now consider the atomic orbitals entering into Eqn.(3). In the course of more than two decades (since the end of the 1920's) Slater type functions (STO≡Slater type orbitals) have been used in all quantum-mechanical calculations on molecules:

$$\varphi = Ar^{n^*-1}e^{-\zeta r}Y_{l,m}(\theta, \varphi) \qquad (4)$$

where n^* is the effective principal quantum number, A a

normalising factor, and $Yl,m(\theta,\varphi)$ are spherical harmonics. In the radial component of the STO r is the distance from the centre and ζ the orbital exponent. The STO are known to be close in form to the true Hartree–Fock atomic orbitals which are in turn obtained by a numerical calculation and have been tabulated long ago for many atoms: at any rate, at short and long distances from nuclei, the STO are virtually identical with the tabulated data. The search for the STO contants most effective in molecular calculations has continued, since the 1930's, i.e. since the time when Slater[7] proposed formulae for the calculation of n^* and the screening constants γ entering into the orbital exponents [$\xi = (Z_e - \gamma)/n^*$, where Ze is the nuclear charge]. Clementi and Raimondi[8] tabulated the STO constants found by minimising the atomic energy up to krypton inclusive. In later studies[9,10] the STO constants were selected by taking into account the properties of the atoms in molecules.

It would appear that the STO should be ideally suitable for calculations on polyatomic molecules, since the use of a slightly extended basis set makes it possible to obtain a wave function close to the true Hartree–Fock function and on energy differing only slightly from the Hartree–Fock limit. However, the application of the STO involves mathematical difficulties associated with the calculation of many-centre integrals. Indeed it has been shown[1] that the matrix elements of the Hartree–Fock operator include the integrals $(\mu\nu/\lambda\delta)$

$$(\mu\nu/\lambda\sigma) = \int\int \varphi_\mu^*(1)\varphi_\nu(1)(r_{12})^{-1}\varphi_\lambda^*(2)\varphi_\sigma(2)\,d\tau_1 \cdot d\tau_2 \qquad (5)$$

in which there are orbitals centred on different atoms. The evaluation of one- and two-centre integrals does not present special difficulties: as a rule, they can be estimated rapidly and accurately[11–13]. However, the evaluation of three- and four-centre integrals is difficult. Although several methods have been proposed for their estimation[14,15], until recently the evaluation of each integral required on average about 1 s even on the most powerful modern computers. Moreover, the number of two-electron integrals arising in the solution of the Hartree–Fock LCAO-MO problem is of the order of N^4, where N is the number of orbitals; for example, in the case of a basis set of 20 orbitals the number of integrals is 22 155 and for a basis set of 50 orbitals the number is 814 725. The total time required for the solution of the Roothaan equations using the STO for polyatomic molecules naturally becomes very long. Therefore in the last decade Gaussian type orbitals, in which the radial component is proportional to $\exp(-\alpha r^2)$ and not to $\exp(-\zeta r)$, have come to be widely used. Namely

$$\varphi = A(\alpha)\, r^{n-1} \exp(-\alpha r^2)\, Y_{l,m}(\theta, \varphi) \qquad (6)$$

where

$$A(\alpha) = 2^{n+1}[(2n-1)!!]^{-1/2}(2\pi)^{-1/4}\alpha^{(2n+1)/4}, \qquad (7)$$

and the functions $Yl,m(\theta,\varphi)$ are in this case exactly the same as in Eqn.(4).

Although the Gaussian type orbitals (GTO Gaussian type orbitals) describe incorrectly the distribution of electron density near the nuclei and at long distance from them, the evaluation of the $(\mu\nu/\lambda\delta)$ integrals no longer presents special difficulties. It is probable that the GTO, introduced into practical molecular calculations by Boys[16] and Meckler[17], have in fact made it possible to achieve in quantum chemistry an approach to the solution of the Hartree–Fock problem for polyatomic molecules, including organic molecules[18].

It is not surprising that generally speaking the Slater basis set gives a more adequate description of molecular properties than the Gaussian basis set because the STO are close in form to the Hartree–Fock orbitals. The use of the minimal Guassian basis set (one function for each electron) results in a difference of 10–20 eV between the total energy of comparatively small molecules and the Hartree–Fock limit, whereas the difference for the minimal STO basis set is only 1–2 eV. Thus much effort has been expended in attempts to approximate the Slater orbitals in terms of the Gaussian orbitals and thereby achieve the best approximation to the Hartree–Fock limit. This idea constitutes the basis of the STO-N G method[19,20], in which each STO is replaced by N GTO.

The expansion of the Slater functions φ_S in terms of the Gaussian functions φ_G can be represented in the form

$$\varphi_s = \sum_{i=1}^{N} c_i \varphi_{g,i}, \qquad (8)$$

where c_i are the expansion coefficients and N is the parameter of the STO-N G method. Huzinaga[21] showed that, for the hydrogen atom, 6–10 GTO of 1s and 2p types yield virtually the same energy as a single STO, and determined the coefficients c_i. Subsequently Stewart[32] obtained the c_i constants also for other atoms.

The choice of N in non-empirical calculations by the STO-N G method constitutes a special problem and depends on the property which must be estimated. Experiment shows that the average time required for the evaluation of many-centre integrals with GTO is approximately 1000 times less than for computation with STO. Thus, on replacing each STO by N Gaussian type orbitals, the time gain is approximately by the factor $1000/N^4$. It is easy to calculate that the STO-2G method leads to a reduction of the time of computation by a factor of 60, the STO-3G method by a factor of 12, and the STO-4G method by a factor of 4. The STO-N G methods with $N = 5, 6, \ldots$ are no longer effective and, in order to obtain the required accuracy, it is necessary to employ the STO or, even better, an extended basis set which can be made up of both STO and GTO. Subsequently it will be shown that, for adequate estimates of many properties of polyatomic molecules including their geometry, it is sufficient to introduce 3–4 GTO for each STO.

However it is absolutely obligatory to select Gaussian basis sets in such a way that they are close to the corresponding Slater basis sets. One can begin with the condition that, provided that the Gaussian basis sets are sufficiently large, they yield a fair approximation to the Hartree–Fock limit and make it possible to predict with satisfactory accuracy the properties of polyatomic molecules. Several methods of formulating such basis sets are discussed below.

Finally one should note that comparatively recently considerable advances have been achieved in the evaluation of many-centre integrals $(\mu\nu/\lambda\delta)$ in which $\varphi\mu$, $\varphi\nu\ldots$ are the STO.[23–25] Therefore in the near future one may expect the resumption of non-empirical calculations of electronic structure, geometries, conformation energies, and other properties of polyatomic molecules with the aid of Slater basis sets. Examples of such calculations already exist[26,27].

We shall now enumerate several methods of formulating the basis set which have become common in calculations of the geometries and energies of polyatomic molecules. The results of their application and the comparative assessment of their effectiveness are discussed in succeeding sections.

1. The Slater basis set. The orbital exponents ζ are optimised with respect to the atomic energies and are assumed to be unchanged in molecular calculations; in the solution of the Roothaan equations only the coefficients $c_{i\nu}$ in Eqn. (3) are varied. Both limited (minimal)[28,29] and expanded[27] basis sets are employed in the calculations.

2. The "double-zeta" basis set. The exponential factor in the STO, $\exp(-\zeta r)$, is replaced by a linear combination of two exponents—$\exp(-\zeta_1 r)$ and $\exp(-\zeta_2 r)$. The optimal values of ζ_1 and ζ_2 have been found[30,31] for atoms with $Z \leqslant 36$ and they are assumed to be fixed in molecular calculations, only the LCAO coefficients being varied.

The basis sets discussed below are constructed from Gaussian type functions.

3. Basis sets of the STO-N G type. The problem of which values of N are to be adopted in order to obtain satisfactory estimates of molecular properties was investigated by Pople and coworkers[32-35] in relation to such properties as the geometry, barriers to internal rotation, dipole moments, and Mulliken populations. It was found that the STO-3G method yields a satisafactory approximation of the STO.

4. The LEMAO-N G basis sets (LEMAO ≡ least energy minimal atomic orbitals)[36,37]. For each atomic orbital, one introduces N GTO, the parameters of which correspond to the minimum energy of the atom. For $N \to \infty$, the energy of the molecule calculated using this basis set must necessarily tend to the Hartree–Fock limit, while in the STO-N G method the Hartree–Fock limit cannot be attained in principle for $N \to \infty$ when the Slater basis set is limited. However, specific calculations have shown[37] that the convergence of the LEMAO-N G method with increase of N is extremely slow: for low values of N (3, 4, 5), the STO-N G method is more effective; on the other hand, there is no point in a further increase of N, since the time required to calculate the total energy increases rapidly and it is then better to employ an extended Slater basis set.

5. The 4-31 G basis set[38,39]. It is constructed as follows: each orbital of the inner shell is represented by the sum of four Gaussian type functions and the valence shell orbitals are divided into two groups. The orbitals of the first group are described by three GTO and those of the second group by one GTO (in particular four GTO are required for the H atom and twenty GTO are required for the C atom). The coefficients of the expansion in terms of GTO are found from the condition for the minimum energy of the atom in the ground state. The 4-31 G basis set is more flexible than STO-3G but at the same time it is much more "expensive". This basis set yields a lower energy and, what is most important, gives satisfactory differences between the energies of various nuclear configurations. Therefore, as shown in Sections II and III, it is entirely suitable for very accurate calculations of molecular geometry, conformational energies, and particularly barriers to internal rotation.

6. The contracted Gaussian basis set. Apart from the 4-31 G basis set, one can of course employ also other extended Gaussian basis sets, and the greater the number of functions introduced for each orbital the greater the accuracy of the prediction of various molecular properties. However, an increase of the basis set entails a sharp increase of computer time. It has therefore been suggested that the Gaussian functions be grouped and that not all the coefficients $c_{i\nu}$ entering into Eqn. (3) be varied, but only those which refer to the given groups of functions[40-43]. The number of Hartree–Fock equations is then significantly reduced.

The employment of contracted basis sets permits the calculation of the structures and properties of large organic molecules. For example, the energies of various conformations of cyclo-octatetraene, whose molecule consists of 8 carbon atoms and 8 hydrogen atoms, have been calculated[44]. The authors employed five s-type and two p-type Gaussian functions for each carbon atom and two s-type functions for each hydrogen atom. This basis set can be naturally designated by (5.2/2). As a result of the "contraction" procedure, this basis set was reduced to (2.1/1) and the number of Hartree–Fock equations was decreased from 72 to 32. The coefficients within each group and the orbital exponents are usually taken from calculations for simpler molecules and are assumed to be fixed. Thus the same group functions were employed for cyclo-octatetraene as for ethylene.

7. The "lobe" GTO basis set. Whitten[40] proposed Gaussian type basis sets the orbitals of which are not centred on atoms but on certain other points in space. The possibility of employing such basis sets depends on the fact that spherically asymmetric orbitals can be imitated with some approximation by a linear combination of spherically symmetrical Gaussian functions. The spherical harmonics $Yl,\mathrm{m}(\theta,\varphi)$ in quantum-mechanical calculations then disappear and the calculation of the integrals is significantly simplified. Thus instead of p orbitals it is possible to introduce two s-type "lobes" or two "petals" the centres of which are located on a straight line passing through the nucleus at equal distances from the latter; instead of d orbitals, it is necessary to introduce now at least four "lobes". Calculations with such basis sets then yield a fairly low total energy, provided that the number of "lobes" is fairly large. Examples of the calculation of the geometry of polyatomic molecules using the "lobe" GTO basis sets have been described[45-50].

8. The "floating orbital" basis set. So far we have considered atomic orbitals with fixed exponents and centres and the molecular orbitals were optimised only with respect to the LCAO coefficients. Nevertheless it is clear that, when the molecular orbitals are also optimised in respect of the orbital exponents and the positions of the centres of the atomic orbitals, one can achieve a closer approximation to the Hartree–Fock wave function. However, this complicates the procedure in the adjustment for self-consistency: it is necessary to solve the Roothaan equation separately for various exponents or to carry out a direct minimisation of the Hartree–Fock functional by numerical methods.

Frost[51-53] proposed a model constructed on the basis of a one orbital–one Gaussian function principle. The limitation of the basis set of this model is to some extent compensated by its flexibility, since, together with the LCAO coefficients, the parameters α_i in Eqn. (6) and the positions of the atomic orbital centres are varied. The geometry of the molecule is determined by direct minimisation of the total energy with respect to independent geometrical parameters describing the positions of the nuclei and with respect to the orbital exponents α_i. As

shown in Section II, the model of "floating Gaussian orbitals" leads to surprisingly satisfactory results owing to the "liberation" of the parameter α_i, despite the fact that, in consequence of the vast limitation of the basis set, one is still a long way from the Hartree–Fock limit.

9. Ellipsoidal Gaussian basis sets. If instead of traditional Gaussian functions (6) one employs ellipsoidal Gaussian functions[54,55], then inclusion of a comparatively small number of orbitals will presumably yield even more satisfactory geometry and energy, which do not differ markedly from the Hartree–Fock parameters. Such functions are of the form

$$\varphi_l = x_l^{\lambda_l} \exp[\alpha_l x_l^2 + \beta_l y_l^2 + \gamma_l z_l^2], \quad (9)$$

where x, y, and z are the local cartesian coordinates of the ith function and α, β, γ, and λ are the parameters varied. The ellipsoidal basis set is more flexible than the floating orbital basis set and it can therefore probably find application in conformational problems.

II. CALCULATION OF THE EQUILIBRIUM GEOMETRY OF POLYATOMIC MOLECULES

Among all the molecular properties, geometry is the most "predictable". "Predictability" must be understood in the sense that, even for very small basis sets and for very unsatisfactory orbitals, the solution of the Hartree–Fock problem yields a reasonable agreement with experiment: the deviations rarely exceed 0.1 Å in bond lengths and several degrees in valence angles. The only difficulty is that in the calculation of the geometry the total energy must be calculated more than once. If there are several geometrical parameters, it is either necessary to plot a network of values of a very complex function (total energy) or direct minimisation methods must be employed. The solution of the latter problem for molecules of any complexity is still unrealistic and therefore in non-empirical calculations one must restrict the treatment to the simplest systems. Apart from the multidimensionality of the problems, one must bear in mind that the time required to calculate the energy increases very rapidly with molecular size—much more rapidly than in empirical and semiempirical methods.

Nevertheless it is easier to calculate the geometry than any other molecular property: the total energy may be approached only by very laborious calculations by the method of configuration interaction; even an approach to the Hartree–Fock limit requires calculations with very large and very carefully selected basis sets; nor is it easy to predict with satisfactory accuracy the distribution of electron density and dipole moments; finally, in order to obtain satisfactory energy differences (bond energies, barriers to internal rotation, and conformational energies), large and fairly reliable basis sets are necessary (in estimates of bond energies one must also take into account correlation effects).

The accuracy of the prediction of molecular geometry depends on the type and size of the basis set employed in the Roothaan equations. The use of Slater orbitals permits a greater accuracy of the calculation of the bond lengths and valence angles corresponding to the total energy minimum. Even better results are obtained when one uses an extended Slater basis set taking into account the polarisation of electrons, i.e. $2p$ functions are included in addition to the s functions of the hydrogen atom and d functions are included in addition to the $2s$ and $2p$ functions of the carbon atom. However, both allowance for polarisation and calculations with STO are too "expensive". Therefore the majority of quantum-mechanical calculations on polyatomic molecules have been carried out with Gaussian type basis sets.

In the search for the equilibrium geometry of polyatomic molecules, it is reasonable to try to restrict the treatment to comparatively small basis sets, since the total energy must be calculated many times. Thus Pople and coworkers[36,56] constructed a network of total energy values at 0.05 Å intervals for bond lengths and at 5° intervals for valence angles; they then subdivided the network at 0.01 Å and 0.1° intervals after which they carried out a quadratic interpolation, which resulted in an average error of about 0.001 Å in bond lengths and about 0.1° in valence angles. Frost[52,53] sought the minimum in the Hartree–Fock functional with respect to natural molecular coordinates (bond lengths, valence angles, and angles of rotation) and orbital exponents using the extremely effective Powell method[57]. Minimisation methods designed specially for quantum-mechanical calculations on molecules have been proposed[58,59]. The use of these methods makes it possible to reduce significantly the number of returns to the procedure function (total energy) and thereby reduce computer time compared with the time required to construct the network. The advantage of direct minimisation consists also in the fact that the derivatives of the Hartree–Fock function required for the selection of the direction of the descent contain the same integrals as the function itself and therefore a considerable proportion of the expensive minimisation process is carried out "free".

Table 1. Comparison of the bond lengths and valence angles calculated using different Gaussian basis sets.

Molecule	Bond or angle	Bond length (Å) or valence angle						
		LEMAO-3G[36]	LEMAO-5G[36]	STO-2G[60]	STO-3G[56]	STO-4G[24]	4-31G[38]	expt.
H_2	H—H	—	—	0.74	0.712	—	0.730	0.742
HF	H—F	0.952	0.966	0.93	0.956	0.955	—	0.917
N_2	N—N	—	—	1.10	1.134	—	—	1.094
NH_3	N—H HNH	1.009 112.8°	1.010 115.0°	— —	1.033 104.2°	1.029 104.4°	0.991 115.9°	1.012 106.7°
H_2O	O—H HOH	0.980 107.3°	0.987 109.1°	—	0.990 100.0°	0.987 100.0°	0.951 111.2°	0.957 104.5°
HCCH	C≡C C—H	1.191 1.055	1.197 1.060	— —	1.168 1.065	1.168 1.063	1.316 1.073	1.203 1.061
H_2CCH_2	C=C C—H HCH	1.332 1.063 116.2°	1.339 1.066 116.3°	1.33 — —	1.305 1.079 115.4°	1.307 1.079 115.7°	1.316 1.073 116.0°	1.330 1.076 116.6°
$H_3C—CH_3$	C—C C—H HCH	1.566 1.065 108.6°	1.581 1.068 108.5°	— — —	1.538 1.085 108.2°	1.535 1.083 108.2°	1.529 1.083 107.7°	1.531 1.096 107.8°
H_2CO	C=O C—H HCH	1.281 1.086 118.7°	1.293 1.087 119.9°	1.21 — —	1.217 1.101 114.5°	1.217 1.099 114.8°	1.206 1.081 116.4°	1.203 1.101 116.5°

We shall now consider the results of calculations of the geometries of certain simple polyatomic molecules and shall attempt to determine which basis sets are adequate

for satisfactory estimates of bond lengths and valence angles. Table 1, which is based on a number of literature data [32,36,56,60], compares the geometrical parameters obtained with the aid of various Gaussian type basis sets—LEMAO-3G, LEMAO-5G, STO-2G, STO-3G, STO-4G, and 4-31G. Table 1 shows that the LEMAO-5G method, let alone the LEMAO-3G method, is somewhat inferior to the STO-3G and 4-31G methods in terms of agreement with experiment: the HNH valence angle in the ammonia molecule is unduly high and the C–C bond in the ethane molecule and the C=O bond in the formaldehyde molecule are too long. Consequently preference must be given to the STO expansion compared with the Gaussian type orbitals even when the latter are optimised with respect to the atoms. The convergence of the STO-N G methods with increase of N is very rapid: judging from the few data obtained by Baird [60], even within the framework of the STO-2G method, it is possible to achieve a fairly satisfactory agreement with experiment and with further approximations by the STO-N G method. One can therefore formulate the problem of the calculation of the equilibrium geometry by the relatively rough STO-2G method with the aim of investigating "less predictable" properties for this geometry—the energy, electron density, etc.—by the STO-N G method with $N > 2$ and the very "expensive" 4-31 G method.

Table 2. Bond lengths and valence angles calculated by the STO-3G method [56].

Molecule	Bond or angle	Bond length (A) or valence angle		Molecule	Bond or angle	Bond length (A) or valence angle	
		calc.	expt.			calc.	expt.
CH_4	C—H	1.083	1.085	F_2N_2	N—F	1.277	1.384
					N=N	1.373	1.214
					FNN	111.5°	114.5°
CH_3F	C—H	1.097	1.105		φ	0° (*cis*)	0° (*cis*)
	C—F	1.384	1.385				
CH_2F_2	C—H	1.109	1.091	H_2O_2	O—H	1.001	0.950
	C—F	1.378	1.358		O—O	1.396	1.475
	HCH	108.8°	112.1°		HOO	101.1°	94.8°
	FCF	108.7°	108.2°		φ	125°	111.5°
CHF_3	C—H	1.119	1.098	F_2O_2	O—F	1.358	1.575
	C—F	1.371	1.332		O—O	1.392	1.217
	FCF	108.6°	108.8°		FOO	109.5°	109.5°
					φ	88.1°	87.5°
NF_3	N—F	1.386	1.365				
	FNF	102.1°	102.3°				

We shall consider in greater detail the results obtained with the aid of the STO-3G method. They are presented in Tables 1 and 2, the latter of which is based on the results of Newton et al. [56] In the first place mention must be made of the satisfactory agreement between the calculated and experimental bond lengths and valence angles in hydrocarbon molecules. Consequently, for the prediction of the structures of these molecules, the minimal Slater basis set (or a slightly "degraded" STO-3G basis set) prove to be entirely satisfactory. The situation is worse for molecules containing electronegative atoms or atoms with lone electron pairs. Thus the changes in the C–F bond lengths in fluoroethanes are not quite accurately represented; the bond length in the HF molecule is also excessive. The calculation does not predict the sharp shortening of the O–O bond on passing from H_2O_2 to O_2F_2; the theoretical O–F bond length in the O_2F_2 molecule is much smaller than the experimental value. The calculated valence angles do not nevertheless differ much from the experimental values even in the most unfavourable cases. However, the greatest discrepancies are again characteristic of the fluorine-and oxygen-containing molecules; in particular the calculated HOO angle in the hydrogen peroxide molecule is 6% greater than the experimental value.

The question arises of the causes of the unsatisfactory agreement with experiment for fluorine- and oxygen-containing molecules. The calculations carried out by Allen's group for simple molecules [45–50] have shown that the main reason is the limitation of the basis series: when orbitals for vacant shells are introduced, the agreement with experiment can be greatly improved. Another reason is of course the correlation effects, but these are probably small. Presumably, after the attainment of the Hartree–Fock limit, the calculated molecular geometry, including that of fluorine- and oxygen-containing derivatives, should virtually agree with the experimental geometry.

Yet another confirmation of the above hypothesis is provided by a study [61] in which the Hartree–Fock calculations were carried out for molecules as complex as that of formamide ($HCONH_2$). The basis series of these calculations included eleven s-type and seven p-type Gaussian functions for the C, N, and O atoms (one d orbital was taken into account for each of the three nuclear configurations): five s-type functions and three p-type functions were considered for the hydrogen atom. After carrying out the calculations for 44 nuclear configurations, the authors showed that the minimum total energy does indeed correspond to the observed experimental geometry of the formamide molecule.

Returning now to the assessment of the results obtained by the STO-3G method, we may note that, despite the observed deviations for several molecules, the agreement between the calculation and experiment is very good. For thirty molecules incorporating 75 individual bonds and angles, Pople and coworkers [56] obtained average deviations of 0.035 Å in the bond length and 1.7° in the valence angles. This is of course much better than can be obtained by different versions of the ZDO method [1] and particularly the CNDO method. Yet another evident advantage of the STO-3G method compared with ZDO is the absence of an arbitrary choice of parameters; the *ab initio* calculations employ only the fundamental constants e, m, and h.

Thus the STO-3G method is entirely satisfactory for the prediction of molecular geometries, at least those of hydrocarbons. The STO-2G method is apparently also fairly satisfactory. The question arises whether one could make do with only one Gaussian type function. Frost [51–53,62,63], who investigated this interesting problem, was able to show that the basis constructed from "floating orbitals" leads to a fairly acceptable accuracy of the calculation of the geometries of simple hydrocarbons, despite the fact that the total energy calculated in terms of this approximation amounts to only 85% of the Hartree–Fock energy. Table 3 presents the geometrical parameters of the five molecules found by Frost [53] by direct minimisation of the Hartree–Fock functional. It is readily seen that the calculations with a very small but flexible basis set yield an entirely reasonable agreement with experiment, which is only slightly worse than that obtained by the STO-3G method. Thus an increase of the sensitivity of the basis set achieved by varying the exponent can lead to a no less effective improvement of the calculations than an increase in the size of the basis set. For STO, this procedure is probably not quite so

effective, since the atomic exponents in the STO do not differ markedly from the optimal exponents of the atomic orbitals in molecules.

The use of floating orbitals is particularly promising in studies on the geometries of large hydrocarbon molecules. Nelson and Frost[64] found the optimal parameters of the wave function of propane and, having transferred them to n-butane and isobutane, obtained entirely satisfactory geometries of these molecules: the calculated CCC angle in n-butane was found to be 112.5° compared with the experimental value of 112.2°,[65] the corresponding values for isobutane being 111° and 111.5°.[66] The total energy was minimised only with respect to the natural molecular coordinates and the orbital exponents and even the expansion coefficients of the molecular orbitals in terms of the atomic orbitals were assumed to be fixed.

Table 3. Geometrical parameters of hydrocarbons calculated by the method of "floating Gaussian orbitals"[53].

Molecule	Bond or angle	Bond length (Å) or angle	
		calc.	expt.
Methane	C—H	1.115	1.085
Ethane	C—C	1.501	1.531
	C—H	1.120	1.096
	HCH	108.2°	107.8°
Ethylene	C=C	1.351	1.330
	C—H	1.101	1.076
	HCH	118.7°	116.6°
Acetylene	C≡C	1.214	1.203
	C—H	1.079	1.061
Cyclopropane	C—C	1.533	1.51
	HCH	114.4°	114.4—115.1°

The calculation on cyclobutane, the molecular geometry of which has been the subject of controversy for a long time, is very interesting. Only comparatively recent studies[67-69] demonstrated the non-planar structure of the four-membered ring (according to experimental data, the dihedral angle is 27—35°). Calculation[64] by the floating orbital method showed that, for the non-sectorial disposition of the HCH valence angle (Fig. 1), the planar form is less favourable than the non-planar form and only when the "tilting" of this angle is introduced as an independent parameter does the non-planar form with a dihedral angle of 32° correspond to the minimum total energy. Calculation predicts a 7° tilt (which can be readily seen from the angle shown in Fig. 1), while the experimental value[70] is 4°.

Thus calculations with very small basis sets in many cases yield an approximately correct geometry. One must not of course overestimate the scope of the floating orbital method. This method is virtually unsuitable for calculations on molecules containing lone electron pairs and molecules with conjugated bonds. The barriers and conformational energies are as a rule found to be twice as high as they should be. Thus the planar form of cyclobutane is found to be less stable than the non-planar form by 3.5 kcal mole^{-1}, while the experimental barrier to ring inversion is 1.48 kcal mole^{-1}.[68]

One should note that during the last 2—3 years many non-empirical calculations have been made on the geometry of molecules of moderate dimensions. 1,4-Dioxane[71], the planar structure of which has been predicted by the method of floating Gaussian type orbitals, and also cyclooctatetraene mentioned above[44] may be quoted as examples. The theoretical equilibrium geometry of cyclo-octatetraene in the boat conformation (D_{2h}) is defined by the following parameters: r(C=C) = 1.340 Å, r(C—C) = 1.507 Å, and $\angle$CCC = 127.37°: these agree extremely well with the experimental parameters[72] 1.340 Å, 1.476 Å, and 126.1° respectively. The planar form of this molecule has an energy higher by 17.8 kcal mole^{-1} than that of the boat form, which is in good agreement with the experimental activation energy for ring inversion (12—15 kcal mole^{-1}).[73-76] Finally, mention should be made of calculations of the geometries of bicyclic and tricyclic hydrocarbon systems[77]: bicyclobutane, tricyclo[1,1,1,0^{1,3}]pentane, and bicyclo[1,1,1]pentane. These systems are interesting because their valence angles are highly deformed and the non-bonded atoms are very close to one another. Within the framework of the molecular force field model, it is impossible to achieve for these systems an adequate agreement between calculation and experiment[78]. Nevertheless, the employment of a contracted Gaussian basis set makes it possible to estimate the equilibrium geometry with a fairly high accuracy.

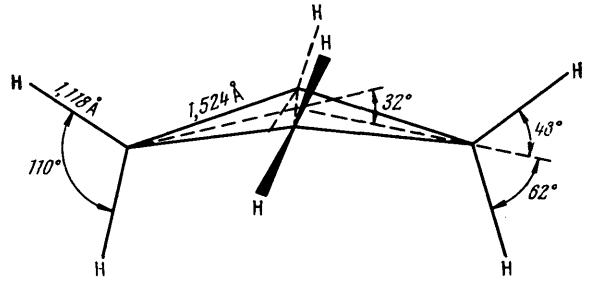


Figure 1. The calculated equilibrium geometry of the cyclobutane molecule.

III. BARRIERS TO INTERNAL ROTATION AND CONFORMATIONAL ENERGIES

Experience gained in quantum-mechanical calculations has shown that the energy associated with a molecular geometry is more sensitive in relation to the choice of the basis than the equilibrium geometry itself. Therefore, generally speaking, a satisfactory prediction of conformational energies and in particular of barriers to internal rotation requires fairly large basis sets. At any rate, the floating orbital method, constructed on the basis of the one orbital—one function principle, is clearly inadequate in this instance. It will be shown in this section that the conformational energy of any molecule can be predicted in very good agreement with experiment, provided that the chosen basis set is fairly large. This means that, when the wave function is such that the total energy is very close to the Hartree—Fock limit, the total energy differences correspond to the experimental conformational energies

and consequently the correlation effects play virtually no role.

We shall consider initially ethane—the "classical" molecule for which non-empirical calculations have been made more frequently than for any other. The complete calculation of the Hartree–Fock energies of the eclipsed and staggered forms of ethane was made for the first time by Pitzer and Lipscomb [28], who employed 16 STO: 1*s* functions for the hydrogen atom and 1*s*, 2*s*, and 2*p* functions for the carbon atom. For this basis set, taking into account the intrinsic molecular symmetry, it was necessary to calculate more than 1200 integrals in each form, a problem which appeared exceptionally difficult at the time. This was the first non-empirical calculation of a barrier to internal rotation and the resulting good agreement with experiment (3.3 compared with 2.93 kcal $mole^{-1}$) appeared promising.

Clementi and Davis [79] were the first to employ Gaussian type orbitals. After carrying out calculations with various basis sets, they concluded that the barrier is almost insensitive to a change of basis set. After this, it became clear that the agreement with experiment achieved by Pitzer and Lipscomb was by no means fortuitous: the Clementi and Davis basis sets led to a higher total energy (which was reasonable to expect from GTO), but the barrier differed from the experimental value by not more than 20% in all cases.

Table 4 summarises the results of seven computations of the total energies of the staggered and eclipsed forms of ethane. Veillard[84], who employed a very large Gaussian basis set with eleven *s*-type and seven *p*-type orbitals for the carbon atom and six *s*-type functions for the hydrogen atoms, obtained the smallest energy; moreover, $3d_{xz}$ and $3d_{yz}$ correlation functions for carbon atoms with an exponent of 1.5 and $2p_x$, $2p_y$, and $2p_z$ functions for the hydrogen atoms with an exponent of 1.0 were introduced. The resulting basis set, consisting of 122 functions, was contracted to 68 independent functions.

We may note that in all the calculations, except those of Stevens [83] and Veillard [84], experimental bond lengths and valence angles were employed and were seen to be unchanged on rotation. Nevertheless empirical theories predict a slight extension of the C–C bond and a decrease of the HCH angle in the eclipsed conformation. Thus Sovers and Karplus [86] calculated the equilibrium geometry of each form using the atom–atom potentials and spectroscopic deformation functions and minimising the strain energy.

They employed two types of potential: (1) the usual H...H and C...H potentials obtained from molecular beam scattering data or any other physicochemical properties and (2) the "effective" potentials yielding the barrier in ethane without taking into account the torsional term. The calculations showed that the C–C bond length increases in the eclipsed conformation by 0.01 Å when potentials of the first type are used and up to 0.1 Å for potentials of the second type; the HCH valence angle in the eclipsed conformation should be smaller approximately by 0.5° than in the staggered conformation.

In the calculations of Veillard [84] and Stevens [83] account was taken of the change in geometry, i.e. the total energy minimum was found for each conformation. The estimates of Sovers and Karplus were confirmed by non-empirical calculations: according to Veillard, the C–C bond in the eclipsed conformation increases by 0.019 Å (from 1.551 Å in the staggered form to 1.570 Å in the eclipsed form), while according to Stevens the increase is by 0.011 Å (from 1.518 Å to 1.529 Å); the HCH angle is close to the experimental value (107.8°) in both calculations, being reduced by 0.3–0.4° in the eclipsed conformation.

Veillard achieved the closest approach to the Hartree–Fock limit—according to his estimate the remaining distance to the "limit" was only 0.09 a.u. However, Levy and Moireau [87] believe that an infinite basis set would yield a further 0.3–0.4 a.u. Despite the fact that the Hartree–Fock limit has been virtually attained, it is still not clear what should be the "limiting" C–C bond length. Indeed C–C bond lengths of 1.501, 1.581, 1.538, 1.529, 1.518, and 1.551 Å have been obtained respectively by Frost's method, the LEMAO-5G method, the STO-3G method, the 4-31G method, the method based on 16 optimised STO (Stevens), and finally the method of 68 GTO based on 122 GTO (Veillard). If an accuracy of bond length of the order of 0.02–0.03 Å is required, the latter may be provided by the Hartree–Fock method with fairly large basis sets. However the question arises whether correlation effects can alter the "limiting" Hartree–Fock bond lengths by hundredths or thousandths of an Ångstrom. So far an answer to this question has not been obtained.

Table 4. Total energies of the eclipsed and staggered forms of the ethane molecule.

Basis set	Total energy, a.u.		Barrier, kcal $mole^{-1}$	References
	staggered form	eclipsed form		
16 STO; Slater exponents	−78.9912	−79.9859	3.3	28
16 STO; exponents optimised for CH_4	−79.0980	−79.0923	3.5	80
34 GTO	−78.5090	−78.5044	2.9	81
32 GTO based on 86 GTO	−79.1082	−79.1025	3.6	79
18 GTO based on 110 GTO	−79.1478	−79.1438	2.5	82
16 GTO with optimisation of exponents and geometry	−79.0999	−79.0946	3.3	83
68 GTO based on 122 GTO with optimisation of geometry	−79.2377	−79.2327	3.1	84
Experiment			2.93	85

"Moderate" basis sets lead to an entirely satisfactory agreement with experiment for other hydrocarbon molecules. Hoyland [88–90], who employed Gaussian type function basis sets, made a detailed study of the internal rotation in alkanes. The calculations for propane and n-butane were made with two basis sets: (5,2,2) and (7,3,3). Five *s*-type and six *p*-type orbitals ($2p_x$, $2p_y$, and $2p_z$) for the carbon atoms and two *s*-type orbitals for the hydrogen atoms were used in the (5,2,2) basis sets. [The (7,3,3) basis set yields the same total energy as the basis sets constructed from the STO with optimised exponents.] The Hartree–Fock calculations for alkanes showed that both basis sets, (5,2,2) and (7,3,3), yield virtually indistinguishable results. Consequently it is reasonable to restrict the treatment to comparatively small basis sets for estimating the conformational energies and barriers to internal rotation of hydrocarbons.

Table 5, which is based on Hoyland's results [89], presents the results of the calculation of the conformational

energies of n-butane using two Gaussian type basis sets—(5,2,2) and (7,3,3). The most striking fact is the identity of the results obtained with different basis sets. The agreement with experiment is so good that it is impossible to say which of the two basis sets is better in this sense. Therefore the calculated values of certain properties can actually be regarded as more accurate than the experimental values. Hoyland's results constitute an undoubted achievement of theoretical methods, especially when one remembers that the n-butane molecule is by no means a trivial object for empirical schemes (the conformations of n-butane were considered in particular by Borisova and Vol'kenshtein [96] and Scott and Scheraga [97]).

Table 5. Results of the non-empirical calculations of the conformational energies of the n-butane molecule.

Property	Calc. (5,2,2) basis set	Calc. (7,3,3) basis set	Expt.	References
Barrier to rotation of methyl group, kcal mole^{-1}	2.92	2.94	3.2—3.4	91
Trans-gauche barrier, kcal mole^{-1}	3.536	3.619	3.6	91
Barrier to interconversion of two *gauche*-forms, kcal mole^{-1}	6.824	6.834	5.3 6.5—6.7	92 93
ΔE (*gauche-trans*), kcal mole^{-1}	0.822	0.761	0.770±0.09	94
Equilibrium angle of *gauche*-form	70.9°	71.3°	72.5±1.1°	95

The calculations of the conformational energies of cycloalkanes carried out by Hoyland in another study [90] are also of considerable interest. Using the experimental bond lengths and valence angles and calculating the total energies with the (5,2,2) basis set, Hoyland obtained approximately identical energies for the envelope and half-chair cyclopentane conformations, in agreement with both experimental data [98] and with the results of empirical calculations [99]. According to the calculation, the twist conformation of cyclohexane is less stable than the chair conformation by 6.05 kcal mole^{-1} and the boat conformation is less stable by 7.19 kcal mole^{-1}; the transition state is less stable by 11.22 kcal mole^{-1} relative to the chair form. These figures are also close to various experimental estimates (about 5.6, about 6.6, and about 11 kcal mole^{-1} respectively [100]).

We shall now consider molecules containing heteroatoms or lone electron pairs. Calculations of the conformational energies and barriers to internal rotation of such molecules generally speaking require larger basis sets than hydrocarbons [101]. Table 6 presents the results of the calculation of the barriers to internal rotation in several molecules of this type. The total energies of propene and its fluoro-derivatives [102] were calculated with two basis sets (A and B); basis set B was constructed by a linear combination of the orbitals of basis set A, i.e. it was less flexible. Table 6 shows that the agreement with experiment leaves something to be desired. Even the direction in which the barrier changes in the fluoroderivatives is not reflected by the calculation: the calculated barrier in 2-fluoropropene is too small and that in *cis*-fluoropropene (with the A basis) is too large.

The reason for the not entirely satisfactory agreement with experiment is probably inadequacy of the basis set. As we have already seen for fluorine- and oxygen-containing molecules, the smallness of the basis set leads to inaccurate estimates of molecular geometries. However, such smallness affects the barriers even more. Therefore reliable calculations of the barriers to internal rotation (to within about 20%), since the remaining discrepancy may be due to correlation effects) require larger basis sets than do calculations of the geometry.

Table 6. Barriers to internal rotation in molecules with a favourable eclipsed conformation.

Molecule	Barrier, kcal mole^{-1}		Expt.
	A basis set	B basis set	
Propene	1.48	1.25	1.98
cis-Fluoropropene	1.58	1.07	1.06
trans-Fluoropropene	1.53	1.34	2.20
2-Fluoropropene	1.20	—	2.45
Acetaldehyde		1.09[82,103]	1.16

In connection with the question of the role of the basis set and the need to improve accuracy, it is interesting to examine non-empirical calculations of the energies of internal rotation in the hydrogen peroxide molecule. Table 7, which presents the results of calculations by different workers, shows that the agreement with experiment depends in a very unusual manner on the completeness of the basis set: small basis sets predict a reasonable *cis*-barrier; then, as the basis set is improved, the calculated barrier becomes too large, becoming reduced to an acceptable value only in Veillard's very exact calculation [105]. On the other hand, the *trans*-barrier is predicted only by the most accurate calculations; in other cases the energy minimum corresponds to the *trans*-form (admittedly the $E-\varphi$ curve, where φ is the angle of rotation reckoned from the *cis*-form, acquires a very low slope for $\varphi > 100°$).

Table 7. Non-empirical calculations of the barriers to internal rotation in the hydrogen peroxide molecule.

Basis set	Total energy in *trans*-form, a.u.	Barrier, kcal mole^{-1} *cis*	Barrier, kcal mole^{-1} *trans*	References
12 STO with Slater exponents	—150.1457	9.4	0	104
12 STO with exponents optimised in relation to H_2O	—150.2232	13.1	0	104
12 STO with total optimisation	—150.2353	9.4	0	83
26 GTO	—149.2641	15.9	0	81
14 "lobe" GTO	—150.7078	13.7	0	82
Extended GTO basis set	—150.7224	13.2	0.3	82
Extended GTO basis set with optimisation of geometry	—150.7992	10.9	0.6	105
22 GTO based on 40 GTO with optimisation of geometry	—150.8202	8.34	1.09	106
32 STO	—150.8319	10.9	0.72	27
Experiment		7.0	1.1	108

The optimisation of the geometry for hydrogen peroxide is more important than for ethane. Veillard's calculation showed that, on passing from the *trans*-form of H_2O_2 to the *cis*-form, the O—O bond length increases by 0.025 Å and the HOO valence angle increases by 5.35°. The angle $\varphi = 123°$ corresponds to the equilibrium concentration, which is quite close to the experimental value [107] (111.5°).

Similar results were obtained by Dunning and Winter[106], who employed an even larger Gaussian type basis set and obtained the equilibrium value $\varphi = 113.7°$. It is remarkable that the calculation carred out with 52 STO,[57] which yielded the lowest total energy, did not give rise to entirely satisfactory barriers. The reason for this is failure to optimise the geometry.

The problem of internal rotation in yet another simple molecule—disulphane (H_2S_2)—is also interesting. The study of microwave spectra[108] showed that in this molecule there should be two barriers of approximately equal height (the *cis*- and *trans*-barriers), the equilibrium angle of rotation being $\varphi = 90°36'$. The calculation[109] performed with an extended and subsequently contracted Gaussian type basis set (58 GTO based on 106 GTO) gave 9.33 kcal mole^{-1} for the *cis*-barrier, 5.99 kcal mole^{-1} for the *trans*-barrier, and an equilibrium angle of 91°16'.

Non-empirical calculations have not been made solely for molecules with "small" barriers. Various Gaussian type basis sets (with and without *d*-type functions) lead to a barrier in formamide[61] ranging from 19.4 to 21.7 kcal mole^{-1}, while the experimental values obtained from NMR spectra are in the range from 16.8 to 21.3 kcal mole^{-1} (see the previous review[1]).

Lehn et al. investigated the mechanism of inversion in aziridine and oxaziridine[110] and also in methyleneimine and the vinyl anion[111]. Using fairly large Gaussian type basis sets, they estimated the barrier to inversion of nitrogen in aziridine CH_2-CH_2-NH as 18.3 kcal mole^{-1} and in oxaziridine CH_2-O-NH as 32.4 kcal mole^{-1}. These figures agree extremely well with the enthalpies of activation obtained from the analysis of the NMR spectra of substituted aziridines and oxaziridines: 16–19 kcal mole^{-1} [112-114] and 32 kcal mole^{-1} [115] respectively.

Methyleneimine ($H_2C=NH$), which was examined in another study by Lehn[111], can undergo inversion in two ways—by rotation about the C=N bond and by the "bending" of the N–H bond. Calculations[111] carried out with a large Gaussian type basis set showed that saddle point for the "tilting" mechanism corresponds to an energy of 26 to 28 kcal mole^{-1} and the saddle point for the rotation mechanism corresponds to 57 kcal mole^{-1}. The first of these figures is virtually identical with the barriers found experimentally for similar compounds (25–27 kcal mole^{-1} [116-119]).

Finally a few words should be said about the simplest molecule in which the inversion phenomenon occurs—the ammonia molecule. Since non-empirical calculations with limited basis sets yielded low or altogether unlikely values of the barrier[120-128], it was believed for a long time that at least half of the barrier is due to correlation effects. However a recent calculation by Rauk et al.[129], taking into account the *d* orbitals of the nitrogen atom, yielded a value very close to the experimental barrier (5.08 kcal mole^{-1} compared with the experimental value of 5.8 kcal mole^{-1} [130]). This demonstrates yet again that not only rotation barriers but also inversion barriers can be fairly satisfactorily predicted within the framework of the Hartree–Fock approximation, provided that the chosen basis set is sufficiently large.

The question arises whether it is possible to make any recommendations concerning the desirability of employing particular basis sets by analysing the results of quantum-mechanical calculations. Naturally the larger the basis set the better and basis sets of the type (11.7/6), including eleven *s* and seven Gaussian *p*-type functions for each carbon or oxygen atom, which were employed by Veillard[84,124], are best in this sense. Even better is the (13.8.2/8.1) basis set, which includes three *d*-type polarisation functions of the nitrogen atom and two *p* functions of the hydrogen atom. The above calculation of the barrier to ammonia inversion was in fact performed with this basis set[129]. However the computer time at the disposal of investigators is limited and therefore a compromise must be resorted to—it is necessary to employ "moderate" basis sets and accept a reduced accuracy of the calculations.

The 4-31G basis set is regarded as a "moderate" basis set of this type.

Pople and coworkers[131] recently employed this basis set to calculate the conformational energies of twenty organic molecules containing methyl, carbonyl, and carboxy-groups and showed that in the vast majority of cases this basis set yields results close to the experimental values. Several examples of the comparison of the calculated and experimental values of the barriers to internal rotation are given below (the experimental data in kcal mole^{-1} are indicated in brackets): ethane 3.26 (2.93); methanol 1.12 (1.07); acetaldehyde 0.74 (1.16); formamide 24.7 (19); methyl ether 3.0 (2.7); acetone 0.75 (0.78–0.83). Evidently the agreement between the calculation and experiment is moderately satisfactory and therefore basis sets of this type may be recommended for large-scale estimates of conformational energies of small molecules and for conformational analysis in organic chemistry. Admittedly, as we have already seen for the ammonia molecule, one cannot always be certain that the error of the calculation is sufficiently small. However, "moderate" basis sets in all probability yield entirely satisfactory results for hydrocarbon molecules.

Table 8. Bond separation energies.

Molecule	Reaction	Bond separation energy, kcal mole^{-1}	
		calc.	expt.
Propane	$CH_3CH_2CH_3 + CH_4 \rightarrow 2C_2H_6$	1.0	1.5
Propene	$CH_3CHCH_2 + CH_4 \rightarrow C_2H_6 + C_2H_4$	4.1	5.0
Propyl	$CH_3CH + CH_4 \rightarrow C_2H_6 + C_2H_2$	8.0	7.2
Allene	$CH_2CCH_2 + CH_4 \rightarrow 2C_2H_4$	−4.6	−4.0
Cyclopropane	$C_3H_6 + 3CH_4 \rightarrow 3C_2H_6$	−30.4	−23.5
Cyclopropene	$C_3H_4 + 3CH_4 \rightarrow 2C_2H_6 + C_2H_4$	−58.0	−45.2

The differences between the energies of rotational isomers are probably just as sensitive to the basis set as the barriers to internal rotation; admittedly few calculations of this kind have been made. We shall mention in particular the work of Pople and coworkers[132], who calculated the energies of two or several conformers with two basis sets—STO-3G and 4-31G. Thus the *gauche*-form of substituted methylamines (XCH_2-NH_2) was found to be more favourable than the *trans*-form (the C–X bond in the *trans*-form is located in the same plane as the bisector of the HNH angle), when X = CH_3, while the *trans*-form is more favourable for X = OH and F. Spectroscopic data, which are available only for ethylamine[133], show that the two forms are in equilibrium. In substituted hydrazines (NH_2-NHX), the "outer" form (the N–X bond is rotated 180° relative to the bisector of the HNH angle) is more favourable than the "inner" form when X = CH_3 and less favourable for X = OH and F. Indeed infrared spectra[134] show the advantage of the "outer"

form for methylhydrazine—it constitutes more than 90% of the mixture. Calculations predict that in compounds of the type Y=N−O−H the *trans*-form is more stable for all Y (Y = CH_2, NH, or O). The experimental data on nitrous acid (Y = O) [135,136] demonstrate the preponderance of the *trans*-form. Finally, we may mention substituted di-imides (X−N=N−H) whose *trans*-form is more favourable than the *cis*-form for all X except OH. Experimental data demonstrating the advantage of the *trans*-form are available only for di-imide itself [137].

The thermochemical properties of substances are known to bear a definite relation to molecular structure and to steric hindrance. However, absolute values cannot be obtained with adequate precision within the framework of the Hartree−Fock model: the correlation corrections to the total energies are too large. However, if we are interested in the comparative thermochemical properties of a series of molecules with similar structures, such properties can be estimated assuming mutual cancellation of the correlation corrections.

Pople and coworkers [138] introduced the concept of the "bond separation" energy: these are the heats of reactions occurring with retention of the total number of formal bonds. The "bond separation" energies are a measure of the intramolecular interactions including steric strains (on the assumption of exact additivity of the bond energies, the "bond separation" energies should be zero).

Table 8 presents several examples of reactions and the results achieved by the STO-3G and 4-31G methods are compared with experimental data adjusted to 0°K and corrected for zero point vibrations. Bearing in mind that the Hartree−Fock limit is far from being attained when using Gaussian type basis sets, the agreement between the calculations and experiment must be recognised as satisfactory (the correlation corrections can indeed cancel out in systems with identical formal bonds). The "bond separation" energies are particularly large in absolute magnitude in cyclopropane and cyclopropene in consequence of the large angular deformations.

IV. THE NATURE OF THE BARRIERS TO INTERNAL ROTATION

The "nature" of the barriers to internal rotation has been the subject of discussion for a long time at the level of empirical and semi-empirical theories. Since the interatomic potentials "do not explain" the barrier in a simple molecule such as ethane, yielding an unduly low value, many theories in which one factor or another is emphasised have been put forward. Thus the breakdown of the cylindrical symmetry of electron density in rotation about the C−C bond has been treated [139,140] as the cause of the inhibiting potential [139,140]. Pauling [141,142] attributed the barrier to the presence of hybrid orbitals of the *d*- and *f*-types assuming that pure sp^3 hybridisation does not give rise to a barrier; however, 4% of *d*-states and 2% of *f*-states give rise to a barrier of about 3 kcal mole^{-1}. Calculations of the barrier on the basis of the classical electrostatic model [143−145] taking into account the interactions between the dipole and higher moments of the C−H bond also did not yield unambiguous results.

From the standpoint of modern computational methods, these theories appear naive and can be readily criticised. Actually the fact that the correct value of the barrier to internal rotation in ethane is obtained with minimal STO basis sets or extended GTO basis sets but not including vacant orbitals is sufficient to demonstrate the lack of validity of Pauling's theory.

However, despite the considerable achievements of non-empirical methods, the problem of the nature of the inhibition of internal rotation in molecules can still not be regarded as finally elucidated. The ambiguity of the interpretation of the nature of the interactions is primarily related to the fact that the integrals arising in the Roothaan equations can be reasonably combined into certain groups in several ways. Nevertheless only two fundamentally different approaches exist.

1. The repulsion energy of the nuclei V_{nn}, the repulsion energy of the electrons V_{ee}, the kinetic energy of the electrons T, and the attraction energy between the electrons and the nuclei V_{ne} are considered separately. The total repulsion energy is written in the form

$$V_{rep} = V_{nn} + V_{ee} + T \tag{10}$$

and the attraction energy in the form

$$V_{att} = V_{ne}. \tag{11}$$

After calculating in this way the attraction and repulsion energies, one can conclude that V_{rep} and V_{att} change on passing from one conformation to another, and particularly on passing from the staggered to the eclipsed form: if ΔV_{rep} is large and ΔV_{att} is small, repulsion predominates; on the other hand, if ΔV_{att} is large and ΔV_{rep} is small, attraction predominates. One cannot rule out the possibility that both terms play equally important roles.

Apart from the above resolution of the total energy, the resolution into one- and two-electron components is also of interest. $V_{nn} + T + V_{ne}$ may be regarded as the one-electron component and V_{ee} as the two-electron component. Such representation makes it possible to understand, in the first place, the role of the repulsion of electrons and, in the second place, the possibility, scope, and disadvantages of the semi-empirical one-electron approximations, in particular the extended Hückel method.

2. Instead of investigating the interelectronic and electron−nucleus interactions, the individual contributions to the total energy from the localised bond orbitals are analysed. Thus, in discussing the nature of the barrier in ethane, one speaks of the repulsion of the localised orbitals of the C−H bond (when the calculations are carried out with such orbitals) or of the repulsion of the *p* orbitals of the carbon atoms in the eclipsed conformation [146]. This approach can be naturally referred to as the "orbital" approach. It is of course less objective than the "electronic-nuclear" approach, but the degree of involvement of particular interactions is determined to a considerable degree by the choice of the basis set; however, this approach is frequently used to justify various semi-empirical and empirical theories.

Allen, who investigated both the competition between attraction and repulsion [102,103,147] and the relative effects of the one- and two-electron components [82], has been a consistent adherent of the first approach. Table 9 presents the individual components of the total energy of ethane (V_{nn}, V_{ee}, T, and V_{ne}), whence one can also see their relative changes on passing from the eclipsed to the staggered conformation (the values of the total energy components for $\varphi = 90°$, i.e. in the intermediate conformation, are also indicated). Fig. 2, which is based on data of Fink and Allen [82], presents the ΔV_{rep} and ΔV_{att} curves (*a*), the skew conformation being adopted as the starting point of the readings ($\varphi = 0$) and also curves characterising the changes in the one- and two-electron components (*b*). It is interesting that in both representations the individual components vary with different phases

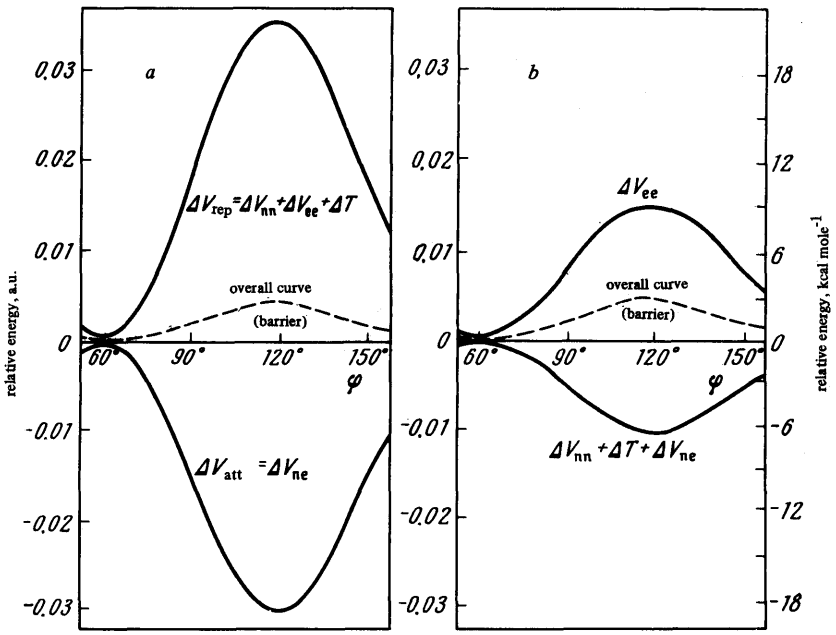


Figure 2. Variation of various components of the total energy of ethane with the internal rotation angle φ.

and the true barrier, illustrated in Fig. 2 by the dashed line, is given by a small difference between fairly large quantities. This situation is characteristic not only of ethane but also of the vast majority of molecules. This is why the experimental barriers to rotation are frequently unexpected and it is by no means always possible to make them fit any empirical rules.

The origin of the barrier in ethane can be most readily understood by examining the repulsion and attraction (Fig. 2*a*). Both terms increase markedly in absolute magnitude in the eclipsed conformation but the repulsion is nevertheless stronger. A detailed study[147] has shown that, in the space between the hydrogen atom, the electron density is significantly reduced. This leads, on the one hand, to an increase of the repulsion of nuclei in consequence of their descreening and, on the other hand, to enhanced attraction of the electrons to the nuclei. On the other hand, the repulsion of atoms constitutes a pure effect. Thus the nature of the barrier in ethane is ultimately the same as the nature of the repulsion of helium atoms at short distances[148].

Evidently the nature of the barriers in propane, n-butane, and cycloalkanes is the same (indeed, in the empirical conformational calculations used to describe these systems, one employs "ethane-like" torsional potentials). However, in molecules with a favourable eclipsed conformation, attraction is more likely to be responsible for the barrier than repulsion. In fact, it has been shown[147] that in the eclipsed conformation of the acetaldehyde molecules (CH_3CHO) the distribution of electron density between the methyl group and the oxygen atom resembles the distribution for a weak chemical bond; but on passing to the staggered form the bond is weakened.

Component-by-component analysis makes it possible to refer the barriers to internal rotation and inversion of molecules to one of two groups—R (repulsive dominant) or A (attractive dominant): if on passing from the state corresponding to the energy minimum to one corresponding to the saddle point on the energy surface, $|\Delta V_{rep}| > |\Delta V_{att}|$, then the barrier refers to group R; for opposite inequality sign, the barrier belongs to group A. In terms of this property, the barriers to rotation in methanol, methylamine, ethyl fluoride, hydrazine, ammonia, etc. belong to group R and the barriers in hydroxylamine, aziridine, hydrogen peroxide, di-imide, etc. belong to group A.[101]

Table 9. Contributions of the individual components to the total Hartree–Fock energy of ethane (in a.u.).

Conformation	V_{nn}	V_{ee}	T	V_{ne}
Eclipsed	41.93845	67.22699	79.00441	−267.3136
Intermediate ($\varphi = 90°$)	41.93469	67.21900	78.99798	−267.2972
Staggered	41.93098	67.21208	78.99142	−267.2823
Δ (eclipsed-intermediate)	0.00376	0.00799	0.00643	−0.0164
Δ (eclipsed-staggered)	0.00747	0.01491	0.01299	−0.0313

Unfortunately it is impossible to say that the component-by-component analysis does indeed reveal the "nature" of the barriers, at least in the sense which would satisfy the chemist who is unable to carry out the calculations *ab initio*. In fact having looked at the structural formula of the compound and even knowing many of its properties, the chemist is hardly able to guess whether the barrier in the given compound belongs to group R or A, let alone being able to predict the magnitude of the barrier. Component-by-component analysis is useful *aposteriori*, i.e. when the quantum-mechanical calculation has already

been performed. However, in this case too it is not always unambiguous, since the sign of the above inequality has been shown to depend for H_2O_2, H_2S_2, and PH_3 on the basis set and on whether or not the geometry has been optimised [101].

The second, "orbital" approach can also be hardly recommended, at least at the present time, since the interpretation of the results depends significantly on the choice of the basis set. We may note, in particular, that Veillard and Demuyck [109], who investigated internal rotation in disulphane (58 independent GTO based on 106 GTO), found that the cause of the *trans*-barrier is the interaction of the electrons of the S–H σ bond with the π electrons of another S atom, which may be classified as hyperconjugation. It may be that this kind of interpretation will find many supporters in the future and will even acquire some predictive power but for this it is necessary that the calculations of the barrier and the analysis of the overlap populations for a large set of molecules are carried out with equivalent basis sets.

Thus the elucidation of the nature of the barriers *aposteriori* is still hardly likely to be of serious interest to the chemist. However, accumulation of new data from quantum-mechanical calculations as well as new experimental data makes it possible to refine and in many cases reformulate the concepts established previously. An attempt to formulate rules which help to predict the least stable conformations has been made [149]: (1) the lone electron pair–lone electron pair, lone electron pair–polar bond, and polar bond–polar bond interactions lead to a considerable increase of the barrier and (2) if the lone electron pairs are located at neighbouring pyramidal atoms (or the polar bonds adjoin these atoms) then the *syn*- and *anti*-periplanar orientations are energetically unfavourable compared with the structure having the maximum number of *gauche*-interactions.

It is possible to quote many examples concerning rule (1): these are the conformations of almost all the halogenoethanes, bis-1,3-dioxolane, [150] etc. However, contrary to expectation, 1,1,2-trichloro- and tribromoethanes exist in the *gauche*-form and not the *trans*-form [151,152]. Rule (2), which Wolfe [153] called the *gauche*-effect, is confirmed both by experimental data and by non-empirical calculations on H_2O_2, H_2S_2, H_2N_2, [154] and H_2P_2. [155,156] The electron pairs in these molecules can be regarded as ligand, which are just as important as the substituents.

The so called anomeric effect [157–160], which is known in the chemistry of carbohydrates and consists in the fact that axial orientations are preferred for electronegative substituents at the anomeric 1-C centre of the pyranose ring, is an exception to rule (2). However, if one supposes that the lone electron pairs of the oxygen atom have the form of "rabbit ears" and "deviate" from one another by an angle of 120°, then the anomeric effect can be readily explained and is no longer an exception to rule (2) but provides conformation of it.

Evidently the state of affairs in this field is by no means satisfactory: despite the fact that non-empirical calculations make it possible to estimate with good precision the conformational energies and barriers to internal rotation in simple molecules, sufficiently convenient methods for the interpretation of the results have not yet been found. Neither have theories satisfactory from the chemist's point of view, whereby one can predict stable and unstable conformers without resorting to laborious computer calculations, yet been established. This is why each new calculation and each new experimental fact are valuable.

V. CALCULATIONS WITH LOCALISED ORBITALS

The ideas of the theory of localised valence bond orbitals (LVBO = localised valence bond orbitals) rest on fundamental empirical chemical postulates. Since the bond energies in molecules are additive with fair accuracy, presumably carefully selected LVBO can be transferred from one molecule to another. This implies that the wave functions for molecules of homologous series can be constructed from the same LVBO. However, the main difficulty of this approach consists in the fact that the transferred orbitals are generally speaking non-orthogonal and when account is taken of the non-orthogonality, the mathematics of the Hartree–Fock method becomes much more complicated [161]. The unitary transformation of molecular orbitals, which does not alter the Slater determinant, makes it possible [162–164] to obtain the localised orbitals b_k from the atomic orbitals φ_i:

$$b_k = \sum_i t_{ki}\varphi_i \,. \tag{12}$$

The localised orbitals of the C–H bonds in the methane molecule are determined by symmetry considerations. However, for molecules whose symmetry is not quite so high, the localised orbitals cannot be found unambiguously and therefore in choosing the localised orbitals it is necessary to resort to particular criteria [165,166]. The criterion, examined in detail by Edmiston and Ruedenberg [166] and consisting in the fact that the b_k orbitals must correspond to the maximum in the function $\Sigma(kk/kk)$, has found the widest practical application.

Pitzer [167] used the criterion of Edmiston and Ruedenberg to calculate the LVBO for the staggered and eclipsed conformations of ethane. The localised C–C, C–H, and inner shell orbitals obtained by an iterative procedure proved to be not entirely identical for the two conformations: the greatest changes occur on internal rotation in the C–H orbitals.

The principal disadvantage of the localised orbitals determined in this way is that it is difficult to use them to explain the nature of the interactions responsible for the nature of the interactions responsible for the barrier, since the localised orbitals of the staggered conformation of ethane differ from the corresponding orbitals of the eclipsed conformation. Therefore, in order to elucidate the nature of the interactions and to prove the validity of additive empirical schemes, it appears more promising to employ orbitals transferred from one molecule to another.

Hoyland [168] attempted to apply the idea of the transferability of orbitals to hydrocarbon molecules—those of methane, ethane, propane, n-butane, and propene. The localised orbitals of the C–H bond in methane were sought in the form

$$b^{(i)}_{C\text{–}H} = N(t_i + \lambda h_i) \tag{13}$$

where t_i are hybrid tetrahedral functions on the carbon atom directed towards the ith hydrogen atom, h_i are the 1s orbitals centred on the same hydrogen atom, and N is a normalising factor. The parameter λ was determined from the condition of the correspondence of the calculated and experimental C–H bond lengths: $\lambda = 1.097$ for the (5,2,2) Gaussian basis set and $\lambda = 1.056$ for the (5,3,3) basis set.

The orbital of the C–C bond in ethane was defined thus:

$$b_{C\text{–}C} = N(t_1 + t_2) \tag{14}$$

where t_1 and t_2 are the hybrid orbitals on the two carbon

atoms directed to the central point in the molecule. The b_{C-H} orbitals were assumed to be exactly the same as in methane.

Calculation of the total energy of ethane using the LVBO yielded −78.493 a.u. for the (5,2,2) basis set and −78.696 a.u. for the (5,3,3) basis set, which are a little higher than the values quoted in Table 4. The calculated barrier amounts to 2.66 kcal mole^{-1} for the (5,2,2) basis set and 2.83 kcal mole^{-1} for the (5,3,3) basis set.

The results for the barrier to internal rotation in propene were not so satisfactory: 0.46 kcal mole^{-1} for the (5,2,2) basis set and 0.80 kcal mole^{-1} for the (5,3,3) basis set (the experimental value is 1.98 kcal mole^{-1}). The reason for the poor agreement between the calculation and experiment becomes understandable if one takes into account the fact that each term V_{ee} and V_{ne} in Eqn. (10) for propene changes on passing from the eclipsed to the staggered conformation by 12−26 kcal mole^{-1} (only ΔT is small), which is a factor of ten greater than the barrier. The errors associated with the inadequacy of the orbitals are fairly large for each total energy component and there is no reason to expect their mutual cancellation.

In another study[169] Hoyland employed the extended (7,3,3) Gaussian basis set and sought the localised orbitals of the C−H bond in methane in the form

$$b^{(i)}_{C-H} = N(2s + \lambda 2p_i + \delta h_i) \qquad (15)$$

where $2p_i$ are linear combinations of the $2p_x$, $2p_y$, and $2p_z$ orbitals. Instead of the single parameter (λ), two parameters (λ and δ) were varied. After transferring the localised orbitals b_{C-H} from methane to ethane, Hoyland obtained for the latter a total energy of −79.093 a.u. and a barrier to internal rotation of 2.40 kcal mole^{-1}. The author explains the comparatively low barrier by the fact that in the eclipsed conformation the wave function constructed from the LVBO is closer to the LCAO-MO wave function for the eclipsed conformation than for the staggered conformation.

Table 10 compares the calculated conformational energies of propane obtained by the LCAO-MO and LVBO methods. In the LVBO method the b_{C-H} orbitals were transferred from methane and the b_{C-C} orbitals from ethane. The closeness of the results obtained by the two methods shows that in many respects the LVBO are entirely satisfactory. However, it is clear that from a quantitative standpoint a better approximation to experiment can be achieved with delocalised LCAO-MO. This is not in fact surprising, since in using the orthogonalised valence bond orbitals one does not take into account satisfactorily the weak interactions which determine the conformational energies and the isomerisation energies of alkanes. However, the agreement with experiment for alkanes may be improved by distinguishing the C−C and C−H bonds as a function of the immediate environment as is done in Tatevskii's method[170,171]. But in this case the non-empirical calculations are reduced to the level of empirical schemes: in fact this is equivalent to postulating the desired result.

VI. CONCLUDING REMARKS

As shown in the previous sections, molecular geometry and conformational energies are quite satisfactorily predicted within the framework of the Hartree−Fock method, provided that one employs delocalised orbitals and fairly large basis sets. Since the Hartree−Fock limit has been approached for only 2−3 molecules, it is still difficult to say what corrections are introduced by allowance for correlation effects; it is only clear that these corrections are small for delocalised orbitals and very large when localised valence bond orbitals are employed.

Table 10. Barriers to internal rotation in propane calculated with delocalised and localised orbitals.

Angles of rotation, deg		ΔE, kcal mole^{-1}	
φ_1	φ_2	LCAO-MO[83]	LVBO[167]
60	60	0	0
60	0	3.134	2.616
0	0	6.971	6.097

The Hartree−Fock model, in which the electrons are considered to move in the effective field due to other electrons and nuclei, does not take into account the "collisions" of electrons, which, as shown by Gruninger et al.[172], makes the average kinetic energy too low and the average electron repulsion energy too high. The correlation energy, which is by definition[173] that difference between the exact non-relativistic energy and the Hartree−Fock energy, amounts on average to 1% of the total energy of the molecules (for example, it is 230 kcal mole^{-1} for the ammonia molecule[126]). Apart from correlation, one could also take into account relativistic corrections, but in calculations on molecules, at least those with fairly light atoms, such corrections are quite insignificant. Thus the relativistic correction for the ammonia molecule is 15 kcal mole^{-1}; however, it is determined mainly by the motion of electrons in atoms and one must suppose that it is the same for different conformations and in general for different relative positions of the nuclei.

In the calculation of the correlation energy, the many-configuration approximation or perturbation methods are employed. In the many-configuration approximation the wave function of the molecule Ψ is represented by a linear combination of functions made up of Slater determinants.

For the function to be exact, it is necessary to employ an infinitely large number of expansion terms. However, one usually restricts the treatment to finite sums and the expansion coefficients are determined from the condition for the energy minimum. The methods of perturbation theory are less accurate, but they make it possible to estimate a considerable proportion of the correlation energy by a relatively simple procedure[174].

It has been known for a long time that the second-order correlation energy $E^{(2)}$, found using perturbation theory, is small for delocalised orbitals and large for localised orbitals (although no one has found a simple explanation for this finding). Levy and Moireau[87], who investigated the effect of the correlation energy on the barrier to internal rotation in ethane, found that $E^{(2)}$ is of the order of 0.01 kcal mole^{-1} for the Slater basis set employed by Pitzer and Lipscomb[28], about 0.1 kcal mole^{-1} for the basis set constructed from the LVBO satisfying the minimal exchange conditions[167], and 0.6−0.8 kcal mole^{-1} for the basis set constructed from hybrid molecular orbitals.

Thus allowance for correlation corrections is important only for localised orbitals. Incidentally, it is precisely in this case that the correlation corrections are most

readily applied and the main idea of the semi-empirical PCILO method discussed in the author's previous review[1] does in fact consist in applying perturbation theory to localised orbitals. The correlation corrections in the non-empirical methods based on atomic orbitals should probably be small and a further approach to the Hartree–Fock limit by extending the basis set and optimising the STO or GTO exponents may serve as the main means of achieving the required accuracy.

The question arises of the prospects for the non-empirical conformational analysis. In the first place one must say that calculations of the electronic structures of molecules with average dimensions, such as those of benzene or pyridine, require several hours of computer time for a single nuclear configuration. It is also significant that such calculations require a large set of programs available hitherto only to individual specialists working in this field. Nevertheless examples are already appearing of predictions of the geometries of complex molecules such as those of bicyclobutane and bicyclopentane. Presumably in the immediate future the number of such examples will increase significantly and towards the end of the 1970's and the beginning of the 1980's, when the speed of computers is increased to 10^9 operations per second, theoretical conformation analysis of organic molecules with average dimensions will become an important instrument in the hands of chemists and physical chemists. However even then, as long as significantly new methods are not devised, the non-empirical calculations of the conformations of complex systems such as steriods, alkaloids, peptides, sugars, nucleic acids, etc. will be hardly possible. Therefore empirical models based on atom–atom potentials and semi-empirical quantum-mechanical methods retain their importance.

REFERENCES

1. V. G. Dashevskii, Uspekhi Khim., 42, 2097 (1973) [Russ. Chem. Rev., No. 12 (1973)].
2. R. K. Nesbet, Adv. Chem. Phys., 9, 321 (1965).
3. O. Sinanoglu (Editor), "Many-electron Theory of Atoms, Molecules, and Their Interactions" (Translated into Russian), Izd. Mir, Moscow, 1966.
4. E. Clementi, J. Chem. Phys., 46, 3842 (1967).
5. A. Veillard and E. Clementi, Theoret. Chim. Acta, 7, 133 (1967).
6. B. J. Ransil, Rev. Mod. Phys., 32, 239, 245 (1960).
7. J. C. Slater, Phys. Rev., 36, 57 (1930).
8. E. Clementi and D. L. Raimondi, J. Chem. Phys., 38, 2686 (1963).
9. L. C. Cusachs, D. L. Carrol, B. L. Trus, and S. P. McGlynn, Internat. J. Quantum Chem., 1, 159 (1967).
10. L. C. Cusachs and J. H. Corrington, in "Sigma Molecular Orbital Theory" (by O. Sinanoglu and K. B. Wiberg), Yale Univ. Press, New Haven and London, 1970, p. 256.
11. C. C. Roothaan, J. Chem. Phys., 19, 1445 (1951).
12. K. Ruedenberg, J. Chem. Phys., 19, 1459 (1951).
13. K. Ruedenberg, C. C. Roothaan, and W. Jaunzemis, J. Chem. Phys., 24, 201 (1956).
14. M. P. Barnett and C. A. Coulson, Phil. Trans., 243, 221 (1951).
15. I. Shavitt, Methods in Comput. Phys., 2, 1 (1963).
16. S. F. Boys, Proc. Roy. Soc. A, 200, 542 (1950).
17. A. Meckler, J. Chem. Phys., 21, 1750 (1953).
18. J. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, Theoret. Chim. Acta, 6, 191 (1966).
19. M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 52, 4064 (1970).
20. W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys., 52, 5001 (1970).
21. S. Huzinaga, J. Chem. Phys., 42, 1293 (1965).
22. R. F. Stewart, J. Chem. Phys., 50, 2485 (1969).
23. R. E. Christoffersen and K. Ruedenberg, J. Chem. Phys., 49, 4285 (1968).
24. L. S. Salmon, F. W. Birss, and K. Ruedenberg, J. Chem. Phys., 49, 4283 (1968).
25. D. M. Silver and K. Ruedenberg, J. Chem. Phys., 49, 4301, 4306 (1968).
26. P. E. Stevenson and W. N. Lipscomb, J. Chem. Phys., 50, 3306 (1969).
27. C. Guidotti, U. Lamanna, M. Maestro, and R. Moccia, Theoret. Chim. Acta, 27, 55 (1972).
28. R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys., 39, 1995 (1963).
29. W. E. Palke and R. M. Pitzer, J. Chem. Phys., 46, 3948 (1967).
30. E. Clementi, J. Chem. Phys., 40, 1944 (1964).
31. E. Clementi, R. Matcha, and A. Veillard, J. Chem. Phys., 47, 1865 (1967).
32. W. J. Hehre, F. R. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2657 (1969).
33. M. D. Newton, J. Chem. Phys., 51, 3917 (1969).
34. M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 51, 3927 (1969).
35. W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 52, 2769 (1970).
36. W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys., 53, 932 (1970).
37. R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 52, 5001 (1970).
38. R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 54, 724 (1971).
39. W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc., 93, 808 (1971).
40. J. L. Whitten, J. Chem. Phys., 44, 359 (1966).
41. E. Clementi and D. R. Davis, J. Chem. Phys., 45, 2593 (1966).
42. J. M. Schulman, J. W. Moskowitz, and C. Hollister, J. Chem. Phys., 46, 2759 (1967).
43. J. M. Schulman, C. J. Hornback, and J. W. Moskowitz, Chem. Phys. Letters, 8, 361 (1971).
44. G. Wipff, U. Wahlgren, E. Kohanski, and J. M. Lehn, Chem. Phys. Letters, 11, 350 (1971).
45. S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, J. Chem. Phys., 45, 734 (1966).
46. R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, J. Chem. Phys., 45, 2835 (1967).
47. R. J. Buenker and S. D. Peyerimhoff, J. Chem. Phys., 45, 3682 (1967).
48. S. D. Peyerimhoff, J. Chem. Phys., 47, 349 (1967).
49. S. D. Peyerimhoff, R. J. Buenker, and J. L. Whitten, J. Chem. Phys., 46, 2029 (1967).
50. S. Peyerimhoff and R. J. Buenker, J. Chem. Phys., 49, 2473 (1968).
51. A. A. Frost, J. Chem. Phys., 47, 3707, 3714 (1967).
52. A. A. Frost, J. Phys. Chem., 72, 1283 (1968).
53. A. A. Frost, B. Prentice III, and R. A. Rouse, J. Amer. Chem. Soc., 89, 3064 (1967); A. A. Frost and R. A. Rouse, J. Amer. Chem. Soc., 90, 1965 (1968).
54. P. Th. van Duijen and D. B. Cook, Mol. Phys., 21, 475 (1971); 22, 637 (1971).

55. D.B. Cook and P.Th. van Duijen, Chem. Phys. Letters, 8, 201 (1971).
56. M.D. Newton, W.A. Lathan, W.J. Hehre, and J.A. Pople, J. Chem. Phys., 52, 4064 (1970).
57. M.J.D. Powell, Computer J., 5, 147 (1962).
58. T.A. Claxton and N.A. Smith, Theoret. Chim. Acta, 22, 399 (1971).
59. J.W. McIver and A. Komornicki, Chem. Phys. Letters, 10, 303 (1971).
60. N.C. Baird, Chem. Phys. Letters, 6, 61 (1970).
61. D.H. Christensen, R.N. Kortzeborn, B. Bak, and J.J. Led, J. Chem. Phys., 53, 3912 (1970).
62. A.A. Frost, R.A. Rouse, and L. Viselius, Internat. J. Quantum Chem., 2S, 43 (1968).
63. A.A. Frost, Theoret. Chim. Acta, 18, 156 (1970).
64. J.L. Nelson and A.A. Frost, J. Amer. Chem. Soc., 94, 3727 (1972).
65. R.A. Bonham and L.S. Bartell, J. Amer. Chem. Soc., 81, 3491 (1959).
66. D.R. Lide, J. Chem. Phys., 33, 1519 (1960).
67. T. Ueda and T. Shimanouchi, J. Chem. Phys., 49, 470 (1968).
68. M.R. Stone and I.M. Mills, Mol. Phys., 18, 631 (1970).
69. V.T. Aleksanyan, G.M. Kuz'yants, M.Yu. Lukina, S.V. Zotova, and E.I. Vostokova, Zhur. Strukt. Khim., 9, 141 (1968).
70. S. Meiboom and L.C. Snyder, J. Chem. Phys., 52, 3857 (1970).
71. B. Tinland, J. Mol. Struct., 9, 205 (1971).
72. O. Bastiansen, L. Hedberg, and K. Hedberg, J. Chem. Phys., 27, 1311 (1957).
73. F.A.L. Anet, J. Amer. Chem. Soc., 84, 671 (1962).
74. F.A.L. Anet, A.J.R. Bourn, and Y.S. Lin, J. Amer. Chem. Soc., 86, 3576 (1964).
75. D.E. Gwinn, G.M. Whitesides, and J.D. Roberts, J. Amer. Chem. Soc., 87, 2862 (1965).
76. J.F.M. Oth, R. Merenyi, Th. Martini, and G. Schröder, Tetrahedron Letters, 3087 (1966).
77. M.D. Newton and J.M. Schulman, J. Amer. Chem. Soc., 94, 767, 773 (1972).
78. N.M. Zaripov, V.G. Dashevskii, and V.A. Naumov, Izv. Akad. Nauk SSSR, Ser. Khim., 1863 (1970).
79. E. Clementi and D.R. Davis, J. Chem. Phys., 45, 2593 (1966).
80. R.M. Pitzer, J. Chem. Phys., 47, 965 (1967).
81. L. Pedersen and K. Morokuma, J. Chem. Phys., 46, 3941 (1967).
82. W.H. Fink and L.C. Allen, J. Chem. Phys., 46, 2261, 2276 (1967).
83. R.M. Stevens, J. Chem. Phys., 52, 1397 (1970).
84. A. Veillard, Chem. Phys. Letters, 3, 128 (1969).
85. S. Weiss and G.E. Leroi, J. Chem. Phys., 48, 962 (1968).
86. O.J. Sovers and M. Karplus, J. Chem. Phys., 44, 3033 (1966).
87. B. Levy and M.C. Moireau, J. Chem. Phys., 54, 3316 (1971).
88. J.R. Hoyland, J. Chem. Phys., 49, 1908 (1968).
89. J.R. Hoyland, J. Chem. Phys., 49, 2563 (1968).
90. J.R. Hoyland, J. Chem. Phys., 50, 2775 (1969).
91. K.S. Pitzer, J. Chem. Phys., 8, 711 (1940).
92. K. Ito, J. Amer. Chem. Soc., 75, 2430 (1953).
93. J.E. Piercy and M.G.S. Rao, J. Chem. Phys., 46, 3951 (1967).
94. G.J. Szasz, N. Sheppard, and D.H. Rank, J. Chem. Phys., 16, 704 (1948).
95. K. Kuchitsu, Bull. Chem. Soc. Japan, 32, 748 (1959).
96. N.P. Borisova and M.V. Vol'kenshtein, Zhur. Strukt. Khim., 2, 346, 469 (1961).
97. R.A. Scott and H.A. Scheraga, J. Chem. Phys., 44, 3054 (1966).
98. W.J. Adams, H.J. Geise, and L.S. Bartell, J. Chem. Phys., 92, 5013 (1970).
99. S. Lifson and A. Warshel, J. Chem. Phys., 49, 5116 (1968).
100. E.L. Eliel, N.L. Allinger, S.J. Angyal, and G.A. Morrison, "Conformational Analysis" (Translated into Russian), Izd. Mir, Moscow, 1969.
101. J.-M. Lehn, in "Conformational Analysis. Scope and Present Limitations" (Edited by G. Chiurdoglu), Academic Press, New York–London, 1971, p. 129.
102. E. Scarzafava and L.C. Allen, J. Amer. Chem. Soc., 93, 311 (1971).
103. R.B. Davidson and L.C. Allen, J. Chem. Phys., 54, 2828 (1971).
104. W.E. Palke and R.M. Pitzer, J. Chem. Phys., 46, 3948 (1967).
105. A. Veillard, Chem. Phys. Letters, 4, 51 (1969).
106. T.H. Dunning, Jnr. and N.W. Winter, Chem. Phys. Letters, 11, 194 (1971).
107. C.S. Ewig and D.O. Harris, J. Chem. Phys., 52, 6268 (1970).
108. G. Winnewisser, M. Winnewisser, and W. Gordy, J. Chem. Phys., 49, 3465 (1968).
109. A. Veillard and J. Demuyck, Chem. Phys. Letters, 4, 476 (1970).
110. J.M. Lehn, B. Munsch, P. Millié, and A. Veillard, Theoret. Chim. Acta, 13, 313 (1969).
111. J.M. Lehn, B. Munsch, and P. Millié, Theoret. Chim. Acta, 16, 351 (1970).
112. H.S. Gutowsky, Ann. N.Y. Acad. Sci., 70, 786 (1958).
113. T.J. Bardos, C. Szantay, and C.K. Navada, J. Amer. Chem. Soc., 87, 5796 (1965).
114. S.J. Brois, J. Amer. Chem. Soc., 89, 4242 (1967).
115. J.M. Lehn and J. Wagner, quoted after Ref. 110.
116. D.Y. Curtin, E.J. Grubbs, and C.G. McCarty, J. Amer. Chem. Soc., 88, 2775 (1966).
117. D.Y. Curtin and J.W. Hausser, J. Amer. Chem. Soc. 88, 3474 (1966).
118. D. Wurmb-Gerlich, F. Vögtle, A. Mannschreck, and H.A. Staab, Annalen, 708, 36 (1967).
119. G.W. Koeppl, D.S. Sagatys, G.S. Krishnamurthy, and S.I. Miller, J. Amer. Chem. Soc., 89, 3396 (1967).
120. R. Moccia, J. Chem. Phys., 40, 2176 (1964).
121. R.D. Joshi, J. Chem. Phys., 43, S40 (1965).
122. V. Kaldor and I. Shavitt, J. Chem. Phys., 45, 888 (1966).
123. D.M. Bishop, J. Chem. Phys., 45, 1787 (1966).
124. A. Veillard, J.M. Lehn, and B. Munsch, Theoret. Chim. Acta, 9, 275 (1968).
125. B. Tinland, Chem. Phys. Letters, 2, 433 (1968).
126. R.G. Body, D.S. McClure, and E. Clementi, J. Chem. Phys., 49, 4916 (1968).
127. A. Pipano, R.R. Gilman, C.F. Bender, and I. Shavitt, Chem. Phys. Letters, 4, 583 (1970).
128. C.F. Bender, Theoret. Chim. Acta, 16, 401 (1970).
129. A. Rauk, L.C. Allen, and E. Clementi, J. Chem. Phys., 52, 4133 (1970).
130. J.D. Swalen and J.A. Ibers, J. Chem. Phys., 36, 1914 (1962).
131. L. Radom, W.A. Lathan, W.J. Hehre, and J.A. Pople, Austral. J. Chem., 25, 1601 (1972).
132. L. Radom, W.J. Hehre, and J.A. Pople, J. Amer. Chem. Soc., 93, 289 (1971).

133. T. Masamichi, A. Y. Nirakawa, and K. Tamagake, J. Chem. Soc. Japan, 89, 821 (1968).
134. J. R. Durig, W. C. Harris, and D. W. Wertz, J. Chem. Phys., 50, 1449 (1969).
135. A. P. Cox and R. L. Kuczowski, J. Amer. Chem. Soc., 88, 5071 (1966).
136. G. E. Graw, D. L. Bernitt, and I. C. Hisatsune, J. Chem. Phys., 45, 1392 (1966).
137. A. Trombetti, Canad. J. Phys., 46, 1005 (1968).
138. R. Ditchfield, W. J. Hehre, J. A. Pople, and L. Radom, Chem. Phys. Letters, 5, 13 (1970).
139. E. B. Wilson, Proc. Nat. Acad. Sci. U. S., 43, 816 (1957).
140. E. B. Wilson, Adv. Chem. Phys., 2, 367 (1958).
141. L. Pauling, Proc. Nat. Acad. Sci. U. S., 44, 211 (1958).
142. L. Pauling, in "Theoretical Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 7.
143. E. Lassetre and L. Dean, J. Chem. Phys., 16, 151, 553 (1948); 17, 317 (1949).
144. J. Oosterhoff, Discuss. Faraday Soc., No. 10, 79 (1951).
145. Au Chin Tang, J. Chin. Chem. Soc., 18, 1 (1951); 19, 33 (1952); Scientia Sinica, 3, 279 (1951).
146. V. Magnasco and G. F. Musso, J. Chem. Phys., 54, 2925 (1971).
147. W. L. Jørgensen and L. C. Allen, J. Amer. Chem. Soc., 93, 567 (1971).
148. H. Margenau and N. R. Kestner, "Theory of Intermolecular Forces", 2nd Edition, Pergamon Press, Oxford, 1971.
149. S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, J. Chem. Soc. (B), 136 (1971).
150. C. Altona and A. P. M. Van der Meer, Tetrahedron, 24, 4377 (1963).
151. R. J. Abraham and M. A. Cooper, J. Chem. Soc. (B), 202 (1967).
152. H. R. Buys, C. Altona, and E. Havinga, Tetrahedron Letters, 3067 (1967).
153. S. Wolfe, Accounts Chem. Res., 5, 102 (1972).
154. W. H. Fink, D. C. Pan, and L. C. Allen, J. Chem. Phys., 47, 895 (1967).
155. J.-B. Robert, H. Marsman, and J. R. Van Wazer, Chem. Comm., 356 (1970).
156. E. L. Wagner, Theoret. Chim. Acta, 23, 115, 127 (1972).
157. J. T. Edward, Chem. Ind. (London), 1102 (1955).
158. P. K. Morand and I. Puskas, Canad. J. Chem., 39, 2069 (1961).
159. F. G. Riddel, Quart. Rev., 21, 364 (1967).
160. E. L. Eliel and C. A. Giza, J. Org. Chem., 33, 3754 (1968).
161. E. Kapuy, Acta Phys. Hung., 9, 237 (1958); 10, 125 (1959); 12, 185 (1960); 13, 345, 461 (1961); 15, 177 (1962); 27, 179 (1969); Theoret. Chim. Acta, 3, 379 (1965).
162. J. E. Lennard-Jones, Proc. Roy. Soc. A, 198, 1, 14 (1949).
163. J. E. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. A, 202, 166 (1950).
164. G. G. Hall, Proc. Roy. Soc. A, 202, 155 (1950); A, 205, 357, 541 (1951); A, 213, 102 (1953).
165. S. F. Boys, Rev. Mod. Phys., 32, 296 (1960).
166. C. Edmiston and K. Ruedenberg, Rev. Mod. Phys., 35, 457 (1963).
167. R. M. Pitzer, J. Chem. Phys., 41, 2216 (1964).
168. J. R. Hoyland, J. Amer. Chem. Soc., 90, 2227 (1968).
169. J. R. Hoyland, J. Chem. Phys., 49, 1908 (1968).
170. V. M. Tatevskii, Dokl. Akad. Nauk SSSR, 75, 819 (1950); 78, 67 (1961); Zhur. Fiz. Khim., 25, 241 (1951).
171. V. M. Tatevskii, N. F. Stepanov, and S. M. Yarovoi, "Metody Rashcheta Fiziko-khimicheskikh Svoistv Parafinovykh Uglevodorodov" (Methods for the Calculation of the Physicochemical Properties of Paraffinic Hydrocarbons), Gostoptekhizdat, Moscow, 1960.
172. J. Gruninger, Y. Öhrn, and P.-O. Löwdin, J. Chem. Phys., 52, 5551 (1970).
173. P.-O. Lödin, Adv. Chem. Phys., 2, 207 (1959).
174. R. K. Nesbet, Proc. Roy. Soc. A, 230, 312, 322 (1955).

Institute of Organic
Derivatives of the
Elements, USSR
Academy of Sciences,
Moscow