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Semi-empirical Quantum-mechanical Methods for the Calculation of Molecular Geometry and Conformational Energies

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The LCAO-MO approximation is considered in the Hartree-Fock problem for many-electron systems, and Roothaan's equations are given, various "simplifications" of which form the foundation for most current semi-empirical methods for calculating the electronic structure of polyatomic molecules. Accounts are given of the most popular semi-empirical schemes enabling the geometry of a molecule to be predicted and several related properties—conformational energies, barriers to internal rotation, and energies of formation—to be calculated. The possibilities and limits of application of these methods are discussed. A list of 171 references is included.

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I. INTRODUCTION

The geometry of the ground state of a molecule is not only of purely structural interest but also, in the broad sense of the word, of chemical interest. Indeed, the thermochemical properties of molecules—differences in energy between rotational isomers, barriers to internal rotation, and heats of formation, hydrogenation, and structural isomerisation—are related to their geometry; frequencies of the vibrational spectra of polyatomic molecules, absorption in the microwave range due to transitions from one rotational level to another, and even electronic spectra are directly dependent on geometry; and finally the effect of the steric factor in reactions, especially organic, is only rarely negligible. Hence it is not surprising that calculations of molecular geometry, conformations, and the energies associated with confirmational transitions occupy an important place in current theoretical investigations.

The present Review covers calculations of bond lengths, valency angles, and conformations, mainly of polyatomic organic molecules. If a method is available for calculating the total energy of a molecule, the equilibrium geometry will clearly correspond to an absolute minimum in the total energy expressed in terms of independent geometric variables, in particular bond lengths, valency angles, and angles of rotation. The total energy surface may have not one but several minima, which, when they appear with variation of angles of rotation about bonds, are claimed to correspond to stable conformers. The difference in energy between conformers determines their

equilibrium in the gas phase (when interactions between molecules can be neglected). Saddle-points in the total energy surface, encountered on the way from one minimum to another, correspond to barriers to internal rotation or inversion, which are measured by various physicochemical methods.

Until the mid-1960s almost the sole method for calculating geometry and conformational energies was the classical model of a molecule, in which the potential energy is regarded as the sum of several contributions—deformation energies of valency bonds and angles, torsional stresses, etc.—and which has several names—the mechanical model of a molecule, the molecular force field model, and the Hill–Westheimer–Kitaigorodskii–Hendrickson–Wiberg model—the last name indicating the workers who have made the most significant contribution to the creation and development of the model[1-5]. The mechanical model has been used for numerous calculations of the conformations of organic molecules (see reviews[6-8]), macromolecules, and biopolymers[9-12], as well as energies of formation of molecules from atoms[13-15], vibrational frequencies in the spectra of polyatomic molecules[16,17], etc. Without doubt this simple model will for a long time yet be a powerful tool in the hands of physical chemists: it may be just as necessary in the present stage of the development of theoretical chemistry as three-dimensional models of molecules were necessary fifteen years ago (when methods of calculation were in a rudimentary state). It must be borne in mind, however, that a mechanical model of a molecule cannot be rigorously based on the fundamental laws of physics: it does not follow directly from the Schrödinger equation, and its constants are chosen by a purely empirical procedure. Although the predictive power of this model is very great, the fact that the nature of the interactions between electrons and nuclei is concealed in empirical constants often leaves a feeling of dissatisfaction.

Quantum-mechanical methods of calculation—both semi-empirical and non-empirical (calculations *ab initio*)—have become widespread during the past decade. This is due primarily to the creation of effective algorithms for evaluating quantum-mechanical integrals, to the elaboration of new semi-empirical methods, and finally to the development of computational technique (though electronic computers are required also for calculations based on the mechanical model) and the founding of the International Exchange Fund for Programmes on Quantum Chemistry. Quantum-mechanical methods are based on seeking approximate solutions of the Schrödinger equation, with many integrals neglected in semi-empirical methods, while many are parametrised by means of experimental data. Of course, calculations *ab initio*, in which no constants other than the fundamental physical constants—e, m, and h, (the charge and mass of the electron and Planck's constant)—are used, are preferable from any point of view, but the rapid action and the memory of present-day computers enable such computations to be made only for relatively simple molecules. Hence the need to work out semi-empirical methods, enabling results of importance for the chemist to be obtained with a relatively short machine time and by means of not very complicated programmes.

II. ROOTHAAN'S EQUATIONS AND POSSIBLE MODES OF "SIMPLIFICATION"

The non-relativistic "electronic" Schrödinger equation for a molecule containing N electrons can be written

$$H\Psi = E\Psi, \qquad (1)$$

$$H = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{\alpha} Z_\alpha/R_{\alpha i} + \sum_{i=1}^{N}\sum_{j=i+1}^{N} 1/r_{ij}, \qquad (2)$$

where $\Psi \equiv \Psi(x_1, x_2, \ldots, x_N)$ is the wave function depending on the spatial and spin coordinates x_i of the electrons. E is the energy, and H is the electronic Hamiltonian, representing the sum (2) of the kinetic energy operators of the electrons, the potential energy of attraction of electrons to nuclei, and the potential energy of mutual repulsion of the electrons. Atomic units in which $m = e = h = 1$, have been used in Eqn. (2): the eigenvalues obtained for the energy operator H will then also be expressed in atomic units or hartrees (1 a.u. $\equiv$ 1 hartree = 27.210 eV = 627.46 kcal mole^{-1}). Furthermore, Z, R, and r in (2) denote respectively the charge on the nucleus, the distance between electrons and nucleus, and the distance between electrons; the subscripts i and j refer to electrons, and the subscript α indicates nuclei; and ∇_i^2 is the Laplace operator for the ith electron.

The electronic Schrödinger equation emerges in the Born–Oppenheimer approximation, according to which the motions of electrons and nuclei in a molecule can be regarded with sufficient accuracy as independent. In order to obtain the total energy of the molecule, however, the eigenvalue E of the electronic equation (1) must be supplemented by the potential energy of repulsion of the nuclei V_{nn}, which is given by the formula

$$V_{nn} = \sum_{\alpha}\sum_{\beta(\neq\alpha)} Z_\alpha Z_\beta/R_{\alpha\beta}, \qquad (3)$$

where the subscripts α and β refer to nuclei. Thus the Born–Oppenheimer approximation enables the problem of the quantum-mechanical calculation of a molecule to be solved with fixed nuclei, their interaction being taken into account only after the "electronic" calculation.

The difficulty in solving Eqn. (1) with the Hamiltonian (2) is due mainly to the large number of independent variables and the presence of terms of the form $1/r_{ij}$. The model of independent electrons (the Hartree–Fock model) permits considerable simplification of the problem, by introducing for each electron the mean potential V_i produced by the other electrons and the nuclei. Instead of (2) we can then write

$$H = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \sum_{\alpha}\frac{Z_i}{R_{\alpha i}} + \bar{V}_i\right] = \sum_{i=1}^{N} h_i^{\text{eff}}. \qquad (4)$$

The total energy calculated with the self-consistent field (Hartree–Fock) approximation differs substantially from the true total energy, owing to the neglect of "instantaneous" interactions of the electrons (or collisions): thus for the ethane molecule this difference amounts to 0.8 a.u. or ~ 500 kcal mole^{-1}![18] However, many properties of molecules are reproduced quite well by Hartree–Fock calculation. We first note that bond angles and lengths, angles of rotation, energy differences between rotational isomers, and barriers to internal rotation can be obtained in terms of a model of independent electrons (non-empirical calculations with large basis-sets are envisaged) with an accuracy only slightly inferior to that of the best experiments. We shall therefore regard the self-consistent field approximation as almost the exact Schrödinger equation for the molecule, and use it as a basis for comparing the various semi-empirical methods.

A solution of the Hartree–Fock problem is usually sought in the form of spin orbitals ψ, each of which is written as a product $\psi_i(x_\rho)\sigma_i$, where $\psi_i(x_j) \equiv \psi_i$ is the ith molecular orbital (MO), depending only on the spatial

coordinates x_j of the jth electron, and σ_j is the spin coordinate, assuming the value either $\eta_+(j)$ or $\eta_-(j)$. The molecular orbital ψ_i is presented as a linear combination of atomic orbitals (LCAO) $\varphi\nu \equiv \varphi_\nu(x_j)$:

$$\psi_i = \sum_\nu c_{i\nu}\varphi_\nu. \tag{5}$$

Denoting the ith spin orbital of the jth electron with the spin coordinate $\eta_+(j)$ as

$$\psi_i(j) = (\Sigma_\nu c_{i\nu}\varphi_\nu)\,\eta_+(j),$$

and with the spin coordinate $\eta_-(j)$ as

$$\psi_i(j) = (\Sigma_\nu c_{i\nu}\varphi_\nu)\,\eta_-(j),$$

we write the approximate wave function Ψ for a molecule with a closed electron shell (even number of electrons N) as the antisymmetrised product of the spin orbitals or the Slater determinant

$$\Psi = A\begin{vmatrix} \psi_1(1)\,\psi_1(2) & \dots & \psi_1(N) \\ \bar{\psi}_1(1)\,\bar{\psi}_1(2) & \dots & \bar{\psi}_1(N) \\ \dots & \dots & \dots \\ \psi_{\frac{N}{2}}(1)\,\psi_{\frac{N}{2}}(2) & \dots & \psi_{\frac{N}{2}}(N) \\ \bar{\psi}_{\frac{N}{2}}(1)\,\bar{\psi}_{\frac{N}{2}}(2) & \dots & \bar{\psi}_{\frac{N}{2}}(N) \end{vmatrix} \equiv A|\psi_1\bar{\psi}_1, \dots, \psi_{\frac{N}{2}}\bar{\psi}_{\frac{N}{2}}| = A\left(1,\bar{1}, \dots, \frac{N}{2}, \frac{\bar{N}}{2}\right), \tag{6}$$

where A is a normalised coefficient determined from the condition

$$\int \Psi\Psi^* d\tau = 0.$$

The variational LCAO-MO method yields Roothaan's equations[19,20], which make it possible to determine the coefficients $c_{i\nu}$, i.e. the fractional involvement of each atomic orbital in the molecular orbitals:

$$\sum_\nu F_{\mu\nu}c_{i\nu} = E_i \sum_\nu S_{\mu\nu}c_{i\nu}. \tag{7}$$

Where the E_i are the orbital energies or eigenvalues of the molecular orbital,

$$S_{\mu\nu} = \int \varphi_\mu^*\varphi_\nu\, d\tau \tag{8}$$

are the overlap integrals, and the

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \tag{9}$$

are the matrix elements of the Fock operator, in which

$$H_{\mu\nu} = \int \varphi_\mu^*\left[-\frac{1}{2}\nabla^2 - \sum V_\alpha(r)\right]\varphi_\nu\, d\tau, \tag{10}$$

$$G_{\mu\nu} = \sum_{\lambda,\sigma} P_{\lambda\sigma}\left[(\mu\nu/\lambda\sigma) - \frac{1}{2}(\mu\sigma/\nu\lambda)\right], \tag{11}$$

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

$$P_{\lambda\sigma} = 2\sum_i^{\text{occup}} c_{i\lambda}^* c_{i\sigma}, \tag{13}$$

and φ_μ^* is a complex conjugate function with respect to $\varphi\mu$. The $H\mu\nu$ in Eqns. (10)–(13) are matrix elements of the one-electron Hamiltonian, and include both kinetic and potential energy. In conformity with the fundamental idea of the self-consistent field, the potential energy is the energy of the effective electrostatic field $\Sigma V_\alpha(r)$ produced by the nuclei and by the other electrons (the summation extends over all nuclei α). The $G\mu\nu$ are the matrix elements of the effective potential resulting from interelectronic interaction. The dependence of $G_{\mu\nu}$ on the molecular orbitals is determined through the population matrix (the bond-order matrix) $P_{\lambda\sigma}$ in which the summation is made only over occupied molecular orbitals (the factor 2 indicates that each orbital is doubly occupied).

The concept of self-consistency is evident from Eqn. (13): the population matrix depends on the molecular orbitals, whereas Eqn. (7) is intended for determining the coefficients of the molecular orbitals. Self-consistency involves seeking coefficients with which these equations are satisfied. In practice self-consistency is achieved by iteration procedures.

The orbital energies E_i are roots of the secular equation

$$|F_{\mu\nu} - ES_{\mu\nu}| = 0, \tag{14}$$

while the total electronic energy is given by the formula

$$E_{\text{el.}} = \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}(H_{\mu\nu} - F_{\mu\nu}). \tag{15}$$

Since (15) is a solution only of the "electronic" Schrödinger equation, the energy of interaction of the nuclei must be added to the energy of the electrons to give the total energy:

$$E = E_{\text{el.}} + \sum_{\alpha>\beta}\sum Z_\alpha Z_\beta / R_{\alpha\beta}. \tag{16}$$

The matrix elements $G\mu\nu$ are usually expressed in terms of Coulombic and exchange operators $K\mu\nu$ and $I\mu\nu$:

$$G_{\mu\nu} = I_{\mu\nu} - K_{\mu\nu}/2, \tag{17}$$

where explicit expressions for $I\mu\nu$ and $K\mu\nu$ can easily be found from Eqns. (11)–(13). Now writing the matrix elements of the kinetic-energy operator $T\mu\nu$ from (10) in the form

$$T_{\mu\nu} = \int \varphi_\mu^*|-\nabla^2/2|\varphi_\nu\, d\tau, \tag{18}$$

we obtain the matrix form of the Roothaan equations

$$\mathbf{F}c_i = (\mathbf{H}+\mathbf{G})\,\mathbf{c}_i = (\mathbf{T} + \sum_\alpha \mathbf{V}_\alpha + \mathbf{I} - \mathbf{K}/2)\,\mathbf{c}_i = \mathbf{E}_i\mathbf{S}\mathbf{c}_i \tag{19}$$

where **F**, **H**, **G**, **T**, $\mathbf{V}_\alpha$, **I**, **K**, and **S** are the matrices whose elements have been discussed above and $\mathbf{c}_i$ is a column of the matrix $\mathbf{c}\nu\mathbf{i}$.

A few comments on the basis-sets used in quantum-mechanical calculations. The limited (minimal) basal series corresponds to 1s orbitals of hydrogen atoms; 1s, 2s, and 2p ($2p_x$, $2p_y$, $2p_z$) orbitals of carbon, nitrogen, and oxygen atoms; etc. Extended basis-sets may involve the use of two or more functions of 1s, 2s, etc. types (i.e. there may be various orbital exponents) and also polarisation functions, e.g. functions of d- and f-types for carbon atoms. It is clear that, the larger the basal series, the better the approximation obtainable to the Hartree–Fock limit.

Semi-empirical calculations usually have a valency basis: in this case the electrons of the inner shells are assigned to the core, and are assumed to introduce a correction to the electrostatic field produced by the nucleus. In π-electron theories it is assumed, moreover, that all σ-electrons belong to the core, and only the properties of the π-electron system are examined.

Thus the first and most important "simplification" in the Roothaan equations is the general use of the valency approximation in semi-empirical theories. With regard to the resulting change in structure of the equations it is obvious that formula (10) for the effective Hamiltonian $H\mu\nu$ can then be rewritten

$$H_{\mu\nu} = \int \varphi_\mu^*\left[-\frac{1}{2}\nabla^2 - \sum_A V_A(r)\right]\varphi_\nu\, d\tau, \tag{20}$$

where the operator in the integrand is the effective potential energy of the electrostatic field due to the atomic cores $V_A(r)$ summed over all atoms A belonging to the molecule (the core of the atom is taken to be its nucleus together with the electrons of its inner shells). It therefore makes sense to replace the nuclear charges Z_α and Z_β by the core charges Z'_A and Z'_B, so that Eqn. (16) will become

$$E = E_{el.} + \sum_{A>B}\sum Z'_A Z'_B / R_{AB} . \qquad (16a)$$

In most semi-empirical methods functions of the Slater type

$$\varphi(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi), \qquad (21)$$

(where n, l, m are quantum numbers (principal, azimuthal, magnetic) and r, θ, φ are the spherical coordinates of the electron) are used as atomic orbitals. For the radial part R_{nl} with $n \leq 3$ we have

$$R_{nl}(r) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} \exp(-\zeta r), \qquad (22)$$

where ζ is the orbital exponent. The spherical functions $Y_{lm}(\theta, \varphi)$ characterising the angular distribution, however, are expressed in terms of Legendre polynomials. In conformity with Slater's view, the orbital exponentials are written

$$\zeta = (Z - s)/n^*, \qquad (23)$$

where Z is the nuclear charge, s the shielding constant, and n^* the effective principal quantum number. Values of s and n^* for the orbitals used in quantum-mechanical calculations of molecules have been tabulated and are given in several monographs[21-23].

Further "simplifications" of the Roothaan equations involve neglecting some integrals in Eqns. (10) and (11) and parametrising several other integrals. There would be no need for this, but for the great bulk of calculations caused by a total number of integrals of the order of N^4 (where N is the number of basal orbitals), as is readily seen from formula (11). In the evaluation of the equilibrium geometry corresponding to an absolute energy minimum or of barriers to internal rotation, however, energy calculations should be repeated several and sometimes many times (it is necessary to vary the geometric parameters). By neglecting certain integrals, semi-empirical methods enable the time, required to calculate on a computer (BESM-6 type) the "total" energy of a molecule with a fixed geometry, to be reduced to a few minutes, and then it really becomes possible to investigate various conformations for a large set of molecules.

The evolution of quantum chemistry can be regarded as a gradual transition from simple to more complicated methods, taking into account a larger number of integrals: with the years an increasingly distinct tendency has developed to obtain the best possible approximation to the Hartree–Fock limit even for organic molecules of "average" dimensions. The non-empirical calculations of the electronic structure of the pyrrole, pyridine, and pyrazine molecules made by Clementi and Davis[24,25] may be cited as example.

Ten to fifteen years ago, of course, such calculations were technically impracticable, and the Roothaan equations were applied only to diatomic molecules. The electronic structure of large unsaturated organic molecules was usually investigated by the simple Hückel method[26,27] on the hypothesis of σ–π separation. More complicated π-electron schemes then acquired popularity, in particular the Pariser–Parr–Pople (PPP) method[28,29], which took into account a rather larger number of integrals, but as before included the σ-electrons in the core. The next considerable advance was to include the σ-electrons in the scheme of calculation by means of the extended Hückel method[30]. Finally, methods appeared using the valency approximation and involving partial or complete neglect of differential overlap[22,31-34]. Since, with a sufficiently large basis-set, non-empirical calculations by Roothaan's method give reliable predictions of geometric parameters and barriers to internal rotation, as has been mentioned, it is not surprising that the improvement of semi-empirical theories has been accompanied by an increasing rôle in calculations of the geometry of polyatomic molecules.

Methods based on localised orbitals, and originating in the "old-fashioned" valence-bond method[35], were developed in parallel with LCAO-MO methods. As early as the beginning of the 1950s Lennard-Jones and Hall[36-38] showed that unitary transformations of molecular orbitals preserve the Slater determinant and enable localised to be expressed in terms of delocalised molecular orbitals (the molecular wave function remaining unchanged). Ideas developed by the above workers and independently by Fock[39] gave rise to the theory of separated electron pairs[40-43], in which the wave function is represented by an antisymmetrised product of two-electron functions (biorbitals or geminals). Although equations similar in meaning to the Roothaan equations could be obtained for such functions, for a long time no appreciable progress was made in specific calculations. Only comparatively recently have methods based on localised orbitals become widely used both in non-empirical and in semi-empirical calculations.

The following Sections will examine semi-empirical methods in order of increasing complexity. The simplest methods (of the Hückel type) make no explicit allowance for interaction between electrons, and utilise only a few of the most important integrals. Since, however, these integrals are too remote in meaning from those in the Roothaan equations, they must be parametrised by means of experimental data (the parameters are mostly found from a comparison of calculated and experimental properties of simple molecules). More complicated methods, in which interelectronic interaction is explicit (methods involving complete or partial neglect of differential overlap), require the evaluation of a considerably larger number of integrals together with a self-consistency procedure. Finally, the last Section will examine calculations with localised molecular orbitals, which in principle are already beyond the scope of the Hartree–Fock approximation. The aim is not to investigate in which cases and for which molecular characteristics a particular method should be employed: the more modest aim is pursued of discussing the results obtained by various methods for the geometry of molecules and conformational energies, and of giving a comparative assessment of the reliability and the accuracy of these methods.

III. SIMPLE HÜCKEL METHOD

The simple Hückel method is used in the π-electron approximation to investigate the electronic structure of unsaturated systems. The idea behind this method is extremely simple. If a self-consistency procedure is applied to the Hartree–Fock equations for π-electrons, the molecular orbitals will be solutions of Eqn. (9), in which the matrix elements $F_{\mu\nu}$ can be regarded as constants:

$$F_{\mu\mu} = \alpha_\mu; \; F_{\mu\nu} = \beta_{\mu\nu} \qquad (24)$$

where $\alpha\mu$ is termed a Coulombic integral, and $\beta\mu\nu$ a resonance integral.

In the Hückel method $\alpha\mu$ and $\beta\mu\nu$ are usually regarded as empirical parameters. It is assumed furthermore that the matrix of the overlap integrals is identical with the unit matrix, while the resonance integrals, corresponding to non-bonded atoms, are assumed to be zero. Since no explicit allowance for interelectronic interaction is made in the Hückel method, there is no need for a complicated self-consistency procedure. Solving the problem now reduces to finding the roots of the secular equation (14) and determining the coefficients of the molecular orbitals.

Without considering the further simplifications introduced for π-electron systems or methods of estimating the parameters $\alpha\mu$ and $\beta\mu\nu$, we merely note that this method is unsuitable for completely calculating the geometry of a molecule. In several cases, however, empirical relations between bond length and bond order, which were especially popular fifteen years ago, can be used to assess e.g. carbon–carbon bond lengths in fused aromatic systems such as naphthalene, phenanthrene, etc.

Table 1. Dependence of resonance integral (25) on internuclear distance.

Å	k^{14}	k^{15}	Å	k^{14}	k^{15}
1.20	1.71	1.38	1.45	0.83	0.91
1.33	1.23	1.11	1.54	0.57	0.78
1.397	1.00	1.00			

The Hückel method is usually applied to molecules having a planar conjugated system. If the length of a bond which transmits the conjugation (e.g. the central carbon–carbon bond in biphenyl) is changed by the repulsion of non-bonded atoms, the resonance integral is represented by the formula

$$\beta = k\beta_0, \tag{25}$$

where β_0 is the "standard" value of the resonance integral and k is a constant, whose variation with the carbon–carbon bond length is given in Table 1. If, however, the repulsion of non-bonded atoms leads to a loss of coplanarity, a correction is made to the resonance integral of the bond relative to which the parts of the molecule are rotated. The resonance integral is then regarded as a function of the angle of rotation φ (e.g. between the planes of the phenyl rings in biphenyl) and is calculated by means of the formulae

$$\beta_\varphi = \beta_{\varphi=0}\cos\varphi \tag{26}$$

and

$$\beta_\varphi = \beta_{\varphi=0}\cos^2\varphi\,. \tag{27}$$

These equations are based on the proportionality noted by Mulliken[41–46] between resonance and overlap integrals; probably their first applications were reported in Refs. 47 and 48.

Neither in accuracy nor in relative validity do expressions of such type differ from the empirical formulae used in classical calculations[49,50], where the analogue of the resonance integral is the empirical constant U_0. Nor can attempts to obtain more complicated formulae for the resonance integral by the simple Hückel method be regarded as sufficiently soundly based. This applies in particular to the suggested[51] relation

$$\beta = \beta_0\frac{S/(1+S)}{S_0/(1+S_0)}, \tag{28}$$

which follows from Mulliken's "magic" formula[46] (S and S_0 are overlap integrals).

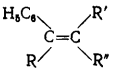
Adrian[52] computed the equilibrium conformations of the triphenylmethyl radical (I), biphenyl (II), *cis*-stilbene (III), *cis*-azobenzene (IV), and the *pp'*-dimethoxyphenylnitric oxide radical (V). Resonance integrals for the carbon–carbon bonds about which rotation occurs were estimated by Wheland's method[53], which gave relations between β and φ closely similar to (27). Repulsions of non-bonded atoms compete with conjugation in these molecules (I)–(V). The H...H interactions were allowed for by means of Hirschfelder and Linnett's potential curve[54], and the C...H interactions by means of the relation $f_{C...H} = 2.3 f_{H...H}$ (interactions between carbon atoms were disregarded). The calculated angles φ of rotation of the phenyl rings for the five compounds (I)–(V) were respectively 32°, 20–30°, 30–40°, > 40°, and ~ 25°, agreeing quite well with the experimental values.

Goodwin and Morton-Blake[55] tried to solve the "converse" problem–to obtain the parameters of the H...H potential from data on the equilibrium conformation of biphenyl in the vapour (the angle between the phenyl rings is $\varphi = 42°$) and the approximate expression for the conjugation energy[56]

$$\varepsilon_\pi = 0.196\beta^*\cos^2\varphi$$

with respect to a system of two isolated benzene rings. They adopted the value $\beta^* = -32.5$ kcal mole^{-1}. The calculated H...H potential (it has no minimum, of course, since only repulsion was considered) was rather "more rigid" than other published potentials. This is due partly to the neglect of C...C and C...H interactions.

Favini and Simonetta[57] examined the conformations of the phenylated and methylated ethylenes



(R, R', and R'' are hydrogen atoms or phenyl and methyl groups). The ideal bond angles in ethylene and its derivatives were assumed to be 120°, corresponding to sp^2 hybridisation of the carbon atoms. The C–R, C–R', etc. bond lengths were computed by an iteration procedure involving calculating bond orders in the Hückel approximation for some standard geometry, and determining the bond lengths by means of Coulson's dependence[58] of bond length on bond order. Resonance integrals β were then calculated for the resulting geometry, bond orders and lengths were redetermined, and the procedure repeated until changes in bond lengths became less than 0.005 Å. Rotations of the phenyl rings relative to the plane of the ethylene system were allowed for by means of formula (26). Finally, the energy of interaction of non-bonded atoms was calculated by means of Kitaigorodskii potentials[59].

The most interesting calculated results are the angles of rotation of the phenyl rings relative to the plane of the ethylenic system (the distortions of the bond angles lay within the limits of accuracy of the calculation). Twenty compounds of this type gave angles of rotation of 17–60°.

Another paper by Italian authors[60] gave a similar calculation of the equilibrium conformation of the *trans*-$\alpha\beta$-dicyanostilbene molecule. Unfortunately, reliable structural data are as yet lacking for the large majority of these compounds.

The problem of rotation about bonds that transmit conjugation has been investigated not only by the simple Hückel method. Dewar and Harget[61] proposed a method of evaluating resonance integrals from thermochemical data and used Bartell potentials[62] to obtain a dihedral angle of $\varphi = 40°$ in biphenyl, in excellent agreement with experiment (42°).[63] Skancke[64] worked out the parametrisation of the zero differential overlap method for π-electrons (actually for the PPP method), which enabled the conformations of various fluorinated biphenyls to be predicted with good accuracy[65]. In this series of compounds the dihedral angle between the phenyl rings is increased by the entry of substituents at positions 2 and 6, reaching a maximum of 70° in decafluorobiphenyl[66]. This tendency is apparent also in calculations taking into account non-bonded interactions and the π-electron energy. A similar approach, but with use of the CNDO valency approximation (Section V), was made by Sekigawa[67] to investigating the conformations of nitronaphthalenes and certain other compounds of this type. The results of his calculations are almost identical with those obtained for the same compounds by means of the mechanical model of the molecule[49].

In the above examples empirical model methods are ultimately used, since the search for equilibrium conformations is based on the examination of non-bonded interactions. Only conjugation energies, bond orders, and certain other quantities are estimated by semi-empirical methods of quantum chemistry. The term "quantum-mechanical" should properly be applied only to calculations that give the total energy of the molecule. As already mentioned, the optimal conformers would then correspond to minima of the total energy; the heat of isomerisation is given by the difference between the total energies of the isomers; etc. Henceforward we shall consider parametric methods enabling the total energy of the molecule to be estimated.

IV. EXTENDED HÜCKEL METHOD

The extended Hückel method (EHM) uses the valency approximation and the assumption that the matrix elements of the Fock operator $F_{\mu\nu}$ are independent of the coefficients of the molecular orbitals:

$$F_{\mu\nu} = H_{\mu\nu}^{\text{eff}}. \qquad (29)$$

Comparison of Eqn. (29) with (9)–(13) shows firstly that the extended method does not allow explicitly for the interaction of the electrons (11) and secondly that the effective one-electron Hamiltonian takes account both of the kinetic energy of the electrons and of the effect on them of the electrostatic field of the core, but makes no separation of these two completely different kinds of effect. In contrast to the simple Hückel method (24), however, the extended method covers all non-diagonal elements of the one-electron Hamiltonian. This is very important in conformational analysis: it is because the non-diagonal elements differ in different conformations of such molecules as e.g. n-butane that these conformations have different energies. Another virtue of the extended Hückel method is that it takes into account all the valency electrons of the molecule, whereas methods used until the 1960s usually covered only the π-electrons, the σ-electrons being confined to the core.

Hoffmann[68], having demonstrated the great predictive power of this method, suggested using the ionisation potentials of the corresponding valency states of the atoms as the diagonal matrix elements $H_{\mu\mu}$. For hydrocarbon molecules, in particular, he used the values (in kcal mole^{-1}) $H_{\mu\mu}(1s\text{H}) = -313.6$, $H_{\mu\mu}(2s\text{C}) = -493.5$, and $H_{\mu\mu}(2p\text{C}) = -262.9$.[69,70] The non-diagonal matrix elements $H_{\mu\nu}$ are usually obtained by means of the Wolfsberg–Helmholtz relation[71]

$$H_{\mu\nu} = 0.5K(H_{\mu\mu} + H_{\nu\nu}) \cdot S_{\mu\nu}, \qquad (30)$$

where K is an empirical constant and the $S_{\mu\nu}$ are the overlap integrals of the Slater orbitals.

Choosing the value of K is the most difficult part of the whole scheme of calculation[72]. If Mulliken's approximation is adopted[46], K should be unity. But calculations for homonuclear diatomic molecules then give absurd results. It is therefore usually assumed that $K > 1$, and in Hoffmann's work and several other calculations of conformations and conformational energies the value of K is taken to be 1.75.

The non-diagonal elements $H_{\mu\nu}$ are not only estimated by means of formula (30), in which the arithmetic mean of the diagonal elements $H_{\mu\mu}$ and $H_{\nu\nu}$ is used, but sometimes from the geometric mean of these quantities[73,74]:

$$H_{\mu\nu} = K\sqrt{H_{\mu\mu}H_{\nu\nu}} \cdot S_{\mu\nu}. \qquad (31)$$

Formula (31) can be regarded as just as valid as (30). The proportionality coefficient K should exceed unity in this case, and the best agreement with experiment is obtained when $K = 1.75$.

An interesting attempt was made to avoid altogether the empirical constant K, and write the non-diagonal matrix elements of the Hamiltonian in the form[75]

$$H_{\mu\nu} = (2 - |S_{\mu\nu}|)S_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu})/2. \qquad (32)$$

Calculations in the extended Hückel method are quite simple: they merely involve evaluating the overlap integrals $S_{\mu\nu}$, setting up the matrix H, and solving the set of equations

$$\sum_{\mu=1}^{n} [H_{\mu\nu} - ES_{\mu\nu}]c_\mu = 0, \quad \nu = 1, 2, \ldots, n, \qquad (33)$$

where n is the number of atomic orbitals. Allowing for the double occupation of each level, we take the "total" energy to be given by the sum of the orbital energies E_i of the occupied molecular orbitals:

$$E_{\text{total}} = 2\sum_i E_i.$$

The computer time necessary to estimate the coefficients $c_{\mu\nu}$ and compute the "total" energy is of the same order as the time required to calculate empirical potential functions. Thus only 10 s is required to calculate ethane[68]. Within the framework of the extended Hückel method, therefore, it is possible to seek the minimum total energy and calculate energy differences between rotational isomers and barriers to internal rotation.

We return to Hoffmann's parametrisation[68], and examine the results obtained in the calculation of conformations. The three conformations of propane—(I) with both methyl groups in the staggered position with respect to the methylene group, (II) with one methyl in the staggered position and the other in the eclipsed position, and (III) with both methyls in the eclipsed position—have calculated energies of −8022.32, −8016.69, and −8009.91

kcal mole^{-1}, whence it follows that (I) is the most stable form. But the calculated difference in energy between (I) and (II) is 5.63 kcal mole^{-1}, which considerably exceeds the experimental value[76]. The most favourable of the twelve conformations of n-butane is the *trans*(or *anti*)-form with the carbon–hydrogen bonds in the staggered position, which is consistent with electron-diffraction data[77]. However, the barrier to internal rotation (the difference in energy between *cis*- and *trans*-forms) is too large in comparison with the experimental value[78] (27 and 6.92 kcal mole^{-1}). The calculated barrier to internal rotation in ethane is also overestimated: 4.0 in comparison with the experimental value[79] of 2.93 kcal mole^{-1}. Calculated energies of isomerisation are also rather too high: thus for the isomerisation of n-butane into isobutane calculation gives 2.3 kcal mole^{-1}, whereas the experimental value[80] is 1.6 kcal mole^{-1}.

Calculation of the conformations of cycloalkanes has yielded interesting results. Like most empirical theories, the extended Hückel method gives for cyclobutane a minimum corresponding to the planar form. In cyclopentane the planar form is unfavoured, but the half-chair (C_2) is more favoured than the "envelope" (C_S) by 1.8 kcal mole^{-1}. This result agrees neither with empirical estimates nor with electron-diffraction data[81] proving the equivalence of these forms and the absence of hindrance to pseudorotation. The calculated difference in energy between chair and boat conformations of cyclohexane (17.7 kcal mole^{-1}) is about double the experimental value.

Hoffmann's paper was the first of a stream of predictions of the geometry and the conformational energies of molecules, and many workers regarded it as a triumph of quantum chemistry. Other authors, on the other hand, considered that the accuracy of the predictions obtained by the extended method was too poor; in any case, it is substantially inferior to that of model methods using atom–atom potentials. Subsequent Hartree–Fock calculations of the conformations of simple molecules helped to establish a moderate attitude: the extended Hückel method is useful for rough conformational calculations, but gives inaccurate values of conformational energies, and in some cases an incorrect assignment of favoured conformers.

The above examples show that the extended Hückel method in Hoffmann's parametrisation leads to a re-evaluation of the part played by the steric factor. Hoffmann calculated conformational energies for experimental bond lengths and valency angles. Strictly speaking, a minimum total energy should be sought with respect to all internal parameters, including bonds and angles. Unfortunately such a procedure does not lead to agreement with experiment: Table 2 shows that the calculated geometric parameters are far removed from the experimental values†. Conformational energies obtained with the optimised geometry are too low. Thus in Hoffmann's method optimisation of the geometry does not give agreement with experiment. Nor could better agreement be obtained by changing the parametrisation. Thus if the value 1.2 instead of 1.0 is adopted for the Slater exponent 1*s*H, calculation will give the correct barrier in ethane, but strong divergence from experiment for the difference in energy between chair and boat conformations of cyclohexane.

† The reason why the extended method may give reasonable conformational energies, while being completely unsuitable for predicting the geometry of molecules, will be indicated in Section V.

The formalism of the extended Hückel method has been compared[74,83,84] with Roothaan's formalism, and the main sources of error in the extended method have been indicated. According to Allen[74,84] a considerable proportion of the error is due to change in the electrostatic potential $\Sigma_A V_A(r)$ in Eqn. (20) during deformations of bond angles and rotations about bonds. Therefore, whereas the extended method works satisfactorily for hydrocarbons, it often predicts, for molecules whose atoms bear large excess charges, a geometry that is markedly different from the experimental geometry. Thus for the water molecule the extended method yields an HOH equilibrium angle of 140°, whereas the experimental angle is 104.5°. For the same reason the shape of the potential curve for internal rotation in the hydrogen peroxide molecule is opposite to the experimental curve.

Table 2. Geometric parameters corresponding to minimum energy in the extended Hückel method[68,82].

Molecule	Bond	Bond length, Å		Valency angle	Value of angle	
		calc.	expt.		calc.	expt.
CH_4	C—H	1.02	1.09			
$H_3C—CH_3$	C—C	1.92	1.53			
	C—H	1.00	1.10			
$H_2C=CH_2$	C=C	1.47	1.33	HCH	125°	
	C—H	0.95	1.08			
	C=C	1.52	1.33	HCH	120.7°	115.6°
	C—H	0.92	1.08			

A numerical investigation of the dependence of the non-diagonal matrix elements of the one-electron Hamiltonian on the distance between the atoms showed[83] that the proportionality of $H_{\mu\nu}$ and $S_{\mu\nu}$ expressed by Eqn. (30) is satisfied fairly accurately only if the atomic orbitals φ_μ and φ_ν are not immediate neighbours (it is probably for this reason that the extended method is suitable for conformational calculations). However, neighbouring atoms show large departures from proportionality, caused by the kinetic portion $(\varphi_\mu | -\frac{1}{2}\nabla^2 | \varphi_\nu)$ of the Hamiltonian in Eqn. (10). This non-proportionality is primarily responsible for the constant K differing from unity in the Wolfsberg–Helmholtz relation.

In spite of the obvious defects of the extended Hückel method, it is widely used for theoretical investigations of the conformations of structurally similar molecules. Van Eijck[85], who calculated the conformations of numerous carboxylic acids, concluded that the method predicts the correct equilibrium structure for these compounds in nearly every case: only the calculated barriers to internal rotation showed poor agreement with experiment. Pachler and Tollenaere[86] calculated conformational energies for substituted ethanes—fluoroethane, 1,2-difluoroethane, ethanol, propionitrile, ethylene glycol, 2-fluoroethanol, and succinonitrile—and obtained good agreement between calculated and experimental barriers to rotation by using experimental bond lengths and angles and adopting the value 1.2 for the Slater exponent 1*s*H (with exponent of 1.0 the resulting barriers were overestimated by 30–80%). In full agreement with experiment, calculation predicts preference for the gauche forms of 1,2-difluoroethane, ethylene glycol, 2-fluoroethanol, and succinonitrile. However, the calculated energy differences between the gauche and *trans*-forms are too large in comparison with the experimental differences.

Because of the simplicity of programming and the small consumption of computer time, the extended Hückel method rapidly gained popularity with biochemists investigating the conformational states of complicated bio-organic molecules. Thus conformational maps have been calculated[87] for dipeptides, the structural units of protein molecules; the conformations of amino-acids have been investigated[88]; and Long and Goldstein have predicted[89] the conformations of nicotinamide and related amides. Finally, mention may be made of work done by Kier[90], who calculated the molecular conformations of many medicinals, and claimed the start of a new line of scientific advance—quantum pharmacology.

Pullman[91-93] used the extended method to investigate the conformations of nucleosides, photodimers of thymine, and several other molecules related to components of nucleic acids. He was interested not only in the problems of finding the preferred conformers but also in the charge distribution on the atoms. The calculated charges on the atoms in nucleosides were numerically too large: although no experimental methods are available for determining charge, it is improbable that the excess charge on the oxygen atoms in β-D-ribose and in nitrogen bases would reach the calculated 1.5 electron.

An iteration procedure of the extended Hückel method (IEHM) was suggested[94,95] to obtain more realistic values of the charges and refine the conformational energies. Without going into details of the application of this procedure, we note that it yields reasonable charges on the atoms, and in some cases more reliable conformational energies. However, since the time required to calculate the total energy is appreciably increased, while the significance of the Hamiltonian is not essentially changed, the value of the procedure in conformational calculations is not very great.

V. METHODS OF ZERO DIFFERENTIAL OVERLAP

Pople[31-33] and Dewar[97,98] worked out several semi-empirical self-consistent field methods in the valency approximation. These were close in physical meaning to the Hartree–Fock LCAO-MO procedure, but were considerably simpler and accessible to many chemists having an electronic computer at their disposal.

The most laborious stage in solving Roothaan's equations consists in evaluating the two-electron integrals (11) and (12). Semi-empirical schemes have been constructed with the idea of partly or completely avoiding this complicated procedure. But simply neglecting these integrals strongly distorts the structure of Roothaan's equations: the molecular orbitals ψ_i and the orbital energies E_i become non-invariant with respect to (i) transformations of the coordinates—translation and rotation of the axes—and (ii) change in hybridisation: in particular, replacement of the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals of the carbon atom by hybrid sp^3 orbitals will give different solutions of the equations. Although breakdown of hybridisational invariance may still be accepted in several cases, by arranging to use molecular orbitals of a certain type (this procedure is used in calculations by the extended Hückel method), loss of invariance of type (i) is simply intolerable. Indeed, any author is free to choose a system of coordinates in the molecule as he thinks fit, and non-invariance with respect to transformations of the coordinate axes makes it impossible to compare results obtained by different workers. The idea underlying methods of zero differential overlap (ZDO) is the partial or complete neglect of products of atomic orbitals of the type $\varphi_\mu\varphi_\nu$ ($\mu \neq \nu$) and the choice of approximations that leave the Roothaan equations invariant with respect both to orthogonal transformations of the basis and to change in hybridisation.

The method of complete neglect of differential overlap (CNDO)[31,32] involves neglect of integrals of the type (Eqn. 12)

$$(\mu\nu/\lambda\sigma) = 0 \text{ with } \mu \neq \nu, \lambda \neq \sigma \tag{34}$$

but it is assumed that

$$\gamma_{\lambda\mu} = (\lambda\lambda\,|\,\mu\mu) \neq 0. \tag{35}$$

This disrupts the invariance of the Roothaan equations, and only further approximations will restore it. It is assumed firstly that $\gamma_{\mu\nu}$ depends solely on the type of atoms to which the orbitals φ_μ and φ_ν belong, not on the type of orbital. Thus γ_{AB} is a measure of the mean repulsion of electrons in valency orbitals of the atom A and the atom B. Combining this postulate with formulae (34) and (35), we obtain instead of (9)–(13) the equations

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2}P_{\mu\mu}\gamma_{AA} + \sum_{B(\neq A)} P_{BB}\gamma_{AB}, \tag{36}$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}, \tag{37}$$

$$P_{BB} = \sum_{\nu}^{B} P_{\nu\nu}, \tag{38}$$

$$H_{\mu\mu} = \left(\mu\left|-\frac{1}{2}\Delta^2 - V_A\right|\mu\right) - \sum_{B(\neq A)}(\mu\,|\,V_B\,|\,\mu) = U_{\mu\mu} - \sum_{B(\neq A)} V_{AB}, \tag{39}$$

where the subscripts μ refer to the atom A ($\mu \equiv \varphi_\mu$), P_{BB} in (38) is the aggregate electron density of valency electrons on atom B, and $U_{\mu\mu}$ is the energy of the atomic orbital φ_μ regarded as an empirical parameter. Equations (36)–(39) restore the invariance with respect to orthogonal transformations. A further simplification has been introduced into Eqn. (39): the matrix elements $(\mu\,|\,V_B\,|\,\nu)$, where φ_μ and φ_ν belong to the same atom A, are zero if $\mu \neq \nu$; if, however, $\mu = \nu$, we have $(\mu\,|\,V_B\,|\,\mu) = V_{AB}$.

The non-diagonal matrix elements $H_{\mu\nu}$ in (37) are found empirically on the assumption that they are proportional to the overlap integrals $S_{\mu\nu}$:

$$H_{\mu\nu} = \beta_{\mu\nu} = \beta^0_{AB}S_{\mu\nu}, \tag{40}$$

where β^0_{AB} is an empirical parameter depending on the nature of the atoms A and B. Increments β^0_A and β^0_B are adopted for each atom, and β^0_{AB} is then computed as the arithmetic mean of these increments:

$$\beta^0_{AB} = (\beta^0_A + \beta^0_B)/2. \tag{41}$$

The proportional relation (40), in contrast to the Wolfsberg–Helmholtz formula (30), does not disrupt the invariance of the equations with respect to transformations of the basis-set. Bearing in mind that φ_μ refers to atom A, and φ_ν to B, we find from (40) for the non-diagonal elements of the Fock matrix the expression

$$F_{\mu\nu} = \beta^0_{AB}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB}. \tag{42}$$

An expression for the total energy in the CNDO/1 approximation[31] can now be readily obtained:

$$E_{\text{total}} = \sum_A E_A + \sum_{A>B}\sum E_{AB}, \tag{43}$$

where

$$E_A = \sum_{\mu}^{A} P_{\mu\mu}U_{\mu\mu} + \frac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{A}\left(P_{\mu\mu}P_{\nu\nu} - \frac{1}{2}P^2_{\mu\nu}\right)\gamma_{AA} \tag{44}$$

and

$$E_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B}\left(2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2\gamma_{AB}\right) + \\ + (Z'_A Z'_B R_{AB}^{-1} - P_{AA}V_{AB} - P_{BB}V_{BA} + P_{AA}P_{AB}V_{AB}). \quad (45)$$

The energies of the atomic orbitals $U_{\mu\mu}$ are expressed in this approximation in terms of mean ionisation potentials I_μ:

$$U_{\mu\mu} = -I_\mu - (Z - 1)\gamma_{AA}. \quad (46)$$

Calculations by the CNDO/1 method give bond lengths in diatomic molecules that are too short and bond energies that are too large. Polyatomic molecules, however, are, roughly speaking, "too compressed". Pople and Segal[32] therefore proposed a different parametrisation (CNDO/2), which subsequently became widely accepted. Firstly it is assumed that

$$V_{AB} = Z'_B\gamma_{AB}. \quad (47)$$

Application of this relation enables "the effect of 'penetration' of one atom into the electron shell of the other to be diminished" (however, the physical justification for this is weak). Further, the parameter $U_{\mu\mu}$ is estimated by averaging the ionisation potential I_μ and the electron affinity A_μ:

$$U_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + \left(Z' - \frac{1}{2}\right)\gamma_{AA}. \quad (48)$$

For the matrix elements of the Fock operator we then obtain the formulae

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + \left[(P_{AA} - Z'_A) - \frac{1}{2}(P_{\mu\mu} - 1)\right]\gamma_{AB} + \sum_{B(\neq A)}(P_{BB} - Z'_B)\gamma_{AB} \quad (49)$$

$$F_{\mu\nu} = \beta^0_{AB}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB}. \quad (50)$$

The Slater basis-set with exponents 1 and 2 for the hydrogen atoms is used in computing the overlap integrals $S\mu\nu$. In contrast to the extended Hückel method, complete neglect of differential overlap requires self-consistency procedures. The iteration procedure consists in making initial estimates of the coefficients of the linear combination of orbitals from theories of Hückel type

$$F^{(0)}_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu), \quad (51)$$

$$F^{(0)}_{\mu\nu} = \beta^0_{AB}S_{\mu\nu}, \quad (52)$$

and computing the total energy and the matrix elements $F\mu\nu$ until self-consistency is attained.

The success of the CNDO/2 method depends substantially on the parametrisation, especially on the choice of proportionality constants β^0_{AB} in Eqn. (40) (more precisely on the choice of the atomic constants $\beta^0_A, \beta^0_B, \ldots$). Pople and Segal[32] selected these constants to give the best possible reproduction of the results of non-empirical calculations of corresponding diatomic molecules made with the same set of atomic orbitals. Use of their parametrisation yields reasonable geometric parameters, conformational energies, and barriers to internal rotation. In any case, it becomes possible to make a serious search for a minimum total energy in order to obtain the geometry of the molecule and the energy characteristics of the conformers: in the extended Hückel method such a search leads in many cases to absurd results.

Table 3, based on Gordon's results[99], gives an idea of the extent of agreement between calculated and experimental values (bond lengths are given only to hundredths of an Ångström unit; extremal values reached during rotation are given for the calculated valency angles; and references to the experiments will be found in the original paper). Bond lengths are seen to be predicted with a mean accuracy of 0.1 Å, and valency angles to a few degrees. Nevertheless, the divergence between calculation and experiment is in some cases too large—e.g. the oxygen–oxygen bond length and the HOO valency angle in the hydrogen peroxide molecule, and the oxygen–fluorine bond length in the F_2O_2 molecule.

Table 3. Molecular geometry predicted by CNDO/2 method with Pople–Segal parameters.

Molecule	Bond	Bond length, Å		Valency angle	Angle, degrees	
		calc.	expt.		calc.	expt.
H_3C-CH_3	C—C	1.46	1.52	HCH	106.0—106.5	107.8
	C—H	1.12	1.10			
H_3C-NH_2	C—N	1.41	1.47	CNH	108.7—107.5	112.3
	C—H	1.12	1.09	HNH	103.8—104.2	105.8
	N—H	1.07	1.01			
H_3COH	C—C	1.37	1.43	HCO	110.9—110.7	109.5
	C—H	1.12	1.09	HCH	108.0—108.2	109.5
	O—H	1.03	0.94	COH	106.6—105.0	109.5
HO—OH	O—O	1.22	1.47	OOH	110.8—105.0	94.8
	O—H	1.04	0.95			
FO—FO	O—O	1.22	1.22	OOF	109.0—105.6	109.5
	O—F	1.18	1.57			
H_2N-H_2N	N—N	1.34	1.45		106.5—110.6	112.0
	N—H	1.07	1.20	HNH	102.5—103.0	105.8

Table 4. Barriers to internal rotation calculated by CNDO/2 method.

Molecule	Height of barrier, kcal mole^{-1}		Molecule	Height of barrier, kcal mole^{-1}	
	calc.	expt.		calc.	expt.
cis-H_2O_2	5.16 [99]	7.0	CH_3-CH_2F	2.00 [99]	3.30
trans-H_2O_2	0 [99]	1.1			
CH_3OH	0.78 [99]	1.07	CH_3-CHF_2	1.88 [99]	3.18
	0.67 [32]				
CH_3NH_2	1.57 [99]	1.97	CH_3-CF_3	1.76 [99]	3.48
	1.21 [32]				
C_2H_6	2.18 [99]	2.93	CF_3-CHF	1.46 [99]	4.58
	2.32 [32]				
C_3H_8	2.20 [101]	3.6	$CF-CHF_2$	1.22 [99]	3.51
iso-C_4H_{10}	2.64 [101]	3.9	$CF-CF_3$	1.07 [99]	3.92
C_3H_6	1.16 [102]	1.98	*trans*-FCH:$CHCH_3$	1.30 [99]	2.20
	1.00 [101]				
cis-2-C_4H_8	0.44 [101]	0.75	*cis*-FCH:$CHCH_3$	0.93 [99]	1.06
CH_3CHO	0.71 [102]	1.16	CH_2:$CFCH_3$	0.88 [99]	2.43
HCOOH	34.9 [102]	17.0	CF_2:$CHCH_3$	0.96 [99]	1.25

Table 4, compiled from results in several papers (references to the experimental work will be found in a review[100]), gives calculated barriers to internal rotation. Comparison of the values calculated for methanol, methylamine, and ethane shows that the two variants of the method—CNDO/1 and CNDO/2—give closely similar results. It is evident that this method almost always underestimates the barriers, as a consequence of partial neglect of two-electron integrals and/or the parametrisation. Despite the discrepancy between calculated and

experimental values, however, the trend in the variation of the barriers is in the main correctly reproduced. Thus the proportions 3 : 2 : 1 for ethane, methylamine, and methanol are quite well satisfied[100], and the assignment of minima and maxima of the total energy during internal rotation is correct in all cases other than for hydrogen peroxide. With fluorinated derivatives calculation gives the right assignment of stable forms, but poor agreement with experiment both in the numerical values of the barriers and in the trend of their variation on passing from one molecule to another.

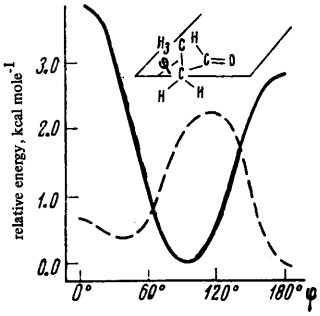


Figure 1. Variation in energy of propionaldehyde molecule during rotation of the methyl group about the C–C bond calculated by different methods: CNDO; extended Hückel method.

Nevertheless, calculations by the CNDO method by no means always give even qualitative agreement with experiment. Fig. 1 illustrates the variation in the total energy of the propionaldehyde molecule with the dihedral angle φ. Microwave[103] and nuclear magnetic resonance[104] spectra have shown the presence of two stable conformers differing in energy by 0.9 kcal mole^{-1}. The more stable conformer corresponds to $\varphi = 49°$, and the barrier separating them is 2.28 kcal mole^{-1}. The CNDO/2 method with Pople and Segal's parameters does not predict the existence of two conformers at all, quite apart from the position of the minimum[102]. In this case the extended Hückel method—which is considerably cruder than CNDO—yields better agreement with experiment.

In all the above examples the energy of internal rotation was calculated with bonds and valency angles fixed at values taken from experiment. This raises the question whether agreement with experiment could not be improved by basing the calculations on the optimum geometry, i.e. by requiring that the energy should be optimised with respect to bond lengths and valency angles for each angle of rotation. This question has been too little investigated for an unambiguous answer to be possible. We note merely that calculation with optimisation of the geometry for the hydrogen peroxide molecule gives two barriers—*cis* and *trans*—with energies of 5.0 and 2.85 kcal mole^{-1} respectively (in non-empirical calculations the *trans*-barrier can be predicted only with large basis-sets). Minimum energy corresponds to an angle of rotation of 87° read from the *cis*-form (the experimental angle is 111.5°).

The CNDO method makes it possible to understand which interactions are responsible for the appearance of barriers. The energy of interaction of the atoms E_{AB} (Eqn. 45) can be written as the sum of three components:

$$E_{AB} = E^{(1)}_{AB} + E^{(2)}_{AB} + E^{(3)}_{AB}, \tag{53}$$

where

$$E^{(1)}_{AB} = 2\sum_{\mu}^{A}\sum_{\nu}^{B} P_{\mu\nu}S_{\mu\nu}\beta^{0}_{AB} \tag{54}$$

$$E^{(2)}_{AB} = -\frac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{B} P^{2}_{\mu\nu}\gamma_{AB} \tag{55}$$

$$E^{(3)}_{AB} = P_{AA}P_{BB}\gamma_{AB} - P_{AA}Z'_{B}\gamma_{AB} - P_{BB}Z'_{A}\gamma_{AB} + Z'_{A}Z'_{B}/R_{AB} \tag{56}$$

and V_{AB} in (45) has been replaced by formula (47) in conformity with the CNDO/2 approximation.

The component $E^{(1)}_{AB}$ represents the main contribution to the energy of bonding made by the atomic orbitals $\varphi\mu$ and $\varphi\nu$ belonging to atoms A and B respectively. Since $\beta^{0}_{AB} < 0$, the inequality $E^{(1)}_{AB} < 0$ implies that this type of interaction between atoms A and B strengthens the bonding; the inequality $E^{(1)}_{AB} > 0$ corresponds to a weakening of bonding.

The component $E^{(2)}_{AB}$ represents stabilisation by exchange interactions.

Finally, $E^{(3)}_{AB}$ is the electrostatic interaction of atoms A and B, since

$$P_{AA} = \sum_{\mu}^{A} P_{\mu\mu}$$

is the total electron density on A. If at large distances $\gamma_{AB} \simeq 1/R_{AB}$, we actually have

$$E^{(3)}_{AB} = (P_{AA} - Z'_{A})(P_{BB} - Z'_{B})/R_{AB} = q_{A}q_{B}/R_{AB} \tag{57}$$

where q_A and q_B are the net charges of atoms A and B: i.e. Eqn. (57) corresponds to purely Coulombic interaction.

The energy E_A introduced by the orbitals of atom A (Eqn. 44) makes a very small contribution to the relative conformational energy. Thus for ethane, methylamine, and methanol $\Sigma_A \Delta E_A$ is respectively 0.08, 0.12, and 0.16 kcal mole^{-1}, and stabilises the eclipsed conformations[99].

Analysis shows[99] that in most cases the term $\Delta E^{(1)}_{AB}$ plays by far the major part in determining the barrier to internal rotation. In ethane, its fluorinated derivatives, methylamine, and methanol the barrier is due to H...H interaction (characterised by the parameter $E^{(1)}_{HH}$) in the eclipsed conformations. The electron density in the space between the hydrogen atoms is small, which leads to their repulsion. In the hydrazine molecule interaction of the lone pairs of the nitrogen atoms prevails over H...H repulsion. In molecules having large excess charges, such as hydroxylamine, the electrostatic contribution $\Delta E^{(3)}_{AB}$ plays an important part as well as $\Delta E^{(1)}_{AB}$.

The nature of the barriers in the hydrogen peroxide molecule is interesting. It is not surprising that H...H interaction, characterised by the parameter $\Delta E^{(1)}_{HH}$, is responsible for the *cis*-barrier. The *trans*-barrier is due mainly to interaction of π-electrons in the non-planar conformations, and is determined by the parameter ΔEOO of the oxygen atoms. These characteristics of interatomic interaction appear only in calculations with optimisation of the geometry: if the experimental bond lengths and HOO valency angle are used, however, the minimum total energy will correspond to the *trans*-form.

Nevertheless, a more reliable assignment of the "nature" of the barriers to internal rotation in molecules can be obtained only on the basis of non-empirical calculations. Indeed, the neglect of many integrals and the replacement of a further series of integrals by empirical

parameters lead firstly to considerable errors in the calculated barriers and secondly to incorrect assessment of the effects of particular factors. Yet even an extremely rough non-empirical calculation (with a small basis-set) yields in most cases a correct idea of the relative importance of various contributions to the barrier. And still, independently of the method of calculation used, a fundamental difficulty arises in interpreting the "nature" of the barriers, because quantum-mechanical integrals can be combined in various groups in quite a number of ways, so that the interpretation will depend on the grouping adopted in a specific calculation.

The resolution of E_{AB} into components—$E_{AB}^{(1)}$, $E_{AB}^{(2)}$, and $E_{AB}^{(3)}$—enables us to understand why the extended Hückel method often gives reasonable conformational energies and barriers to internal rotation, while being completely unsuitable for calculating the geometry and the force constants of polyatomic molecules. Since the effective Hamiltonian of this method contains only terms proportional to $S_{\mu\nu}$, while ionisation potentials are used as diagonal elements, only the components E_A and $E_{AB}^{(1)}$ are taken into consideration, the remaining components being absorbed in empirical parameters. But the equilibrium geometry of the molecule is determined from the condition that the derivatives $\partial E/\partial x_i$ should vanish, where the x_i are independent geometric parameters, while the force constants $K_{ij} = \partial^2 E/\partial x_i \partial x_j$ are second derivatives. The contribution of electrostatic interaction $E_{AB}^{(3)}$ to these derivatives is, however, quite large, as estimates by Fisher and Kollmar[105] have shown. In many cases, therefore, calculation of molecular geometry and force constants by the extended Hückel method does not lead to the end in view.

The CNDO method, because of the presence of a large number of empirical parameters, is extremely flexible, and with appropriate choice of parameters may give good agreement with experiment. In fact, several successful attempts have been made to vary the parametrisation[106-117], especially in calculations of the geometry and the atomisation energies of hydrocarbons.

Table 5. Pople–Segal and Wiberg parameters for CNDO method.

Orbital	Core charge	Slater exponent	Ionisation potential, eV		β^0	
			P-S	W	P-S	W
1s H	1	1.2	7.1761	7.176	9	10.0
2s C	4	1.625	14.051	10.3	21	17.5
2p C		1.625	5.572	6.3		

Too profound significance should not be attached to calculations of energies of atomisation, of course, since correlation corrections amount numerically to an average 20% of the total energy. The LCAO-MO method in Roothaan's approximation does not predict the existence of the F_2 molecule at all[118], contrary to experimental results; in most cases, however, the existence of the equilibrium conformation is correctly predicted, but the calculated bond energies differ greatly from the true values. The same must be expected for the CNDO method, since it is a simplification of the Hartree–Fock model.

For certain homologous series, in particular for hydrocarbons, however, effective parameters can be so chosen that the calculated atomisation energies agree quite well with the experimental values.

Wiberg showed[117] that results calculated by the CNDO method are very sensitive to the proportionality constants β^0 and the mean ionisation potentials of the orbitals. Table 5 compares Pople and Segal's parameters with those of Wiberg. The slight difference in the constants β^0 for carbon atoms (17.5 instead of 21) permits considerable improvement in predicting molecular geometry. In fact, Table 6 shows that the calculations give bond lengths accurate to about 0.02–0.03 Å, and valency angles to 1–2°.

Table 6. Geometry of hydrocarbon molecules calculated by CNDO/2 method with Wiberg's parameters.

Molecule	Bond	Bond length, A		Angle	Angle, degrees	
		calc.	expt.		calc.	expt.
Methane	C—H	1.124	1.085			
Ethane	C—H	1.128	1.096	HCC	111.5	110.5
	C—C	1.506	1.531			
Propane	C—C	1.513	1.526	CCC	113.3	112.4
				HCH	105.6	106.1
Ethylene	C—H	1.120	1.076	CCH	123.3	122.2
	C=C	1.356	1.330			
Benzene	C...C	1.423	1.397			
Acetylene	C—H	1.103	1.061			
	C≡C	1.239	1.203			
Allene	C—H	1.120	1.082	CCH	122.8	120.2
	C=C	1.342	1.312			121.5

Table 7. Comparison between experiment and atomisation energies calculated by CNDO method (all energies in kcal mole^{-1}).

Molecule	$-\Delta E_{at}$, calc.	Zero-point vibrations	$-\Delta H_{at}$, expt.	$-\Delta E_{at}$, expt.*
Methane	419.61	27.11	392.86	419.97
Ethane	713.60	45.18	667.02	712.20
Propane	1006.91	62.46	943.61	1006.07
Butane	1298.62	79.77	1221.43	1301.20
Ethylene	563.14	30.70	532.74	563.44
Benzene	1373.14	62.84	1308.06	1370.90
Allene	710.44	33.23	672.95	706.18
Acetylene	416.33	16.18	389.69	406.50

*Allowing for zero-point vibrations.

Varying the mean ionisation potentials of the orbitals (Table 5) enables quite satisfactory agreement to be attained between calculated and experimental atomisation energies. It is noteworthy that comparison with experiment is based not on the enthalpies (as is mostly done) but on the atomisation energies: i.e. the zero-point vibrational energies of the atoms (Table 7, column 3) are added to the experimental enthalpies with their sign reversed. In order to obtain agreement with experiment (column 5), however, the calculated atomisation energies ΔE_{at} were treated by the method of least squares, to give the relation

$$-\Delta E_{at}(\text{kcal mole}^{-1}) = 218.01[-\Delta E_{at}(\text{a.u.})] + 35.28. \quad (58)$$

The right-hand side of this equation contains atomisation energies found by the CNDO method in atomic units, and the left-hand side the atomisation energies that are to be compared with the experimental values. Equation (58) is clearly not simply a conversion from one type of unit to another. It is a purely empirical relation, which governs the predictive value of the CNDO method with appropriate parametrisation.

As in any semi-empirical method, successful choice of parameters in the CNDO method permits the prediction of many—but by no means all—properties of molecules. Thus Wiberg's parametrisation gives strongly underestimated barriers to internal rotation: the calculated barrier in ethane is only 0.7 kcal mole^{-1}. While yielding good agreement with experiment for atomisation energies, this parametrisation does not give reliable values for the energies of individual bonds, and therefore has recently been re-examined by Ehrenson and Seltzer[119].

As already mentioned, Pople and Segal's original parametrisation, while not leading to agreement with experiment for molecular geometry and atomisation energies, nevertheless indicates the changes in barriers to internal rotation occurring on passing from one molecule to another, although the calculated numerical values are usually considerably lower than the experimental values. In cases in which the barriers in π-electron systems are due mainly to repulsion of non-bonded atoms, however, the CNDO method does not give results agreeing with experiment. Thus a calculation for biphenyl showed[120] that the total energy does not pass through a minimum as a function of the dihedral angle between the phenyl rings, although such a curve should have a minimum at $\sim 40°$. The CNDO method also gives incorrect relations between total energy and equilibrium angle of deflection of the phenyl rings[121] for *cis*- and *trans*-stilbenes: they do not agree with the curves obtained from empirical potential functions and do not lead to equilibrium structures comparable with the results of X-ray diffraction; the calculated barrier to the *cis–trans* isomerisation of stilbene is too high—129 instead of the experimental 43 kcal mole^{-1}.

The above examples of the application of the CNDO method force us to treat the calculated results with caution, especially in the case of energy differences. An attempt to predict the mechanism of the *cis–trans* isomerisation of the difluorodi-imide molecule[122] is interesting in this connection. Both forms (Fig. 2) are stable at room temperature, and their structures have been established by detailed investigations[123,124]. Calculations by the CNDO method showed that they actually corresponded to energy minima, with the *cis*- more stable than the *trans*-form by 4.5 kcal mole^{-1} (the experimental energy difference is 3.0 kcal mole^{-1}). The geometry corresponding to the energy minima is not entirely consistent with experiment: the N=N bond length coincides with the experimental value, but the N–F bond is 0.15 Å shorter (calculated and experimental values 1.26 and 1.41 Å); the calculated valency angles differ from the experimental by 2–3°.

Two routes are obviously possible for *cis–trans* isomerisation in this compound: (i) an N–F bond may "bend back", when the transition state will correspond to a configuration in which the two nitrogen atoms and one fluorine atom lie on a straight line (Fig. 2); (ii) rotation about the N=N bond will give a transition state in which the two F–N=N planes are mutually perpendicular. Calculation gives saddle-point energies respectively of 75 and $\sim$ 80 kcal mole^{-1} for the two paths. However, the experimental kinetic equation[125] is $k = 10^{14} \exp[-32.2\ (\text{kcal})/RT]\ \text{s}^{-1}$. Thus the CNDO method gives an activation energy that is inconsistent with experiment. Since the calculated energies of the transition states were almost identical, however, no preference could be made for either mechanism in this example.

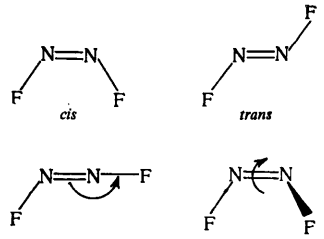


Figure 2. Stable and transitional forms of the difluorodiimide molecule.

The CNDO method bred a whole family of conceptually closely similar semi-empirical methods. Among them may be mentioned the neglect of diatomic differential overlap (NDDO) and partial (intermediate) neglect of differential overlap (INDO). The NDDO method, suggested long ago by Pople et al.,[31] neglects diatomic differential overlap while retaining integrals with the products $\varphi_\mu\varphi_\nu$ for different orbitals on the same atom. The INDO method[33] retains all one-centrel exchange integrals, while neglecting the remaining two-electron integrals. Finally, mention must be made of a few methods "terminating in differential overlap" and occupying a position intermediate between CNDO, NDDO, and INDO[97,98,126–136].

Among all the methods of zero differential overlap, NDDO is the closest approximation to the Roothaan equations[31,137]. The serious defects of NDDO must include the difficulty of parametrisation and the long computer time required. In a detailed examination of the possibilities of this method[101] the parameters β^0 were chosen to give agreement between calculated and experimental bond lengths and valency angles in hydrocarbons. This yielded a geometry agreeing satisfactorily with experiment: deviations in carbon–carbon bond lengths were on the average 0.01 Å and in carbon–hydrogen bond lengths 0.04 Å. But the barriers to internal rotation calculated with the same parameters were unsatisfactory: whereas the CNDO method underestimated all barriers, but gave the correct trend for variations from molecule to molecule, even the trend becomes blurred in the NDDO method. Energies of isomerisation (isobutene → *trans*-but-2-ene → *cis*-but-2-ene; isobutane → n-butane) disagree with experiment even in sign. Thus the introduction of additional integrals into the CNDO method not only does not improve but rather impairs the agreement with experiment. However, such a situation is typical of many semi-empirical methods, and was encountered repeatedly during the period of flowering of π-electron approximations.

The INDO method also does not improve (but does not worsen) the agreement with experiment. Table 8 gives bond lengths and valency angles calculated by this method[138] for several molecules. Comparison with Table 3 shows that, for ethane, methanol, hydrogen peroxide, and dioxygen difluoride, use of a more rigorous approximation has

hardly any effect on the molecular geometry. The impression is produced that optimisation of the parameters of a method is more effective for predicting geometry than are further complications of the theory.

Table 8. Geometry of molecules calculated by INDO method.

Molecule	Bond	Bond length, Å		Angle	Angle, degrees	
		calc.	expt.		calc.	expt.
NH_3	N—H	1.07	1.02	HNH	106.4	109.1
NF_3	N—F	1.25	1.37	FNF	104.4	102.2
CH_4	C—H	1.12	1.09			
CF_4	C—F	1.34	1.32			
H_3COH	C—O	1.37	1.43	COH	107.3	105.9
	C—H	1.12	1.09	HCH	108.2	109.5
	O—H	1.04	0.94			
$H_3C—CH_3$	C—C	1.46	1.53			
	C—H	1.12	1.10	HCH	106.6	107.8
$F_3C—CF_3$	C—F	1.35	1.33	FCF	106.1	108.0
	C—C	1.45	1.51			
HO—OH	O—O	1.22	1.47	HOO	108.8	94.8
	O—H	1.04	0.95	∠φ	83.5	111.5
FO—OF	O—O	1.23	1.22	FOO	108.4	109.5
	O—F	1.19	1.57	∠φ	85.8	87.5

Table 9. Comparison between experiment and energies of formation ΔHform (at 298°K) of cyclic hydrocarbons calculated by MINDO/1 method[129].

Molecule	Heat of formation		Molecule	Heat of formation	
	MINDO/1	expt.		MINDO/1	expt.
Cyclopropane	16.36	12.72	Bicyclo-butane	52.29	51.9
Cyclobutane	11.34	6.35	Cyclopentene	8.11	7.73
Cyclopentane	−19.23	−18.46	Cyclopentadiene	30.16	32.44
Cubane	116.88	148.70			

Special consideration must be given to the MINDO (modified INDO) method proposed by Dewar and his coworkers[129-131]. The main idea of MINDO/1 consisted in selecting empirical parameters designed to reproduce experimental heats of formation of organic molecules from the atoms. This involved the parametrisation of many integrals. Since, however, computer time is mainly devoted to evaluating quantum-mechanical integrals, the MINDO method enabled the duration of the calculation to be shortened by more than 90% in comparison with CNDO. In the MINDO/2 variant[131] the parameters were chosen to obtain agreement with experiment not only for energies of formation but also for the molecular geometry. As a result, the accuracy with which heats of formation could be predicted for most organic molecules became about ±2–3 kcal mole^{-1}, and the accuracy of calculating bond lengths and valency angles ±0.01 Å and ±2–3° respectively. Because of its great accuracy the MINDO method is widely employed[139-144] for calculating geometry, barriers to rotation around bonds, and thermochemical properties of organic molecules, as well as for investigating the paths of organic reactions.

Table 9 lists heats of formation calculated for several cyclic and polycyclic hydrocarbons (by the MINDO/1 variant, which for thermochemical properties gives better agreement with experiment than does MINDO/2). These results show about the same agreement with experiment as in calculations using the interatomic potential model[13,145,146]. This is not surprising, however, for in the MINDO method quantum mechanics has already been brought down almost to the level of empirical models: the parameters of the method are very far from reproducing non-empirical calculations (and this was the idea of parametrisation in the CNDO method); on the other hand, they are very valuable for the chemist who wishes to predict with great accuracy the structures and the properties of complicated organic systems.

VI. APPLICATION OF LOCALISED ORBITALS IN SEMI-EMPIRICAL CALCULATIONS

Hitherto we have been examining methods based on delocalised molecular orbitals, each of which is a linear combination of atomic orbitals. It was precisely from them that the Slater determinant (6) was constructed. However, such a determinant can be constructed also on the basis of localised molecular orbitals, in particular those of valency bonds, representing the stereochemical character of the molecule. If functions set up from hybrid atomic orbitals (of types sp^3, sp^2, and sp) are chosen as these localised molecular orbitals, and the coefficients representing the hybrid state are fixed, there is no need to use the Hartree–Fock equations and hence a self-consistency procedure. Such a mode of action is not very good with a non-empirical approach, of course, for the resulting accuracy is too low. In calculations *ab initio*, therefore, the coefficients of hybrid orbitals are optimised by a variational method. Molecular orbitals of methane, for example, can be sought in the form[147]

$$i = A(i_1 + \lambda i_2) \qquad (59)$$

where i_1 is the hybrid tetrahedral orbital of carbon directed towards one of the hydrogen atoms, i_2 is a 1s orbital centred on the same hydrogen atom, and A is a normalising factor. The parameter λ can be optimised with respect either to the length of the carbon–hydrogen bond (to make the calculation coincide with experiment) or to some other property.

In semi-empirical methods, however, whose accuracy depends significantly on the parametrisation, it hardly makes sense to proceed in this way: the use of pure hybrid orbitals seems more promising, and then the total energy can be calculated without the need for variational procedures, resulting in a considerable saving of time in comparison with self-consistent methods of the zero differential overlap type.

The principal disadvantage of localised orbitals is that the wave function based on them differs significantly from that of the self-consistent field, while the total energy is far from the Hartree–Fock limit. However, by the use of localised orbitals together with a method of "interaction" of configurations, we can go far beyond the scope of the Hartree–Fock approximation and obtain a considerable proportion of the correlation energy due to "instantaneous" interactions of the electrons[148,149]. This represents a considerable advantage of localised molecular orbitals over delocalised LCAO-MO orbitals.

French workers[150] have used perturbation theory to develop a technique for computing the total energy of a molecule. The Slater determinant, constructed from bonding orbitals completely localised on the bonds, is regarded as a wave function of zero order. Antibonding

orbitals are used to construct wave functions of excited states, and a matrix of configurational "interactions" is based on such functions (configurations). The theory of perturbations is then used to find the energy and the eigenfunction of the ground state.

We shall consider in greater detail the above procedure for systems having closed electron shells (even number N of electrons). Let i and i^* be the bonding and the antibonding orbital corresponding to the ith bond, which can be represented by a linear combination of the hybrid orbitals i_1 and i_2:

$$i = \alpha i_1 + \beta i_2, \tag{60}$$

$$i^* = \beta' i_1 - \alpha' i_2. \tag{61}$$

We assume the localised molecular orbitals (60) and (61) to be known (they can be found, for example, from Hartree–Fock calculations of small molecules). The zero-order wave function can then be written as a Slater determinant:

$$\Psi_0 = (1/2n!)^{1/2} |1\bar{1} \ldots i\bar{i} \ldots n\bar{n}|, \tag{62}$$

which coincides with (6) as $n = \frac{1}{2}N$. The energy of this wave function is calculated as the average value of the Hamiltonian H.

We now consider singly excited configurations, by promoting one electron from the orbital i to the antibonding orbital j^*, and also doubly excited configurations, by promoting electrons from orbitals i and k to antibonding orbitals j^* and l^*:

$$\Psi(\bar{j}_i^*) = (1/\sqrt{2n!})^{1/2} |11 \ldots i\bar{j}^* \ldots n\bar{n}|, \tag{63}$$

$$\Psi\left(\frac{\bar{j}^*\bar{l}^*}{ik}\right) = (1/\sqrt{2n!})^{1/2} |1\bar{1} \ldots i\bar{j}^* \ldots k\bar{l}^* \ldots n\bar{n}|. \tag{64}$$

Using the methods of perturbation theory, it was shown[150] that the approximate wave function Ψ and the energy E are given by the formulae

$$\Psi \cong \Psi_0 + \sum_{i,j^*} \frac{\langle \Psi_0 | H | \Psi_0 \left(\frac{j^*}{i}\right) \rangle}{E_0 - E(j_i^*)} \Psi(j_i^*) + \sum_{i,k,j^*,l^*} \frac{\langle \Psi_0 | H | \Psi \left(\frac{j^*l^*}{ik}\right) \rangle}{E_0 - E\left(\frac{j^*l^*}{ik}\right)} \Psi\left(\frac{j^*l^*}{ik}\right) \tag{65}$$

$$E \cong \langle \Psi_0 | H | \Psi_0 \rangle + \sum_{i,j^*} \frac{\langle \Psi_0 | H | \Psi_0 \left(\frac{j^*}{i}\right) \rangle^2}{E_0 - E\left(\frac{j^*}{i}\right)} + \sum_{i,k,j^*,l^*} \frac{\langle \Psi_0 | H | \Psi \left(\frac{j^*l^*}{ik}\right) \rangle}{E_0 - E\left(\frac{j^*l^*}{ik}\right)}, \tag{66}$$

where it is a simple matter to calculate $E(j^*/i)$ and $E(j^*l^*/ik)$. If the approximation of zero differential overlap is now applied, i.e. if n^4 integrals of type $(ij|j^*i^*)$ present in formulae (65) and (66) are equated to zero, it only remains to evaluate n^2 integrals of type $(ij|i^*j^*)$. But the main gain in time of calculation is due to the absence of a self-consistency procedure.

The above method has been termed perturbative configuration interaction using localised orbitals (PCILO). In practical application, this method is usually confined to a minimal basis-set of localised bond orbitals. Thus four bonding and four antibonding carbon–hydrogen orbitals are considered for ethylene, together with σ- and π-orbitals of the C=C bond. Not only valency orbitals but also 1s orbitals of the inner shells are included. Since the number of integrals is large, although considerably smaller than in methods of configurational interactions based on Hartree–Fock LCAO-MO, the method is usually restricted to zero differential overlap by the use of CNDO/2 parametrisation.

The great merit of the PCILO method with CNDO parametrisation is the comparatively short time of computation: the total energy of a molecule, allowing for a considerable proportion of correlation energy, is calculated on an electronic computer in roughly the time required to calculate empirical potential functions or total energy in the extended Hückel method. This makes PCILO suitable for solving relatively complicated conformational problems. Pullman and his coworkers have employed the PCILO method to construct conformational maps of dipeptides[151–156], to investigate the conformations of conjugated systems playing an important part in the mechanism of visual stimulation[157,158], to calculate the relative energies of steroid systems[159], and to make conformational analyses of disaccharides[160].

Although the PCILO method is in principle more accurate than the Hartree–Fock LCAO-MO method, it is still difficult to state whether it yields more reliable calculated geometric parameters and conformational energies. Even with restricted basis-sets Hartree–Fock calculations *ab initio* lead to an entirely reasonable geometry and reasonable barriers to internal rotation[161,162]. Hence correlation need not in general be taken into account. But it is not excluded that the introduction of correlation corrections into CNDO/2 may lead to an improvement of this semi-empirical method.

Certain results of calculations of simple molecules may give an idea of the possibilities of the PCILO method. Barriers to internal rotation calculated[151] for formamide, acetamide, *N*-methylformamide, and *N*-methylacetamide, respectively 20.8, 14.3, 13.1, and 12.8 kcal mole^{-1}, were close to the experimental values: for formamide, in particular, the experimental values lay in the range 16.8–21.9 kcal mole^{-1}[163–165], and those calculated *ab initio* in the range 19.4–24.7 kcal mole^{-1}[166,167]. In this case the PCILO method based on CNDO/2 parametrisation will give the correct height of the barrier (20.8 kcal mole^{-1}), whereas use of the CNDO/2 method in its original form usually underestimates the barriers.

Calculation of conformational energies for such classical systems as cyclohexane, cyclopentane, and decalin has given interesting results[159] (all values in kcal mole^{-1}): in cyclohexane the boat is less stable than the chair by 5.8 (the experimental energy difference is ~ 6); in cyclopentane the half-chair is more stable than the envelope by 0.7 (this result is not entirely satisfactory, as pseudorotation occurs in cyclopentane almost without hindrance[81]); and *trans*-decalin is more stable than the *cis*-isomer by 2.0 (experimental energy of isomerisation 2.7[168]). Further, calculated values[169] of the barrier to internal rotation in propene are 1.31 with second-order perturbation and 1.22 with third-order perturbation (experimental value 1.98[100]). In methylketen $CH_3.CH:C:O$ the calculated barrier to rotation of the methyl group is 1.54 and 1.31 with second- and third-order perturbation respectively (experiment gives 1.18[100]).

Langlet and van der Meer compared the results obtained by calculating the geometry of ethylene, propene, keten, and methylketen by the extended Hückel[170] and PCILO[169] methods. All calculations were made with fixed bond lengths taken from experiment; the ultimate aim was to find valency angles satisfying minimum total energy (such a procedure is not entirely systematic, of course: in principle a minimum should properly be sought with respect to all parameters). Neither method gave satisfactory results. For the H–C=C angle in methylketen, in particular, the extended Hückel method gives a value of 121.4°, and PCILO yields 119.2° and 117.3° with second- and

third-order perturbation respectively. These three values exceed considerably the experimental angle of 113.7°.[171]

Althqugh the PCILO method has been tested only on a small number of simple molecules, it has become clear that, like any semi-empirical method, it may suffer from the imperfections of parametrisation. The rôle of correlation corrections in the PCILO–CNDO/2 scheme has not yet been finally elucidated, and therefore it is at present difficult to know whether the PCILO method is to be preferred to the classical form of CNDO/2. Nevertheless, in contrast to the latter, the PCILO method makes it possible to calculate in a comparatively short time the relative energies of a multitude of conformations of extremely complicated molecules such as dipeptides and disaccharides. This is the chief merit of the new method.

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Summing up, we can state that the semi-empirical methods examined in this Review—extended Hückel method, CNDO, MINDO, PCILO, and certain others—are undoubtedly useful for comparative estimates of the properties of polyatomic molecules. However, the results obtainable by semi-empirical methods depend on the parametrisation adopted, and therefore are not always reliable. In this sense calculations *ab initio* have an undoubted advantage.

But it must not be thought that non-empirical calculations will be able in the forseeable future to replace semi-empirical methods of quantum chemistry completely. Organic molecules of interest to chemists are usually too large for their geometry and conformational energies to be estimated by evaluating all the quantum-mechanical integrals. It is also difficult to envisage the possibility of minimising the Hartree–Fock functional with respect to independent geometric parameters: for molecules of moderate size such a procedure would require an unreasonably long computer time. Yet problems of seeking the equilibrium geometry and calculating conformational energies are easily solved by empirical and semi-empirical methods. This is why such methods, it must be assumed, will acquire still greater popularity among wide circles of chemists.

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