

Model Description of Some Molecular Properties by the Modified-Atom-in-Molecule (MAM) Approach

Zvonimir B. Maksić^{a*}, Mirjana Eckert-Maksić^b, and Krešimir Rupnik^a

^aTheoretical Chemistry Group and ^bDepartment of Organic Chemistry and Biochemistry, The »Ruđer Bošković« Institute, 41001 Zagreb, Yugoslavia

Received February 18, 1985

Conclusive evidence is presented which shows that the concept of modified atoms in molecule (MAM) is a viable model for a good description of numerous molecular properties. Atomic modification can be decomposed to isotropic and anisotropic components. The isotropic change caused by molecular formation is given by the electric monopoles of atoms. It is a consequence of the charge drift accompanying chemical bonding. Atomic monopoles reproduce diamagnetic shielding of the nuclei σ_A^d , diamagnetic susceptibility χ^d and ESCA shifts with an intriguing success. The atomic monopole model is easily extended to include higher local multipoles (*i. e.* anisotropic contribution), thus yielding satisfactory total molecular multipoles and extramolecular electrostatic potentials. Salient directional properties of covalent bonds are well described by the use of polarized atomic orbitals. It was shown that hybridization is the underlying concept which explains interrelations between steric features and local bond properties. Hybridization rationalizes in a natural and simple way the electron pair (Lewis) bond which is one of the corner stones of chemistry being particularly important for the first row atoms. It was concluded that the high information content of hybrid AOs can be ascribed to the fact that they conform to the local symmetry of the immediate molecular environment. Thus the HAOs are local wavefunctions of the zeroth order which describe atomic angular distortions. Although atoms can not be uniquely defined within molecules, the MAM model has high interpretative power yielding reasonable results. Special attention deserves a picture of charged atoms immersed in the »sea« of mixed electron density, because it is free of any arbitrariness in the slicing of molecular volume of partitioning of overlap charge. Finally, the definition of pseudo-observables is given. It was concluded that atomic monopoles and hybridization indices are pseudo-observables *par excellence*.

Apparently there is colour, apparently sweetness, apparently bitterness; actually there are only atoms and the void.

Democritus, 420 B. C.

INTRODUCTION

A complete description of the molecular systems is given by the exact wave function Ψ . Rigorous quantum chemistry provides today results of high

* Also at the Faculty of Sciences and Mathematics, The University of Zagreb, Marulićev trg 19, 41001 Zagreb, Yugoslavia.

accuracy on small molecules, which in turn are severe tests of the quantum mechanics itself. Precision of the contemporary *ab initio* computational methods is in many cases competitive with the experimental data for a number of molecular observables.¹⁻³ Accurate *ab initio* predictions are invaluable for systems not easily accessible to experiment, adding theoretical pieces of information to the mosaic called the properties of matter. Hence, the *ab initio* calculations can be used *ex aequo* with experimental techniques for small molecules and, in fact, they help to overcome limitations of particular experimental methods, *e.g.*, in the determination of molecular geometries.⁴ There are, however, two drawbacks in the *ab initio* approach. The large molecules of chemical interest will still remain beyond its reach even with the next generation of computers. Secondly, the rigorous wavefunctions are so sophisticated that it is difficult to interpret them immediately in simple terms. This applies particularly to the brute force *ab initio* methods. Hence, additional work is needed to recognize and understand the most important features of the studied phenomena. Furthermore, in chemistry one is frequently interested in trends of changes of some properties over a series of related molecules. This is usually prohibitively laborious by the computations from the first principles. Simple and physically well founded models are better suited for this purpose. Their value lies more in the capability to identify the dominant effect(s) than in their ability to accurately reproduce certain physical and chemical quantities. Indeed, a model does not yield a true picture because its object is distorted by simplifications. This is, however, its strength because the model greatly gains in simplicity and conceptual clarity. The well known physicist Ya. I. Frenkel put it succinctly by saying that a good model is a good caricature. It deliberately neglects the less relevant details and emphasizes the most important features. Additionally, by stressing the role of sometimes subtle details, a model can rationalize the variation of some property within the family of compounds, if other contributions, whatever large, remain constant. It turns out that carefully chosen and empirically adjusted models can give not only a qualitative understanding but also semiquantitative estimates of observable entities, as we shall see later. It should be stressed, however, that recognition of the dominant effect(s) and appropriate parametrization is a very delicate problem. An excellent review article on theoretical models used in chemistry was provided by Trindle.⁵

In the present paper we shall discuss the physico-chemical properties of complex molecules by simple models, instead of treating simple systems with complicated methods. A large body of experimental and accurate *ab initio* data will be analyzed and interpreted in a transparent way. Conclusive evidence will be presented which shows that some molecular properties can be well accounted for by conceptually simple models, which in turn have a surprisingly good performance. The underlying pattern of thoughts used in the modelling of the considered properties is close to chemical experience. Chemists have always had the idea that atoms retain their identity within a molecule and that molecular properties could be interpreted in terms of the constituent atoms and their bonds. In other words, a molecule has a memory and knows which atoms are used as building blocks. There are many hints which indicate that a molecule can be reasonably well described by

modified atoms and their interactions. For example, a sum of bond energies is by two orders of magnitude smaller than the total energy of a molecule. Recent X-ray measurements show that deformation density is a very small fraction of the total electron charge distribution in a molecule.⁶ Many global properties can be decomposed to atomic contributions *etc.* Therefore, a picture of distorted atoms in molecules should hold for many purposes. This conjecture is supported by the results of our extensive calculations (*vide infra*). The idea of deformed atoms in molecular systems was theoretically put forward first by Moffitt⁷, modified by Balint-Kurti and Karplus⁸ and discussed recently by Parr⁹ within the local functional theory¹⁰. Strictly speaking, it is impossible to define an atom quantum mechanically in a unique way once it has entered a molecule. The same applies to the notion of the chemical bond, and yet the latter is a well established empirical concept which provides the strongest pillar of the chemical phenomenology. Although the atoms and their bonds can not be unambiguously designed from the first principles, there must be a sensible way of identifying them in molecular environments. An interesting attempt was made by Bader¹¹ by introducing the so called topological atom encompassed by a zero-flux surface. A definition of chemical bonding in terms of properties of the total electron density $\rho(\mathbf{r})$ and local energy density was recently suggested and thoroughly discussed by Cremer and Kraka¹².

Our approach is less rigorous, being at the same time closer to traditional chemical thinking. A molecule will be considered first as an ensemble of spherically symmetric atoms. Particular emphasis will be put on the promolecule model where neutral and spherical atoms are placed at the equilibrium positions supposing that all mutual interactions equal zero. In other words, all bonding effects are neglected. It is surprising how close this apparent idealization reproduces some diamagnetic properties. A charge migration will be allowed next as one of the basic facets of chemical bonding while spherical symmetry of atoms will be still retained. This model explains in the simple monopole (formal atomic charge) form the diamagnetic shielding of nuclei, diamagnetic part of molecular susceptibility, potentials at the nuclei and ESCA chemical shifts with intriguing success. Attention will be focused in particular on alkali halides where intramolecular charge transfer is pronounced. A quite different point of view will be taken when considering hydrocarbons and silanes. Charge migration can be abandoned to the first approximation. However, the redistribution of charge around carbon and silicon atoms, caused by a descent of symmetry determined by the nearest neighbours, is of pivotal importance here. Asymmetry of the atomic charge will be described by local hybrid orbitals which offer a simple interpretation of preferential bonding directions in space. It will turn out that hybridization is very helpful not only in comprehending molecular shapes and sizes but contributes also to the rationalization of a number of properties which can be ascribed to chemical bonds, to mention only bond energies, heats of formation ΔH_f , strain energy in angularly deformed molecules, spin-spin coupling constants *etc.* Finally, the use of hybrid AOs in more sophisticated calculations in molecules and solids will be briefly discussed.

Simplicitas veri forma est.
Cato, 234 B. C.

I. ISOTROPIC ATOMIC DENSITIES. DESCRIPTION OF MOLECULAR
PROPERTIES BY ELECTRIC MONOPOLES

Apportioning of the total electron density $\rho(\mathbf{r})$ to atomic contributions is not unique, due to the presence of the mixed (interatomic) charge. Since any breakdown of $\rho(\mathbf{r})$ to atomic terms is arbitrary, it is condemned by quantum purists. This attitude is, however, not very fruitful. In spite of the fact that there is an infinite number of ways of partitioning the total charge into atomic components, it is intuitively clear that one of them will give the most reasonable description of the properties which are atomic in nature. We shall adopt this optimistic point of view and assume that there is a *bona fide* partitioning which provides sensible atomic charges in molecules. For practical purposes we shall employ the simplest population analysis advocated by Mulliken¹³, which divides the mixed charge on the 50%/0—50%/0 basis. It allows the definition of the formal atomic charge or atomic monopole. One can say *a posteriori* that this composition is usually quite satisfactory, being at the same time very democratic. Other approaches involve, e. g., the »stockholder« principle of Hirshfeld or spatial division of the molecular volume to atomic domains.^{11,14,15} Subsequent integration of the total density $\rho(\mathbf{r})$ encompassed by atomic surfaces yields higher atomic multipoles in addition to monopoles. Since the diamagnetic properties, like σ^d and χ^d , as well as ESCA shifts, are very well reproduced by atomic monopoles, the Mulliken population analysis will suffice.

I.1. Diamagnetic Susceptibility of Molecules

The temperature independent part of the magnetic susceptibility has two contributions

$$\chi_{aa} = \chi_{aa}^d + \chi_{aa}^p \quad (1)$$

The first term gives the so called Langevin's diamagnetism, whilst the second is the Van Vleck's high frequency paramagnetic term. We shall restrict our attention to the former, which is the first order one-electron property. As shown by Van Vleck¹⁶

$$\chi_{aa}^d = K [\langle b^2 \rangle_e + \langle c^2 \rangle_e] \quad (2)$$

where a , b , and c stand for the inertial coordinates. The abbreviation K denotes $K = Ne^2/4mc^2$ where constants have their usual physical meaning. It appears that the diagonal elements of the diamagnetic susceptibility tensor are given by the corresponding second moments of the electronic charge distribution. The latter usually refer to the center of mass of a molecule since they are experimentally deduced mostly by the Zeeman effect on rotational spectra.¹⁷ Within the one-electron MO-LCAO picture, the second moment is easily decomposed into three contributions

$$\begin{aligned} \langle r_\alpha^2 \rangle = & \sum_A \sum_\mu P_{\mu\mu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\mu \rangle + 2 \sum_{\mu < \nu}^A \sum_A P_{\mu\nu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\nu \rangle + \\ & + 2 \sum_A \sum_B \sum_\mu \sum_\nu P_{\mu\nu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\nu \rangle \end{aligned} \quad (3)$$

where $\alpha = a, b$ and c and r_α is the corresponding component of the position vector \mathbf{r} . The integrals appearing in the expression (3) involve, in general, several centers. However, a series of consecutive coordinate translations $r_\alpha = r_{A\alpha} + r_{A\alpha}(i)$ brings the formula (3) to a one-center form:

$$\langle r_\alpha^2 \rangle \cong \sum_A [Q_A r_{A\alpha}^2 + \sum_\mu^A Q_\mu \langle \Phi_\mu(i) | r_{A\alpha}^2(i) | \Phi_\mu(i) \rangle] \quad (4)$$

Here $r_{A\alpha}$ and $r_{A\alpha}(i)$ denote the α -th coordinate of nucleus A from the center of mass and the corresponding coordinate of the i -th electron relative to the host nucleus A, respectively. The total number of electrons apportioned to atom A is given by Q_A , whilst the orbital population is designated by Q_μ . It was tacitly assumed that the Mulliken approximation $\Phi_\mu \Phi_\nu = (1/2) S_{\mu\nu} (\Phi_\mu^2 + \Phi_\nu^2)$ for two-center mixed densities holds to a good approximation. Hence, the second moment is essentially given by the two contributions (4). The first term represents the point-charge or monopole approximation. The second term is a correction of the first and arises from the spatial extension of the AOs. Needless to say, the monopole term is a dominating contribution due to the squares of the atomic coordinates. Careful examination has shown that the spatial term is roughly isotropic and constant for each atom belonging to the same row of the periodic system of elements.¹⁸⁻²⁰ Thus, the approximate formula (4) takes a succinct form:

$$\langle r_\alpha^2 \rangle \cong \sum_A Q_A r_{A\alpha}^2 + \sum_p n_p k_p \quad (5)$$

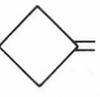
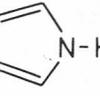
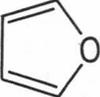
where sum over A is extended over all atoms, n_p is the number of atoms of the p -th row in a molecule and k_p is an adjustable parameter. However, Eq. (5) might be considered as a parameter-free formula because k_p empirical constants correspond very closely to the *ab initio* values for free atoms²¹ averaged over the p -th period of the Mendeleev system of elements. Hence, the second moments depend on the atomic charge densities and structural features (atomic coordinates) in a simple and transparent way. The underlying physical picture behind the formula (5) is that of spherical atoms placed at equilibrium distances. Their charge densities are modified by intramolecular charge drift toward more electronegative atoms. It should be mentioned that the second moments are not critically dependent on the charge redistribution unless atoms with widely different electronegativities are involved.^{20,22} The neutral atom or the so called *promolecule* approach suffices for most cases. Then the charge migration correction is disregarded and $Q_\alpha = Z_A$:

$$\langle r_\alpha^2 \rangle \cong \sum_A Z_A r_{A\alpha}^2 + \sum_p n_p k_p \quad (6)$$

Notice that the second moment of the electronic charge distribution is intrinsically a negative entity. The negative sign is dropped for simplicity. The promolecule (free-atom) treatment has a surprisingly good performance^{18,19}, being a typical pencil and paper approach once the geometry of a molecule is known. Some more examples are provided in Tables I and II. Table I presents the results obtained for some inorganic molecules (H_2S , SOF_2 and SO_2F_2) and several organic four and five membered rings involving heteroatoms. The structural parameters and definition of coordinate axes used in

TABLE I

Comparison of the Second Moments Estimated by the Promolecule Approach and the *ab Initio* Experimental Results^a

Molecule	Promolecule	<i>Ab initio</i>	Exptl.
CS	$\langle x^2 \rangle = \langle y^2 \rangle = 3.5$ $\langle z^2 \rangle = 13.8$	3.9 ^b 14.6	
H ₂ S	$\langle x^2 \rangle = 2.9$ $\langle y^2 \rangle = 4.8$ $\langle z^2 \rangle = 4.5$	3.5 ^b 4.4 4.4	
SOF ₂	$\langle x^2 \rangle = 13.2$ $\langle y^2 \rangle = 27.5$ $\langle z^2 \rangle = 29.2$	11.9 ^c 28.4 29.6	6.9 ^e 36.6 28.9
SO ₂ F ₂	$\langle x^2 \rangle = 31.1$ $\langle y^2 \rangle = 29.8$ $\langle z^2 \rangle = 31.0$	32.3 ^c 30.0 29.2	31.4 ^e 30.5 30.7
	$\langle x^2 \rangle = 10.0^f$ $\langle y^2 \rangle = 29.2$ $\langle z^2 \rangle = 27.3$	9.8 ^d 27.8 28.1	10.0 ^g 29.2 28.3
	$\langle x^2 \rangle = 12.2$ $\langle y^2 \rangle = 46.2$ $\langle z^2 \rangle = 35.0$	12.5 ^d 46.9 34.7	
	$\langle x^2 \rangle = 11.1$ $\langle y^2 \rangle = 33.1$ $\langle z^2 \rangle = 61.5$	10.8 ^d 33.0 63.2	10.8 ± 1.8 ^h 32.8 ± 1.8 63.2 ± 1.8
	$\langle x^2 \rangle = 7.8$ $\langle y^2 \rangle = 42.6$ $\langle z^2 \rangle = 42.5$	8.6 ^b 42.5 42.1	8.2 ± 2.2 ⁱ 42.3 ± 2.2 41.8 ± 2.2
	$\langle x^2 \rangle = 6.0$ $\langle y^2 \rangle = 39.7$ $\langle z^2 \rangle = 40.2$	7.2 ^b 39.2 39.2	7.4 ± 0.6 ^j 38.6 ± 0.6 39.1 ± 0.6
	$\langle x^2 \rangle = 5.8$ $\langle y^2 \rangle = 38.4$ $\langle z^2 \rangle = 35.8$	6.7 ^b 37.4 36.2	6.8 ± 0.7 ^k 37.8 ± 0.7 36.2 ± 0.7
	$\langle x^2 \rangle = 7.3$ $\langle y^2 \rangle = 41.7$ $\langle z^2 \rangle = 58.7$	8.4 ^b 41.2 58.7	8.5 ± 1.2 ^k 44.6 ± 1.2 58.6 ± 1.2
	$\langle x^2 \rangle = 10.9$ $\langle y^2 \rangle = 53.9$ $\langle z^2 \rangle = 63.7$	11.6 ^b 53.2 64.3	

^a In 10⁻¹⁶ cm². All values should be multiplied by -1; ^b Ref. 23; ^c Ref. 24; ^d Ref. 25; ^e Ref. 26; ^f For C₃H₆O the coordinates used by Flygare *et al.*²⁷ were employed (see text); ^g Ref. 27; ^h Ref. 28; ⁱ Ref. 29; ^j Ref. 30; ^k Ref. 31.

the promolecule calculations were those given in theoretical *ab initio* studies, C_3H_6O being an exception (*vide infra*). Perusal of the data presented in Table I shows that the promolecule point-charge model estimates are in good accordance with the measured values and *ab initio* results. It provides a quick albeit approximate test of the experimental data and/or numbers produced by more sophisticated methods. An illustrative example is given by SOF_2 . The experimental second moments²⁶ refer to inertial coordinates while the coordinate frame utilized in calculations is rotated by -57° around the z -axis. Hence, the $\langle z^2 \rangle$ values are comparable (notice, however, that de Brouckere *et al.*²⁴ cite a wrong experimental $\langle z^2 \rangle$ second moment) and in fact they are in good accordance. In order to check the measured values, we calculated $\langle a^2 \rangle$ and $\langle c^2 \rangle$ second moments in the inertial coordinate frame and obtained 9.7 and 30.9 (in 10^{-16} cm²), respectively. The results are in striking disagreement with the corresponding experimental data of 6.9 and 36.6×10^{-16} cm², which indicates that the measured values are erroneous. There are several possible sources of errors. We shall mention two of them. The individual second moments are extracted from Zeeman MW data employing the Pascal estimate of the bulk diamagnetic susceptibility.²⁶ Additionally, negative values of the diagonal elements of the molecular g -tensor were chosen. It would be interesting to reinterpret experimental data by using positive values. The promolecule estimates for $\langle x^2 \rangle$ and $\langle y^2 \rangle$ are in satisfactory agreement with the *ab initio* results obtained in the same coordinate system (Table I). Trimethyleneoxide (C_3H_6O) is another interesting case which illustrates a useful application of the promolecule model in detecting errors. By using the geometric parameters given in the paper of de Brouckere *et al.*²⁵ we found a good agreement with the *ab initio* results, but there was discrepancy with experiment²⁷ for the $\langle y^2 \rangle$ component. Careful examination revealed that the authors used somewhat different y -coordinates of the nuclei, leading to different second moments of atoms $Z_A Y_A^2$, although the same source of structural data was cited.³² It turned out that the coordinates used by Flygare *et al.*²⁷ for the assumed planar configuration of the heavy atoms were correct. Consequently, they were employed in our work and the $\langle y^2 \rangle$ second moment is in excellent agreement with experiment now. Similar simple analyses have led to detection of errors in the measured values of $FCICO$ and PF_3 ³⁰. Reinvestigation of the former molecule established a fair agreement between the experimental data and values offered by the promolecule model.³³ It should be mentioned in this connection that this model is a very helpful aid in determining the sign of the diagonal elements of the molecular g -tensor.³⁴

The intramolecular charge transfer can be estimated by the simple electronegativity arguments or by executing the quantum mechanical calculation accompanied by the subsequent partitioning of the total electron density to atomic portions. Our extensive investigations have shown that the semiempirical SCC-MO (self consistent charge) method⁴⁰ yields a number of one-electron properties which can be favourably compared with experimental data^{41,42} and *ab initio* DZ results.⁴³ The second moments produced by the SCC-MO calculations are compared with the measured or *ab initio* values in Table II. The semiempirical results were obtained by using the Mulliken population analysis and the atomic monopole (point-charge) approximation

TABLE II

Comparison of the Second Moments Obtained by the Point-Charge Model by Using SCC-MO Wavefunctions and *ab Initio* or Experimental Data^a

Molecule	Point-charge (SCC—MO)	<i>Ab initio</i> or Exptl.
ONOH (trans)	$\langle x^2 \rangle = 24.4$	24.3 ^b
	$\langle y^2 \rangle = 6.2$	5.9
	$\langle z^2 \rangle = 2.8$	2.7
ONOH (cis)	$\langle x^2 \rangle = 23.1$	22.9 ^b
	$\langle y^2 \rangle = 6.5$	6.3
	$\langle z^2 \rangle = 2.8$	2.7
HPPH (trans)	$\langle x^2 \rangle = 135.9$	(137.9) ^c
	$\langle y^2 \rangle = 32.4$	(33.6)
	$\langle z^2 \rangle = 19.3$	(21.2)
HPPH (cis)	$\langle x^2 \rangle = 137.6$	(139.4) ^c
	$\langle y^2 \rangle = 32.6$	(33.6)
	$\langle z^2 \rangle = 19.3$	(21.2)
$\begin{array}{c} \text{H} \\ \diagdown \\ \text{P}-\text{P} \text{ (singl.)} \\ \diagup \\ \text{H} \end{array}$	$\langle x^2 \rangle = 140.9$	(140.3) ^c
	$\langle y^2 \rangle = 27.6$	(30.3)
	$\langle z^2 \rangle = 19.3$	(20.9)
HFB ⁺	$\langle r^2 \rangle = 19.8$	18.5 ^d
HBF ⁺	$\langle r^2 \rangle = 14.3$	13.2 ^d
HBS	$\langle r^2 \rangle = 26.7$	27.6(27.2) ^e
ClBS	$\langle r^2 \rangle = 110.7$	112.9(111.8) ^e
HOBS	$\langle r^2 \rangle = 65.1$	64.4(63.7) ^e
H ₃ C—B≡S	$\langle r^2 \rangle = 82.9$	83.8(83.2) ^e
F—C≡P	$\langle r^2 \rangle = 60.9$	(61.2) ^f
H ₃ C—C≡P	$\langle r^2 \rangle = 75.3$	(75.9) ^f
HO—C≡P	$\langle r^2 \rangle = 63.7$	(63.9) ^f

^a In 10⁻⁶ cm². All the values should be multiplied by -1. The *ab initio* results refer to DZ basis set unless they are given within parentheses. The DZ+P basis was employed in the latter case.

^b Experimental data Ref. 35.

^c Ref. 36. ^d Ref. 37. ^e Ref. 38. ^f Ref. 39.

(formula (5)). A survey of the results shows that the monopole model very well discriminates the cis-trans isomers of ONOH and HPPH molecules. Further, the second moments of the unusual H₂P—P molecule are in relatively good agreement with *ab initio* computations, which were obtained by the DZ+P basis set and limited CI (configuration interaction). Unfortunately, the individual components for the rest of compounds are not available. Instead, only $\langle r^2 \rangle$ values are given. They are, however, also informative. The first cations treated so far by the monopole model are HFB⁺ and HBF⁺ isomers.

The $\langle r^2 \rangle$ values are well reproduced by the simple approach. The same conclusion holds for compounds possessing $B \equiv S$ and $C \equiv P$ fragments. It should be noted that the *ab initio* values are basis set dependent and that the second moments are smaller by $\sim 1 \times 10^{-16} \text{ cm}^2$ if the DZ set is augmented by the polarization function as exemplified by the $X-B \equiv S$ compounds ($X=H, Cl, OH, CH_3$).

Finally, the second moments of alkali halides deserve a brief comment. The promolecule and charge migration (estimated by electronegativities) models did not provide satisfactory results.²² It was necessary to assure the existence of the 100% ionic bond in these compounds to reproduce the *ab initio* results of Matcha.⁴⁴ Transfer of the valence electron from the alkali atoms to the halide ones gave a simple and pictorial rationalization of the puzzling *ab initio* finding that the second moments in NaF and KCl are practically independent of the placement of the origin of the coordinate system to alkali or halide atoms. This is however obvious by observing that by the electron transfer NaF and KCl assume the electron configurations of the hypothetical homopolar diatomic molecules Ne_2 and Ar_2 , respectively. This illustrates in a pervasive way the interpretative power of simple but adequate models. Indeed, we can say that the monopole model describes and explains quite satisfactorily the second moments and the related diamagnetic susceptibilities χ^d . It is due to this model that we understand the values provided by experiments and rigorous *ab initio* calculations. The model could be refined by using optimal k_A values for each atom A instead of the k_p value averaged over the p -th period of the Mendeleev system of elements. Sutter *et al.*⁴⁵ suggest for example $k_H = 0.19$, $k_B = 1.24$, $k_C = 1.06$, $k_N = 0.921$, $k_O = 0.811$ and $k_F = 0.725$ (in 10^{-16} cm^2). Furthermore, the k_A constants are not isotropic in linear and planar molecules. We found that the out of plane (or out of straight line) k_A values should be smaller than the in-plane ones. Work on the generalization of the Eqs. (5) and (6) is under way.

A comment on the Flygare's atomic dipole approach for the calculation of molecular second moments is in place here. According to Flygare *et al.*⁴⁶ the second moment is given by

$$\langle r_a^2 \rangle \cong \sum_A Z_A r_{Aa}^2 + \sum_A 2r_{Aa} \langle r_{Aa}' \rangle + \sum_A \langle (r_{Aa}')^2 \rangle \quad (7)$$

where the prime denotes that the electron coordinate is measured from the respective nucleus. Hence, $\langle r_{Aa}' \rangle$ is a component of the atomic dipole. Examination of the terms in (7) reveals that the charge migration is neglected. Comparison with our formula (5) shows that the additional second term in (7) describes polarization of neutral atoms forming chemical bonds. Therefore, Flygare's formula is more general. However, the choice of the empirical atomic dipoles is not free of criticism. They are extracted from experimental dipole and quadrupole moments for a selection of characteristic molecules by using approximate formulae which neglect the monopole terms. Since the monopole contributions to molecular dipole and quadrupole moments are far from negligible, the deduced atomic dipoles are vague. Consequently, the good performance of the Flygare's approach⁴⁷ is somewhat surprising. The whole model should be revisited and put onto a more sound theoretical basis.

I.2. Diamagnetic Shielding of Nuclei

The spherically average magnetic shielding of nuclei can be split into two contributions⁴⁸:

$$\sigma_{av}(A) = \sigma_{av}^d(A) + \sigma_{av}^p(A) \quad (8)$$

where the superscripts d and p refer to diamagnetic and paramagnetic contributions, respectively. We shall focus attention on the former which explicitly reads as follows

$$\sigma_{av}^d = (e^2/3mc^2) \langle 0 | 1/r_A | 0 \rangle \quad (9)$$

According to the early suggestion of Ramsey,⁴⁹ diamagnetic shielding σ_{av}^d can be expressed in a simple form, if the point-charge approximation is used and the intramolecular charge transfer is neglected, *i. e.*, if the promolecule approach is adopted:

$$\sigma_{av}^d(A) = \sigma_{av}^d(\text{FA}) + (e^2/3mc^2) \sum'_B Z_B/R_{AB} \quad (10)$$

where $\sigma_{av}^d(\text{FA})$ refers to the free-atom value of atom A and the prime denotes that $B \neq A$. Ramsey's promolecule formula (10) yields reasonable estimates of the diamagnetic shieldings^{34,50-52}. For the sake of completeness one should mention that $\sigma_{av}^d(\text{FA})$ values are usually approximated by the atomic Hartree-Fock results of Fischer-Froese²¹. Allowing for the charge migration one obtains⁵³:

$$\sigma_{av}^d(A) = \sum_{\mu}^A (\zeta_{A\mu} Q_{\mu}^A/n_{A\mu}) + \sum'_B Q_B/R_{AB} \quad (11)$$

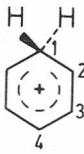
where Q_{μ}^A and Q_A are gross orbital and gross atomic electron populations, respectively, whilst $\zeta_{A\mu}$ is the screening constant. The main quantum number of the corresponding AO is denoted by $n_{A\mu}$. It was tacitly assumed here that the monopole (point-charge) approximation for the calculation of the expectation values of the $1/r$ operator holds to a good accuracy. A careful analysis of the DZ *ab initio* and semiempirical results has conclusively shown that this assumption is fully justified⁵⁴. Since the unparametrized formula (11) usually gives more than 95% of the diamagnetic shieldings, it is quite legal to introduce a few adjustable weighting factors in order to increase the performance and predictability of the model. Thus we obtain

$$\sigma_{av}^d(A) = K_{A1} \sum_{\mu}^A (\zeta_{A\mu} Q_{\mu}^A/n_{A\mu}) + K_{A2} \sum'_B Q_B/R_{AB} + K_{A3} \quad (12)$$

where the parameters K_{Ai} ($i = 1, 2, 3$) depend only on the nature of atom A. Both formulas (11) and (12) hold for *ab initio*, as well as for the semiempirical formalism. The inner-shell electrons are treated in the latter case as highly localized nonpolarizable cores possessing maximal electron occupancy permitted by the Pauli principle. If the diamagnetic shielding of the nuclei is considered in charged species, then the promolecule formula (10) is not suitable because the electron distribution in ions is far from a uniform one. For this purpose the more general formula (12) should be used instead. In Table III we compare diamagnetic shieldings of carbon and hydrogen atoms in some simple ions as obtained by the semiempirical SCC—MO method and full *ab initio* computations. The empirical parameters K_{Ai} in the formula (12) were

TABLE III

Comparison of Nuclear Diamagnetic Shieldings of Carbon and Hydrogen Nuclei in Some Simple Ions and Radicals as Obtained by the SCC-MO Method and Monopole Approximation with Accurate *ab Initio* Results (in ppm)

Molecule	Atom	SCC-MO Monopole Approx.		<i>Ab initio</i>
		Uncorr.	Corr.	
CH ₃ [•]	C	285.4	288.1	287.8 ^a
	H	83.5	81.7	81.7
CH ₃ ⁻	C	296.1	300.5	292.5 ^b
	H	92.5	92.5	86.7
	C ₁	428.7	430.2	433.3 ^c
	C ₂	429.1	430.5	433.1
	C ₃	428.6	430.0	433.0
	C ₄	428.2	429.7	431.9
	H ₁	190.8	189.1	189.9
	H ₂	185.9	185.9	185.1
	H ₃	184.7	184.7	184.0
	H ₄	184.3	184.3	183.1

^a Ref. 55; ^b Ref. 56; ^c Ref. 57.

taken from Ref. 53. The SCC—MO uncorrelated data refer to $K_{A1} = K_{A2} = 1$ and $K_{A3} = 0$. The *ab initio* results were obtained by using large and flexible GTO basis sets⁵⁵⁻⁵⁷ so that the predicted shieldings should be considered as reliable. Additional CI calculations in CH₃[•] and CH₃⁻ compounds did not significantly change the results^{55,56}, indicating that the expectation values of the $1/r$ operator are not very sensitive to the finer details of the total wavefunction. This is concomitant with some earlier findings¹ and provides one of the reasons why $\langle 0 | 1/r | 0 \rangle$ can be well reproduced by the simple monopole approximation at least for the ground states of neutral molecules. The SCC—MO results for the CH₃⁻ anion are less satisfactory, apparently due to the fact that the otherwise minimal basis set becomes a subminimal one by addition of an electron to the neutral molecular system. The agreement with *ab initio* data for CH₃[•] and C₆H₇⁺ systems is good. The parametrized formula (12) improves the results, in particular for carbons. One can conclude that diamagnetic shieldings in neutral molecules, cations and radicals are well accounted for by the monopole model provided that reasonably good semi-empirical wavefunctions are used (SCC—MO). It is noteworthy that the promolecule model works very well in alkali-halides⁵⁸. The estimated nuclear shieldings are in a reasonably good accordance with the *ab initio* results⁵⁸ in contrast with the second moments and diamagnetic susceptibilities case²². The reason behind the good performance of the promolecule approach is of some interest. The unrelaxed ionic monopole M⁺¹ X⁻¹ model where M and X represent alkali metal and halogen atoms, respectively, gave results exhibiting small but significant deviations from the promolecule estimates. However, the use

of the screening constants of neutral atoms in formulas (11) and (12) is not quite justified since we deal with ions. Appropriate relaxation of ζ screenings put the ionic model on line with the promolecule approach. Consequently, the surprisingly good performance of the simple promolecule formula (10) is a result of the opposite effects (charge migration and relaxation of the atomic charge densities) which approximately cancel each other. An interesting relation between the derivatives of the total energy over the nuclear charges, molecular electronegativity and diamagnetic shielding was found by Ray and Parr⁵⁹. It was shown that the molecular electronegativity has small influence on σ_{av}^d in neutral systems, which is compatible with the good performance of the promolecule approach (10). The atomic dipole method advocated by Gierke and Flygare⁶⁰ for the calculation of σ_{av}^d is conceptually not quite acceptable for the reasons discussed earlier (*vide supra*).

I.3. Hartree-Fock Energies of Molecules and other Energetic Properties

It was shown recently that the total SCF molecular energy of a molecular system is approximately given by a sum of potentials exerted on the nuclei⁶¹⁻⁶³

$$E_t = \sum_A k_A Z_A V_A \quad (13)$$

where Z_A are atomic numbers and k_A are adjustable weighting factors, respectively. Formula (13) recovers most of the total SCF energy. If the potentials are calculated in an *ab initio* manner, the error is about 0.5%/⁶³. In our point-charge procedure, the potential takes the form

$$V_A = - \sum_{\mu}^A (\zeta_{\mu} Q_{\mu}^A / n_{A\mu}) + \sum_B (Z_B - Q_B) / R_{AB} \quad (14)$$

where each term has its obvious physical meaning. Utilizing the Q_{μ}^A and Q_A entities produced by the SCC—MO wavefunctions, the *ab initio* DZ total energies of Snyder and Basch⁶⁴ were reproduced by a standard deviation of 0.1 a. u.⁶⁵. The same quality of results was obtained by using the point charges extracted from the Snyder-Basch DZ wavefunctions. This is encouraging because it indicates that slight adjustments of the formula (14), perhaps by small additional terms, might lead to good semiempirical estimates of molecular Hartree-Fock energies. It is worth mentioning that the weighting factors k_A are not far from the 0.5 value which in turn is required by the virial theorem. The formula (13) in conjunction with the expression (14) seems to enjoy better accuracy than the Ruedenberg's relation between the total molecular SCF energy and the sum of orbital energies⁶⁶. The role of atomic charges in determining the enthalpies of formation of organic compounds was studied by several researchers⁶⁷⁻⁶⁹ and discussed at length particularly for hydrocarbons by Fliszar⁶⁹. An appealing bond energy formula was developed by Matcha⁷⁰. It relates the stabilization energy to the asymmetry in bond charge distribution between the participating atoms showing that charge-transfer is the leading term. Matcha's formula represents a generalization and refinement of the early Pauling's expression which gives bond energies in terms of the difference in electronegativity of the constituent atoms⁷¹. Hence, the definition of reliable atomic charges is of wider chemical interest.

We shall briefly consider here the dissociation energies in alkali halides. The most common potential for the alkali halide pair is that suggested by Rittner⁷² (in atomic units):

$$V_{MX}(R) = -R^{-1} - [(\alpha_M + \alpha_X)/2R^4] - [2\alpha_M \alpha_X/R^7] - [C_{MX}/R^6] + A_{MX} \exp(-R/\rho_{MX}) \quad (15)$$

where α_M and α_X are free atom polarizabilities. The first term describes the Coulomb attraction of the pair of MX atoms. The second and the third terms arise from the polarization of the ionic charge clouds, which leads to induced atomic dipoles. Van der Waals attraction is given in the London C_{MX}/R^6 approximation. Finally, penetration of the two charge clouds which correspond to the completed shells yields the repulsive $A_{MX} \exp(-R/\rho_{MX})$ term, where A_{MX} and ρ_{MX} are empirical parameters. It is intuitively clear that the Coulomb R^{-1} term provides a dominating contribution because other interactions decrease either exponentially or by high inverse powers of the internuclear distance R . Additionally, the polarization and dispersion stabilization will approximately cancel the repulsion of full electron shells. Hence, the point charge attraction of alkali and halide atoms should give a reasonable estimate of MX dissociation energies to the ionic limit. This is indeed the case, as shown in Table IV. The $M^{+1}X^{-1}$ model in the monopole form accounts for the

TABLE VI

Comparison of the Dissociation Energies in Alkali-Halides Obtained by the Ionic $M^{+1}X^{-1}$ Model and the Experimental Values

Molecule	Dissociation energies ^a			Exptl.
	Re/Å	$M^{+1}X^{-1}$ model	$M^{+q}X^{-q}$ model ^b	
Li—F	1.564	212.3	81.0	184.1
Li—Cl	2.0207	164.3	43.0	153.3
Li—Br	2.170	153.0	34.8	147.8
Li—I	2.392	138.8	21.1	138.7
Na—F	1.926	172.4	63.1	153.9
Na—Cl	2.361	140.6	31.6	132.6
Na—Br	2.502	132.7	28.2	127.7
Na—I	2.7115	122.5	17.0	120.3
K—F	2.1715	152.9	62.0	139.2
K—Cl	2.667	124.5	32.8	118.0
K—Br	2.821	117.7	29.5	113.6
K—I	3.048	108.9	18.9	106.1
Rb—F	2.2703	146.2	60.5	133.6
Rb—Cl	2.787	119.1	32.5	113.4
Rb—Br	2.945	112.7	29.3	109.0
Rb—I	3.177	104.5	19.0	101.9
Cs—F	2.345	149.6	60.4	130.5
Cs—Cl	2.906	114.2	32.6	112.3
Cs—Br	3.0722	108.1	30.9	108.6
Cs—I	3.3152	100.2	19.4	101.1

^a The experimental dissociation energies refer to the ionic limit and were taken from Ref. 73;

^b Charge migration is estimated by the electronegativity criterion.

changes in the D_e (ion) dissociation energies in alkali halides. For example, the energy decreases along the series MX for a fixed M and X = F, Cl, Br and I. Similarly, if the halogen atom X is kept fixed, the bond strength decreases along the MX family (M = Li, Na, K, Rb and Cs). In both cases the interatomic distance R_e increases, thus diminishing the Coulomb attraction. Further, the monopole $M^{+1}X^{-1}$ model gives, as a rule, too high D_e (ion) values, indicating that the overlap repulsion outweighs the polarization and dispersion interactions. This is particularly pronounced at smaller distances taking place in compounds involving smaller halide ions like F and Cl. The dissociation energies for large halogens Br and I are in good agreement with experiment. It appears that the main features are well reproduced by the point-charge $M^{+1}X^{-1}$ model. The largest relative error of 15% is found in fluorine compounds (Li—F and Cs—F) for the reason mentioned above.

It is interesting to point out that the monopole model involving partial $+q$ and $-q$ charges estimated by the electronegativity criterion

$$q_M = 1 - 2\chi_M/(\chi_M + \chi_X) \quad \text{and} \quad q_X = 1 - 2\chi_X/(\chi_M + \chi_X)$$

is not satisfactory (Table IV). The employed electronegativities were those of Little and Jones⁷⁴. The trend of changes is correct but the absolute values are by far too small. Hence the dissociation energies and second moments require the use of the ionic $M^{+1}X^{-1}$ model for alkali halides whilst diamagnetic shielding is equally well described by both the promolecule M^0X^0 and ionic $M^{+1}X^{-1}$ models.

I.4. ESCA Chemical Shifts

X-ray photoelectron spectroscopy (XPS) developed by Siegbahn and coworkers^{75,76} is a powerful tool for studying the charge distribution in molecules and crystals. Binding energies (BE) of the localized inner core electrons exhibit strong dependence on chemical environment, thus providing a sensitive probe of the electronic structure of compounds. It was observed first by Siegbahn *et al.*⁷⁵ that binding energy shifts (ΔBE) parallel the changes in electrostatic potentials exerted on the nucleus in question. Basch⁷⁷ and Schwartz⁷⁸ have shown subsequently, by both theoretical considerations and *ab initio* calculations, that 1s-binding energies are indeed intimately related to the potentials felt by the host nucleus. The semiempirical work involving the point-charge model based on EHT and CNDO/2 wavefunctions was not quite satisfactory due to relatively large errors, particularly for nitrogen and oxygen atoms^{79,80}. Significant improvement in the performance of the semiempirical point-charge model was achieved by the use of the SCC-MO method^{81,82}. Our approach is succinctly given below because the relevant details can be found in the literature.

Binding energy shifts in the ground state potential approach are given by

$$\Delta BE_A = k_1 Q_{ns}^A + k_2 Q_{np}^A + k_3 \sum_B (Z_B - n_B - Q_B)/R_{AB} + k_4 \quad (16)$$

where Q_{μ}^A is the orbital population, $Q_{\mu}^A = P_{\mu\mu} + \sum_B \sum_{\nu} P_{\mu\nu} S_{\mu\nu}$, and $Q_{np}^A = \sum_{\alpha} Q_{np\alpha}^A$ ($\alpha = x, y, z$) is the population of the np subshell. The valence shell

charge density of atom B is denoted Q_B and the principal quantum number of the valence electrons is given by n . The third term is commonly called the Madelung term. In the formula (16) a provision is made for the difference in screening of the ns and np orbitals because the Clementi-Raimondi⁸³ AOs are used in the SCC-MO computations. The adjustable weighting factors k_i serve to align the potentials with the energy shifts. The last factor, k_4 , is related to the reference level of the gauge molecule. The parameters k_i absorb a portion of the relaxation energy. The first two (k_1 and k_2) account for the part of reorganization energy arising from contraction of the host-atom orbitals whilst k_3 , which multiplies the Madelung term, takes into account some of the charge flow relaxation. The weighting parameters k_1 and k_2 can be contracted to a single constant, simplifying the formula for ΔBE shifts without a significant loss in accuracy

$$\Delta BE_A = k_1 Q_A + k_3 M_A + k_4 \quad (17)$$

In this form the BE s depend directly on the formal atomic charge densities of the studied molecule in its ground state. Formulas (16) and (17) implicitly involve some reorganization energy of the valence electron cloud due to the creation of the positive hole. Better results are obtained if this effect is explicitly taken into account. One way of doing this is to invoke the equivalent core concept^{84,85} leading to the expression (18) if the point-charge model is employed:

$$\Delta BE_A = k_1 (\zeta_A Q_A + \zeta_{\bar{A}} Q_{\bar{A}}) + k_3 (M_A + M_{\bar{A}}) + k_4 \quad (18)$$

Here the bar denotes the equivalent atom possessing the equivalent core. An alternative approach is offered by the transition potential formalism involving the corresponding pseudo-atom instead of the atom hit by the photon⁸⁶. The transition potential formula reads

$$\Delta BE_A = k_1 Q_A^{TP} + k_3 M_A^{TP} + k_4 \quad (19)$$

where the superscript TP refers to pseudo-atom entities. Expressions (18) and (19) have similar performance, providing a semiempirical basis for the relaxation potential model (RPM). On the other hand, formulas (16) and (17) lie within the framework of the ground state potential model (GPM). Extensive SCC-MO calculations supplied conclusive evidence that ESCA shifts are well described by the monopole approximation if the reliable atomic charges are available. This conclusion holds both for gaseous^{81,82} and solid state samples^{87,88}. Since the XPS is a fast experimental technique, it can give an »instantaneous« snap-shot of the charge distribution in a molecule, thus enabling a study of the (*e.g.*) keto-enol tautomers, which in turn are fairly well described by the theoretical procedures based on the monopole model⁸⁹. The accuracy of the point-charge model is worth discussing. The standard deviations for ESCA shifts of B, C, N, O, F, Si, S and Ge atoms are presented in Table V. One observes a dramatic improvement of the quality of the results for Si and Ge when RPM is applied. Additionally, the standard deviation of carbon and sulfur atoms drops by 0.3 eV, which is not insignificant.

TABLE V

Standard Deviations of the ESCA Chemical Shifts as Calculated by the SCC-MO Wavefunctions within the Monopole Approximation (in eV)

Atom	GPM	RPM
B	0.3	—
C	0.6	0.3
N	0.4	0.4
O	0.6	0.6
F	0.2	—
Si	1.1	0.2
S	0.5	0.2
Ge	1.2	0.4

Following Kutzelnigg *et al.*⁹⁰ the accuracy of theoretical calculations can be classified as

- spectroscopical $\sim 1 \text{ cm}^{-1}$ ($3 \cdot 10^{-3} \text{ kcal mol}^{-1}$)
- chemical $\sim 1 \text{ kcal mol}^{-1}$
- moderate $\sim 1 \text{ eV}$ (23 kcal mol^{-1})
- crude $\sim 100 \text{ (kcal mol}^{-1})$

According to this ladder of precision and quality of the results, the SCC-MO computations of ESCA shifts are placed between moderate and chemical accuracy being usually closer to the latter. The underlying reasons for the surprisingly good performance of the monopole approximation accompanied by the SCC-MO atomic charge densities are as follows. The potential at the nucleus is closely related to the total molecular Hartree-Fock energy, as discussed earlier (section I.3). The former can be calculated within the monopole model to a good accuracy⁵⁴. Further, the potential model reproduces ESCA shifts particularly well because: (1) the exchange interactions of inner-shell electrons are relatively small. Their contribution to ΔBEs is of the opposite sign to the correlation effect. (2) The relativistic effects are highly localized. (3) The contributions in (1) and (2) practically disappear when the shift in BEs relative to the reference level is calculated. Finally, the important relaxation effect is fairly well described by the RPM formalism. It follows that the atomic charges in molecules are very intimately related to the basic lines in the XPS spectra. Hence, they prove very useful in interpreting a number of chemical properties revealed by the X-ray PES. Reversing the chain of arguments, one can say that the XPS technique gives the most direct insight into the atomic charge distributions if the relaxation effect is reliably estimated. It is gratifying that suitable methods for this purpose are available nowadays. The first approach is based on the Manne-Åberg theorem⁹¹ which states that the average energy of an inner-shell ionization spectrum taken over the main peak and all shake-up and shake-off satellites equals the ionization energy of the frozen initial state. In other words, it corresponds to the ionization without the rearrangement effect of the valence electrons. Therefore, by measuring this energy and that of the main peak, the relaxation is simply obtained by subtraction⁹². The second route of attack of the rela-

xation problem is by measuring the Auger spectra.⁹²⁻⁹⁴ It turns out that the change in Auger parameter α is proportional to the change in relaxation energy. Hence, the XPS and Auger spectroscopies, in conjunction with the electrostatic atomic monopole model, can provide good estimates of atomic charges in molecules. Work in this area is highly desirable because realistic atomic charges will give interesting relations between the XPS and Auger spectroscopies on one side, and the NMR as well as rotational Zeeman effect on the other side, in the spirit of the discussion of diamagnetic shielding and diamagnetic part of the molecular susceptibility presented in sections I.1 and I.2. They are also of crucial importance in describing electrostatic interactions between very complex chemical systems (*vide infra*).

I.5. *The Scope and Limitations of the Point-Charge Model. Influence of Higher Local Multipoles*

The intimate relation between electric charge and atomic as well as molecular properties was realized already by M. Faraday after his discovery of the laws of electrolysis in 1833. In his book »Experimental Researches in Electricity« M. Faraday writes: »The atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual chemical affinity«. In a later section he continues: »Or if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them«. The quantum theory introduced probabilistic interpretation of the electronic motion or, loosely speaking, continuous charge distribution in molecules. Nevertheless, the concept of point atomic charge played an important role in the early quantum theories of the molecular structure. In the crystal field model, introduced by Bethe⁹⁵ and developed by others^{16,96,97}, ligands are reduced to points carrying positive or negative charges. In spite of this apparent oversimplification, the crystal field model proved extremely useful in rationalizing the properties of complexes due to its high symmetry content. Mulliken's population analysis¹³ within the LCAO-MO framework provided a simple link between the description of a chemical system as a set of N nuclei and M electrons and the traditional notion of a molecule as a set of N atoms. Mulliken's formal atomic charges frequently served as an index of *e. g.* chemical reactivity. In a simple theory, the chemical reaction is charge controlled if the HOMO-LUMO energy gap between reactants is large⁹⁸. It should be pointed out that the modelling of the electronic charge distribution in molecules is not confined only to net atomic charges (monopoles) associated with the nuclei. The point-charge may be generalized and extended in two directions. Namely, one can separately treat portions of the total electron density which are purely atomic in nature and the part involving mixed (overlap) densities. The latter commonly assumes appreciable values in domains between the bonded atoms. Hence, it is sometimes advantageous to consider monopole moments of the atomic and overlap densities separately, *i. e.* avoiding the arbitrary partitioning of the mixed charge. Secondly, neither atomic nor overlap densities possess, in general, spherical symmetry. Consequently, it is rewarding or even necessary in some cases to take into account their higher multipole moments (dipole, quadrupole *etc.*). We shall comment

on that later on. For the time being, some more applications of the atomic monopole (AMo) model will be mentioned here. The formal atomic charges obtained by the modified CNDO/2 method reproduced the stretching force constants of a wide variety of bonds to a good accuracy⁹⁹. The simple formula involved, besides atomic monopoles, the values of the bond index which in turn is similar to Wiberg's index¹⁰⁰. Further, the atomic monopole model is extensively used in the interpretation of quadrupole splitting in the Mössbauer spectra, particularly of complexes involving iron and tin atoms¹⁰¹⁻¹⁰³. The point charge approximation yields only a crude description of the electric field gradients but reproduces correctly the underlying symmetry features being a practical alternative for large compounds and crystals. The AMo model seems to be useful in studying the properties of liquids, *e. g.*, in computer simulation of dipolar fluids¹⁰⁴. Infrared intensities provide another piece of information about AMos. The so called electro-optical (EO) parameters^{105,106} allow determination of atomic charges and charge flows during molecular vibrations¹⁰⁷⁻¹⁰⁹. The extracted charges seem to be quite reasonable and provide a good basis for the calculation of the hydrogen bond stabilization of the weak H-complexes¹¹⁰. Without any intention to make a definite statement, we would like to mention in passing that the physical meaning of the charges derived from the electro-optical (EO) parameters is not quite clear due to the use of the point-charge approximation in the calculation of bond dipole moments and their derivatives. Pertinent discussion on these matters was given by Galabov *et al.*¹¹¹, presented in a recent paper of this volume. It seems that the EO atomic monopoles assume some effective values. We shall return to this point later on by discussing several simple examples.

The expectation values of molecular properties can be usually broken down to several contributions, the atomic monopole term being a dominating member of the series. However, the other contributions could be far from negligible. Typical cases are offered by molecular dipole and quadrupole moments^{14,112}. The same applies to the molecular electrostatic potentials (MEP) which are well represented by the AMo model at very large distances from the molecule. However, at smaller distances the extramolecular potentials require closer scrutiny and a more detailed microscopic picture of the charge distribution. In view of the tremendous importance of the MEP in chemistry^{113,114a}, we shall discuss it in some more detail. Indeed, MEP is a suitable vehicle to explore the protonation sites in large heterocyclic molecules like nucleic acid bases^{115,116}. The same holds for larger cations *e. g.* Li^+ complexes^{114a}. Furthermore, by changing the sign of electrostatic maps, one obtains useful information about the most probable sites of fixation of spherical anions (*e. g.* Cl^-)¹¹⁷. Essential aspects of the hydrogen-bonding phenomenon, like directionality *etc.*, are well accounted for by the electrostatic potentials¹¹⁴. Analyses of the intramolecular electrostatic interactions shed light on the interplay of separate atomic groups in molecules. One can discriminate, for example, between through-bond and through-space substituent effects, distinguish inductive from resonance contributions in planar systems *etc.*^{114a} MEP is an important determinant of biological activity¹¹⁸ and drug-receptor recognition¹¹⁹. The electrostatic approach, of course, has its limitations which are thoroughly discussed by Tomasi^{114a} in terms of the energy decomposition pattern suggested by Morokuma^{120,121}. One of the limitations of the electrostatic hypothesis is the neglect of the polarization, exchange and

charge transfer terms which may sometimes be important. The other limitation is a spatial one because the MEP model gives sensible results for molecular interactions only outside the molecular volume defined by the atomic Van der Waals radii. Nevertheless, the MEP approach provides, within the domain of its validity, valuable chemical information. It is, therefore, gratifying that this information can be obtained simply and inexpensively at a minimal loss of accuracy by using transferable, perfectly localized MOs. It was shown by Tomasi *et al.*¹²² that MEPs of large compounds are well described by fragment local MOs (LMO) taken from smaller molecules possessing similar moieties, in conjunction with a particular form of the point-charge approximation. The latter consists of the two unit point charges placed at the pertinent nuclei in order to preserve electroneutrality, since the -2 charge is associated with the center of gravity of the LMO in question. If the LMO corresponds to the lone pair, then the $+2$ charge is centered at the respective nucleus. This type of polycentric monopole distribution seems to be well suited for the production of useful MEP maps. Further extension of the polycentric point-charge model is possible by inclusion of the higher multipoles. This can be achieved by the multipole expansions at atomic level AMu¹²³ or by the additional multipole series of each mixed charge density¹²⁴. In order to extract atomic multipoles one has to know either experimental or theoretical molecular multipoles with relatively good accuracy. This is not a prerequisite of Stone's overlap multipole expansion OMu¹²⁴ which in turn requires the knowledge of electron density

$$\rho = \sum_{\mu\nu} P_{\mu\nu} \Phi_{\mu} \Phi_{\nu} \quad (20)$$

where φ_{μ} and φ_{ν} are basis functions. Notice that the electron density associated with mixed charge is given by $2P_{\mu\nu} S_{\mu\nu}$ whilst density placed on the φ_{μ} function is $P_{\mu\mu}$ since the overlap $S_{\mu\mu} = 1$. In both AMu and OMu expansions much better convergency is obtained than by the one-center molecular multipole series, offering at the same time a better description of MEPs at smaller distances. This is not surprising because polycentric multipoles represent much better the shape of the molecule and anisotropics of atomic and overlap (bond) charge distribution than the single center multipole expansion. In this connection it should be stressed once again that MEP are well reproduced by atomic monopoles, routinely produced by the Mulliken population analysis, at very large distances from the molecule. At medium and small distances the performance of AMos is not satisfactory. Consequently, the method of deducing atomic monopoles which reproduce accurate MEP in the near vicinity of a molecule is not justified¹²⁵⁻¹²⁸. The fitting of the total molecular dipole moment as an additional constraint in extracting potential derived (PD) charges^{125,129} is not an improvement either, because molecular dipoles and quadrupoles cannot be calculated by the AMos with sufficient accuracy as shown by Hirshfeld.¹⁴ We shall substantiate our criticism by a few examples. For this purpose we compare PD AMos with the corresponding entities obtained by the topological atom approach, electro-optical parameters and stockholder partitioning of the total density (Table VI.). Although the selection of molecules is small, several tentative conclusions emerge. The charges derived from the topological atom and the stockholder principles are similar and predict the smallest intramolecular charge transfer of all

TABLE VI

Comparison of Atomic Monopoles Deduced by Various Extraction Procedures in a.u.^a

Molecule	q (H)	q (C)	q (X)
CH ₄	-0.063 ^b	0.252 ^b	
	0.065 ^c	-0.260 ^c	
	0.139 ^d	-0.556 ^d	
C ₂ H ₆	-0.072 ^b	0.216 ^b	
	0.046 ^e	-0.138 ^e	
C ₂ H ₄	0.134 ^e	-0.268 ^e	
	0.176 ^d	-0.352 ^d	
C ₂ H ₂	0.142 ^f	-0.142 ^f	
	0.094 ^g	-0.094 ^g	
	0.208 ^c	-0.208 ^c	
	0.297 ^d	-0.297 ^d	
	0.312 ^h	-0.312 ^h	
HCN	0.133 ⁱ	0.066 ⁱ	-0.201 ⁱ
	0.220 ^c	0.109 ^c	-0.329 ^c
CO ₂	—	0.414 ⁱ	-0.207 ⁱ
	—	0.820 ^h	-0.410 ^h
	—	0.867 ^d	-0.433 ^d

^a By monopole we mean here the effective net charge of an atom given by the nuclear charge minus total atomic electron density. By $q(X)$ we denote the net charge of nitrogen or oxygen atoms, respectively;

^b The topological atom concept and *ab initio* STO-3G result from Ref. 130;

^c Electro-optical charges¹⁰⁷;

^d Potential derived charges obtained by the *ab initio* 6-31 G** basis set Ref. 126;

^e Electro-optical charges¹⁰⁹;

^f Topological atom concept¹¹ and the wavefunctions of McLean and Yoshimine¹³¹;

^g Stockholder principle and the wavefunctions of McLean and Yoshimine¹³¹. Taken from Ref. 132;

^h Atomic net charges obtained by reproducing the molecular quadrupole moment¹³²;

ⁱ Stockholder principle¹⁴ and the wavefunctions of McLean and Yoshimine¹³¹;

procedures considered here. These estimates are consistent with the electro-neutrality principle. The topological atom approach assigns a small negative charge to hydrogens in CH₄ and C₂H₆ whilst in C₂H₂ the sign is changed and carbon becomes a carrier of the negative charge in accordance with the pronounced acidity of the acetylenic proton. This finding is supported by the careful *ab initio* 6-31G** analysis of Wiberg and Wendoloski¹³³ who explicitly considered the rehybridization effect on IR intensities. The incomplete orbital following seems to be very important, particularly in bending motion. The electro-optical and potential derived (EO and PD) charges ascribe positive charges to the hydrogens in the CH₄, C₂H₆, C₂H₄ and C₂H₂ series. PD charges obviously exaggerate the electron density migration accompanying bond formation apportioning *e.g.* -0.556 |*e*| charge to the carbon atom in CH₄. This impression is enhanced by the perusal of the estimated atomic monopoles for CO₂. The PD charges are too large by a factor of 2 when compared with the charges determined by the stockholder principle.

The same holds for the charges estimated by fitting the molecular quadrupole moment. Hence, it follows that PD charges are stretched on the Procrustean bed indeed. The fact that PD charges reproduce the molecular dipole and quadrupole moments very well¹²⁶ is of course immaterial because these entities are not well described by the AMO approximation. Actually, this is just another indication that PD charges are unrealistic. Therefore, atomic monopoles cannot be determined by fitting the electrostatic potential immediately outside the Van der Waals radii of atoms. Perhaps, useful charges could be deduced by sampling MEP maps at larger distances, particularly if PD charges are to be used for the crystal lattice stabilization calculations. It is also apparent that the polycentric description of molecular charge distribution with concomitant multipole expansions provides a transparent and conceptually appealing procedure for the calculation of ME potentials and higher molecular moments. In this connection, the simple point-charge model based on the floating spherical Gaussian orbitals (FSGO) put forward by Hall¹³⁴ should be mentioned. Its simplicity stems from the central property of the Gaussian functions that their product is again a Gaussian even if they are centered at different places in space. More specifically, if the two FSGOs are denoted by $G_a(\mathbf{A})$ and $G_b(\mathbf{B})$, respectively, the product is given by $G_{a+b}(\mathbf{R}_{AB})$. Here $\mathbf{R}_{AB} = (a\mathbf{A} + b\mathbf{B})/(a + b)$ and nonlinear parameters are assigned by a and b . The electron density associated with the point R_{AB} is determined by the element of the first order density matrix P_{ab} and the overlap integral S_{ab} being equal $2P_{ab} S_{ab}$. The non-linear parameters and positions of FSGOs are found by the variation theorem. The FSGOs can be usually identified with the positions of inner-shell electrons; the lone pairs and bond charge being thus close to chemical intuition. The simplest form of the FSGO approach is given by the Frost model¹³⁵ where each orbital is occupied by two electrons. This sort of subminimal basis set is called the Lewis basis set for an obvious reason. Although the Frost scheme is *ab initio* by nature, the MOs can be simply obtained by the diagonalization of the overlap matrix¹³⁶. Hall's point-charge model has been applied in studies of one-electron properties^{137,138} and second order properties like polarizabilities and diamagnetic susceptibilities^{138,139}. An extension of Hall's model by including higher (Cartesian) Gaussians has been considered¹⁴⁰. The strength of Hall's model is the computational ease and feasibility. Concominantly, it was used in the examination of angular degrees of freedom in solute-solvent interactions yielding reasonable results¹⁴¹. They seem to be better than the earlier representation of the solvent molecules based on the atomic monopoles¹⁴². This is expected due to the polycentric nature of the FSGO model involving a large number of points which reproduce more realistically the continuous charge distribution in molecules. This is exactly the reason why the atomically centered FSGO population analysis of Shipman is less satisfactory¹⁴³. It should be mentioned that point-charge could be employed purely as a convenient computational means in tackling otherwise untractable problems. This type of point-charge modelling was used by Clementi and coworkers¹⁴⁴ in attacking the difficult and very important problem of solvation of large biological molecules. This type of point-charges have no physical significance since they were determined by pure mathematical fitting of accurate Hartree-Fock potentials. Besides the solvation phenomenon, the electrostatic contribution to the crystal lattice energies was considered by a number of

researchers. The adequacy and limitation of electrostatic interactions in determining molecular orientations in crystals was critically examined by van Duijneveldt *et al.*¹⁴⁵. The single-center multipole expansion for each molecule was utilized and the point-charges were generated by the Mulliken population analyses. It was found that the electrostatic component of the lattice energy is the driving force for molecular distortion upon crystallization. Further, it was concluded that the point-charge multipole expansion yields qualitative but not reliable quantitative information about orientational dependence of the crystal lattice energy. It would be interesting to repeat the analysis with the polycentric point-charge multipole expansion. In any case, the simple point-charge calculation at least indicates the domains of angular variables which should be better examined by more accurate methods.

The point-charge model distinguishing atomic and bond electron densities was suggested by Parr *et al.*¹⁴⁶ for the calculation of force constants in two- and three-atomic linear molecules. The model was later extended to include symmetric stretching vibrations of the linear triatomics¹⁴⁷. Since the dipole moment of the central atom seems to play an important role¹⁴⁸, the model was refined accordingly by Simons¹⁴⁹. Parr's bond charge model has not been generalized for a rationalization of force constants of larger polyatomic molecules to the best of our knowledge. We shall, therefore, mention attempts of describing molecular vibrations in terms of the effective nuclear charges^{150,151}. Again, the effective nuclear charges do not have a simple physical interpretation because they involve the relaxation of the electron cloud upon the motion of the nuclei. Finally, the electrostatic effects are explicitly taken into account within the point-charge framework in various force field schemes^{152,153}.

To summarize, previous evidence¹⁵⁴ and present discussion conclusively show that a molecule may be regarded as a superposition of spherical atoms carrying nonintegral charges caused by differences in electronegativity. This simple physical picture suffices for the interpretation of a number of molecular properties, most notably, it reproduces diamagnetic shielding of the nuclei, molecular diamagnetic susceptibility and ESCA shifts in a semiquantitative fashion. Surprisingly, the simple promolecule model of unchanged atoms has a very good performance for many purposes, too. However, for some other features the description of the continuous charge distribution by the monopoles associated with the nuclei is an oversimplification. We have in mind here in the first place the higher molecular multipoles, molecular electrostatic potentials and intermolecular interactions. They require a more detailed microscopic picture. It is gratifying that a simple generalization involving a few of the lowest local multipoles does a decent job in this respect. The local multipoles may be ascribed either to atoms only^{14,123} or they could be produced by mixed densities, too^{124,155}. The polycentric multipole expansion of the molecular charge density opens up a new wide avenue of research in quantum chemistry. The local moments up to quadrupole can be deduced from the abundant experimental data on dipole moments, quadrupole moments and generalized scattering factors¹⁵⁶. Good atomic monopoles could be expected by the combined use of the XPS and Auger measurements. This can aid to find an improved population analysis of the accurate molecular wavefunctions which will replace the common but imperfect Mulliken prescription. More significantly, local multipoles will provide a relatively simple way of treating

electric contributions to the solvent effect and interactions between large molecules of biological importance¹⁵⁷. Hence, they will become both a convenient computational means for the calculation of molecular properties and a very useful interpretative tool in modern chemistry.

Little hybridization goes a long way.
R. S. Mulliken

II. DESCRIPTION OF THE ATOMIC ANISOTROPY BY THE HYBRIDIZATION CONCEPT

In the preceding chapter we discussed the consequences of the intramolecular perturbations leading to the charge redistribution between the atoms. It is rewarding to take the opposite standpoint by neglecting the differences in electronegativities and the concomitant interatomic charge migrations. This will shed some light on the other facets of covalent bonding, essential for a description of compounds exhibiting low polarity *e.g.* hydrocarbons, silanes *etc.* We shall address the question of directionality of chemical bonds which permeates the whole chemistry. Indeed, the spatial arrangement of chemical bonds yields not only a wonderful molecular architecture but has a decisive influence on molecular properties closely related to the very nature of bonding. Hence, the explanation of preferential bonding directions is one of the first tasks of the theoretical chemistry. It is plausible that mutual orientations of bonds are connected with anisotropy of atomic charge densities. An atom in a molecular environment experiences an electrostatic field due to the incomplete screening of the nuclei. The symmetry of the field is determined by the nearest neighbours since their influence prevails. Concomitantly, the spherical charge distribution of the free atom is perturbed and polarized in bonding directions. The simplest description of the local atomic anisotropy is offered by the hybridization of atomic orbitals inaugurated by Pauling in his historical paper¹⁵⁹ which opened new horizons and signified procreation of modern chemistry. It turned out that the hybridization concept has a rich chemical content providing a rationalization of a large number of local bond properties. Hybridization provides an intuitively appealing description of the electron pair bond which is a corner stone of chemical phenomenology. Hybrids are essential ingredients of the perfectly localized orbitals which are to a large extent transferable between similar moieties. Thus, they are bricks for building large molecular systems out of small ones. Being chemically adapted, hybrid AOs offer an excellent basis for efficient approximate schemes. This is the reason why hybridization will never lose its actuality.

II.1. Hybrid Orbitals

Directional properties or polarization of AOs are enhanced by their mixing or, in other words, by sacrificing the angular quantum number l .^{159,160} Let's consider the hybridization of s and p orbitals for the sake of simplicity. The general form of the hybrid placed on atom A is then

$$\chi_{A\mu} = a_{\mu}(ns) + (1 - a_{\mu}^2)^{1/2}(np) \quad (21)$$

where n is the principal quantum number of the valence shell. It was tacitly assumed that s and p orbitals belong to the same shell. Generally, this does not need to be the case. The properly oriented p orbitals are denoted by $(np)_{\mu}$. It is given by the linear combination of Cartesian p orbitals $(np)_{\mu} = \cos \gamma_x (np)_x + \cos \gamma_y (np)_y + \cos \gamma_z (np)_z$ where $\cos \gamma_{\alpha}$ ($\alpha = x, y, z$) are the direction cosines.

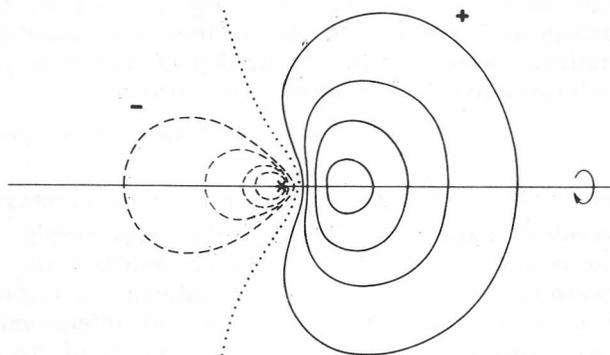


Figure 1. The sp^3 hybrid orbital in CH_4 as obtained by the self-consistent field method (W. Moffit and C. A. Coulson, *Phil. Mag.* **38** (1947) 634). The positive and negative amplitudes are represented by full lines and by dashes. The nodal line is given by dots. Position of the C atom is denoted by an asterisk.

Since the s orbital is spherically symmetric, the polarization and directionality are determined by the p part of the hybrid. If d and higher AOs are present, a closer scrutiny of the directional property of the hybrid is necessary¹⁶¹. Amplitudes of the hybrid χ_{AH} (21) are reinforced in the region of positive signs of s and p AOs and partially cancelled by a destructive interference in the domain of their opposite signs. Hence, a hybrid assumes the familiar axially symmetric mushroom-like shape (Figure 1). It is not only directed along a particular straight line but also localized in a particular region of space. A strong polarization toward the nearest neighbour atom increases favourable bonding interactions. At the same time, the unfavourable non-bonding repulsions with other atoms are diminished. The hybrids residing on the same nucleus are supposed to be orthogonal. This is plausible because electron pairs possessing coupled spins tend to occupy different positions in space. The easiest way of satisfying the Pauli exclusion principle requirement, at least to some extent, is to set overlap integrals of their wave functions equal to zero. It should be kept in mind that this is not a condition imposed by the rigorous theory because hybrids are not eigenfunctions of an atomic hamiltonian. Further, the vanishing overlap integral does not mean that overlapping is zero in each region of space, but simply that positive and negative contributions are exactly cancelled. In other words, the overlapping disappears on average. Hence, other criteria allowing for the avoidance of electrons with parallel spins could be examined. Our semiempirical study of hybridization in hydrocarbons has shown that local hybrid orbitals are almost orthogonal.¹⁶² This finding does not necessarily hold for highly electronegative atoms possessing lone pairs. The nonorthogonality is namely related to the unequal population of AOs.¹⁶³ Concomitant with (approximate) orthogonality is a decrease of the Coulomb repulsion between hybrids as compared to the repulsion of the component free-atom orbitals.¹⁶⁴ Another remarkable property of local hybrids is that they inherently contain a considerable part of the correlation energy¹⁶⁵⁻¹⁶⁷. If the gain in energy outweighs a loss in s - p promotion energy, hybridization is highly pronounced, as in carbon and tetra-

coordinated atoms. However, a large difference between s - p levels can considerably reduce the role of hybridization, like in Se, Te *etc.* atoms.

The hybridization indices are commonly defined as the s -character given by a_{μ}^2 and/or p -content measured relative to the s orbital participation: $n_{\mu} = (1 - a_{\mu}^2)/a_{\mu}^2$. They can be most accurately calculated by the application of the variation theorem. This is usually costly for polyatomic molecules, particularly if much larger atomic basis sets are used. For example, assuming that the z -axis coincides with the symmetry axis of the hybrid (Figure 1) one immediately observes by inspection that the d_z^2 orbital will increase the positive lobe and diminish the negative one. Since the f_z^3 orbital behaves like the p_z orbital, a small admixture of the former can be anticipated. Hence, the general form of the tetrahedral hybrid directed along the z -axis obtained on intuitive grounds reads

$$\chi_t = a(2s) + b(2p_z) + c(3d_z^2) + d(4f_z^3) \quad (22)$$

The use of the group theory allows a selection of AOs suitable for the construction of hybrids belonging to a particular symmetry but it can not determine completely all hybridization parameters¹⁶⁸⁻¹⁷¹. The following groups of AOs can be used as building blocks for hybrids of the T_d symmetry: sp^3 , sd^3 , sf^3 , fp^3 , fd^3 and f^4 . A proper mixture yielding optimal tetrahedral hybrids like the representative one (22) should be therefore obtained by the *ab initio* calculations. If a simple model description of bonding is intended, a more practical procedure is desired. It is provided by the maximum overlap criterion suggested by Pauling¹⁵⁹ and Slater¹⁶⁰ independently. It is equally important as the hybridization concept itself in rationalizing the steric properties of molecules. In order to avoid the calculation of overlap integrals Pauling put forward an even simpler maximum bond strength criterion^{71,159} which states that the optimal hybrid is the one with the maximal angular amplitude in the bond direction. Taking into account the promotion energies, Pauling⁷¹ found that the best tetrahedral hybrid (22) has the following parameters: $a = 0.50$, $b = 0.83$, $c = 0.20$ and $d = 0.14$. Hence, the contribution of the d_z^2 and f_z^3 AOs is 4% and 2%, respectively. Their influence is small but significant. In this paper we shall discuss predominantly the results of the maximum overlap calculation because they are most abundant.

II.2. The Iterative Maximum Overlap IMO Method

The maximum overlap criterion has its limitations but on the whole it gives reasonable results¹⁷²⁻¹⁷⁶. Our extensive studies have shown that the hybrids obtained by the maximum overlap method are comparable to those produced by more accurate criteria giving at the same time sensible estimates for a number of observables in good accordance with experiment. They provide an incomplete but consistent picture of bonding in the class of molecules with low polarity. Therefore, we give here a few salient points of our approach. The iterative maximum overlap method (IMO) stems from the empirical observation¹⁷⁷ and theoretical considerations¹⁷⁸⁻¹⁹⁰ that bond energies are additive. Analyses of the total molecular energies have shown that two-center terms make a dominant contribution to molecular stabilization. It appears also that empirical bond energies are roughly proportional to the overlap

integrals¹⁹¹. This is concomitant with various approximate semiempirical schemes for the calculation of the electronic properties of molecules which employ resonance integrals in a form proportional to the overlap. The resonance integrals occurring due to the mixed electron density have a leading role in determining bond energies¹⁸⁵⁻¹⁸⁸. Hence, it is plausible to express the total binding energy as a sum of scaled bond overlap integrals

$$E_b = \sum_{A-B} K_{AB} S_{AB} + \sum_{A-B} L_{AB} \quad (23)$$

where K_{AB} and L_{AB} are empirical parameters. Summation in the formula (23) is extended only over all bonds or, in other words, the nonbonded interactions are not explicitly treated. Notice that our formula is very similar to that of Ehrenson and Seltzer¹⁸⁶. The basis set in the IMO method is confined to s and p orbitals because they represent the most important AOs in hydrocarbons and silanes. To be more specific, we use the DZ-AOs of Clementi¹⁹². Hybrid orbitals²¹ are occupied by exactly one electron, which means that charge drift is neglected. Atoms are considered to be perfectly neutral. Orthogonality conditions are imposed leading to simple relations between interhybrid angles (Figure 2) and hybridization indices:

$$\cos \vartheta_{\mu\nu} = -(n_\mu n_\nu)^{-1/2} \quad (24)$$

where the square root is to be taken with the positive sign. Interhybrid angles $\vartheta_{\mu\nu}$ are equal to geometric angles if the covalent bonds are axially symmetric. However, if bent bonds appear, then $\vartheta_{\mu\nu}$ includes the deviation angles of the hybrids relative to the straight line passing through the neighbouring nuclei. The optimal hybridization indices are determined by maximizing the expression (23). It is clear that this scheme can describe the shape of the molecules by optimizing angular variables via the formula (24), but it comes short regarding the molecular size. Optimization of overlapping yields interatomic distances which are by far too small, since the nonbonding

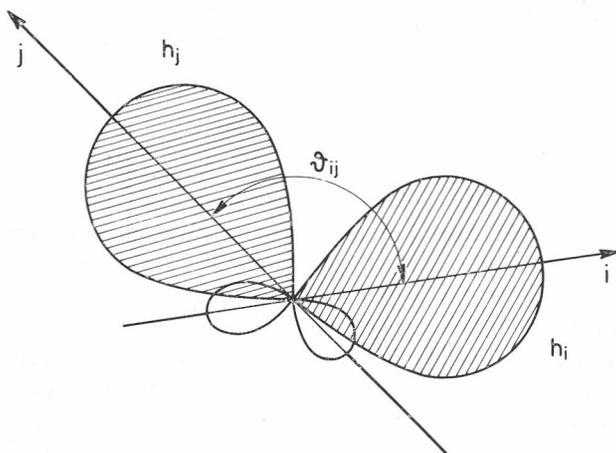


Figure 2. The interhybrid angle is defined as the angle closed by the axial symmetry axes.

interactions, most notably repulsion of the incompletely screened nuclei, are disregarded. One can use the experimental bond distances but this confines the field of applications of the method to molecules of a known structure. An even more serious objection is that one would like to obtain structural parameters as output of the calculations and not use them as input to feed a computer. Prediction of molecular geometries and their rationalization is one of the main issues of theoretical chemistry. A knowledge of atomic positions in space allows a number of statements about molecular properties (*viz.* Eqs. (6) and (10)) and, more importantly, contain intrinsic information about the origin of chemical bonding. This is why the use of standard bond lengths is generally not desirable. It may lead to poor results if they are used in a highly strained system where interatomic distances considerably deviate from standard values¹⁹³. Consequently, these results should be considered with due caution. In order to circumvent this problem and avoid any unnecessary bias introduced by the standard bond distances we have designed an iterative procedure based on the linear relations between the experimental bond distances and calculated bond overlaps^{194,195}. The σ - π separability is adopted and the effect of mobile π -electrons on the already formed σ -skeleton is taken into account by using the maximum overlap molecular orbitals of Lykos and Schmeising¹⁷³. The calculation is started by an arbitrary set of intermolecular bond distances and the sum of weighted overlaps²³ is optimized by varying hybridization indices and independent bond angles. Then a new set of inter-nuclear distances is deduced by using empirical linear relations of the type

$$d(AB) = C_{AB} S_{AB} + D_{AB} \quad (25)$$

where C_{AB} and D_{AB} are known constants. The calculated optimal overlap integral S_{AB} of the previous iteration step determines the bond distance of the next iteration cycle. The process is continued until a consistence in input and output bond distances, compatible with preconceived tolerance, is achieved.

Some related maximum overlap procedures are worth mentioning. Murrell¹⁹⁶ developed a matrix method for determining hybridization of the central atom in compounds of the MX_n type. This approach was subsequently simplified by Golebiewski¹⁹⁷ and generalized to include hybridization of ligands by Czechoslovakian researchers¹⁹⁸⁻²⁰⁰. A general characteristic of these calculations is that they are unable to predict molecular size *i. e.* bond distances. A very interesting discussion of the relation between Löwdin's canonical orthogonalization²⁰¹ and the maximum overlap principle was given by l'Haya and Morikawa²⁰² which throws more light on the maximum localization and hybrid orbitals. Special attention deserves the energy weighted maximum overlap EWMO method^{203,204}. The idea behind the EWMO scheme is that a molecule is essentially a collection of undisturbed atoms. The bonding interactions arise from overlapping of atomic distributions. The one-electron energies of the latter are explicitly taken into account. The method was successfully applied to the calculation of a number of molecular properties particularly of radical species²⁰⁵⁻²⁰⁷. Notice that EWMO, just like the Lykos-Schmeising maximum overlap method, does not employ hybrid orbitals. They can be easily generalized in this sense.

For the sake of completeness we shall mention a particular form of maximum overlap orbitals which exhibit optimal overlapping with exact wave-

functions. They are sometimes called Brueckner or best overlap (BO) orbitals²⁰⁸. A comparison of the Hartree-Fock (HF) and the BO wavefunctions with the true solution of an exactly solvable case gave interesting results²⁰⁹. The HF approximation is better for energetic properties like the total kinetic or potential energy primarily due to the virial theorem, which is satisfied for HF but not for BO wavefunctions. On the other hand, some other operator expectation values were better reproduced by the BO approximation, particularly those sampling outer regions of the electron cloud. This is in accordance with the finding of Larsson²¹⁰, who obtained better results for electron density at the nucleus in He and for the second moment by BO orbitals. It is noteworthy that BO orbitals are very useful in nuclear physics, particularly in considering hard core two-body interactions, because in this case the HF approximation breaks down²¹¹⁻²¹².

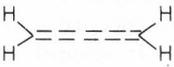
Finally, the overlapping criterion proved useful in the mapping analysis of concerted chemical reactions²¹³. To conclude, the maximum overlap concept is one of the most important criteria for obtaining qualitative and/or semi-quantitative information about chemical bonding. Its strength is its simplicity and ease in modifications which lead towards improved performance. One can say that the concept of optimal overlapping is in full accordance with Ockham's razor principle, which in turn states that conclusions should be reached in a most economical way.

II.3. Hybridization Indices in Hydrocarbons

One of the most striking features of the calculated hybridization parameters is their deviation from the canonical sp^3 , sp^2 and sp^1 values. The latter appear extremely rarely in highly symmetric chemical environments if two conditions are fulfilled: (a) that only the s, p basis set is used, (b) that each AO is occupied by exactly one electron and (c) that the σ - π separation holds. All of these requirements are built in the IMO method and the sp^3 hybridization is found in CH_4 (and diamond); sp^2 in some central sites of fused benzene rings (and graphite) and sp^1 in linear cumulenes. In all these cases the hybridization is completely fixed by symmetry. If a more realistic model, allowing for the difference in energy levels of s and p orbitals (or their electronegativity) is employed, then the canonical hybridization disappears even in these exceptional examples. Hence the canonical hybridization states, which have faithfully served organic chemistry for a long time in the most elementary description of the electron pair (Lewis) covalent bonding, are results of a very large number of simplifications. On the other hand, the hybridization indices offered by the maximum overlap criterion are closest to the original notion of hybridization. If the local symmetry is lower than T_d , D_{3h} or $D_{\infty h}$, then the hybridization deviates from canonical values (Table VII). The degree of deviation depends on the strength of the perturbation. Hybridization in C_2H_6 is very close to the sp^3 state. Significant rehybridization is found in C_2H_4 because the σ -part of the C=C double bond in the σ - π separation picture takes a larger portion of s -character than prescribed by the sp^2 canonical value. Similarly, a shift of s -character to the central multiple bond is found in acetylene. A general conclusion can be drawn that multiple bonds prefer a high s -content in the hybrids forming the corresponding σ -bond. It is worth mentioning that the σ - π

TABLE VII

Some Characteristic Hybridization Parameters as Predicted by the IMO Method

Compound	Hybridization indices
CH ₄ and diamond	sp^3
 and graphite	sp^2
	sp^1
C ₂ H ₆	$\chi_{CC} \equiv sp^{3.21}$ $\chi_{CH} \equiv sp^{2.93}$
C ₂ H ₄	$\chi_{CC} \equiv sp^{1.72}$ $\chi_{CH} \equiv sp^{2.16}$
C ₂ H ₂	$\chi_{CC} \equiv sp^{0.80}$ $\chi_{CH} \equiv sp^{1.25}$
	$\chi_{CC} \equiv sp^{3.69}$ $\chi_{CH} \equiv sp^{2.49}$

picture is easily converted by orthogonal transformations to the bent bond representation of multiple bonds, as originally suggested by Pauling¹⁷, which is advantageous for some purposes. Deviations from the canonical hybridization in cases discussed so far were significant but relatively small. A very pronounced rehybridization takes place in the angularly strained systems. A prototype of the latter is provided by cyclopropane where the existence of bent bonds in the three-membered ring was theoretically predicted first by Förster²¹⁴, Coulson and Moffitt²¹⁵ and confirmed later by X-ray measurements^{216,217}. Bond bending follows directly from the orthogonality requirements and the resulting relation between the interhybrid angle and hybrid composition (24). It appears that two equivalent hybrids cannot form an angle ϑ_{ij} smaller than 90° . This conjecture is valid for real hybrids. If the hybrids are supposed to be complex wavefunctions²¹⁸, then the lower limit $\vartheta_{ij} \geq 90^\circ$ does not necessarily hold. We have shown, however, that complex hybrids have poor overlapping power and that the maximum overlap criterion leads to real hybrids* and consequently to bent bonds²¹⁹. This has a number of chemical consequences, to mention only the considerable angular strain and the pronounced chemical reactivity. Hybrid AOs of the C—C bonds of small rings have a high *p*-content. It is a consequence of the tendency of hybrid orbitals to diminish their bending in order to increase their overlapping. However, a lowering of the *s*-character of hybrids decreases their bonding power. Hence, the resulting hybridization $sp^{3.69}$ is a result of two competing effects. Generalizing the results we can say that *p*-character exhibits a strong shift towards higher values in small rings. Further, maximum overlap crite-

* See also Ref. 220.

tion requires that the neighbouring hybrids forming a bond should assume similar s and p contents²²¹. This finding indicates that the maximum overlap criterion and electronegativity equalization are not widely different. It is well known that electronegativity is a linear function of the s -character. If two hybrids tend to achieve the same composition, *i. e.* s -characters, then they simultaneously try to equalize their electronegativities. If the hybrids are forced by structural reasons to bend from the straight line passing through the nuclei, then the deviation angles of the two overlapping HAOs tend to be the same²²². One of the most important features of hybrid orbitals is their transferability between similar moieties. This finding allows an approximate estimate of hybridization in very large molecular systems without actual calculation, if the HAOs in small molecules, serving as fragmental building blocks, are known. Hybridization in tetracoordinated silanes follows the same general pattern as sketched above²²³. It should be mentioned that hybridization is much more effective for the first row atoms than for other elements for the reasons discussed *in extenso* by Kutzelnigg^{163c}.

II.4. Isopycnic Maps in Strained Rings

Electron isopycnic (isodensity) contours reflect the changes in charge distribution upon the formation of chemical bonds.^{6,224} Particularly informative are for this purpose the deformation density maps defined as the difference between the total molecular electron density and the superposition of densities of neutral atoms placed at the equilibrium position. The latter reflects the promolecule charge distribution which is provided by the accurate *ab initio* calculations. Thus, strictly speaking, the deformation isopycnic maps are not observable by experiment. Nevertheless, they are very useful because they transparently visualize the charge distribution changes caused by bonding. If the bonded atoms have moderate electronegativities, then humps of electron density are observed in the regions between atoms. Concomitantly, a depletion of the charge density in the peripheral parts of the molecule takes place. These changes are, as a rule, quite small, thus supporting the concept of distorted atoms in a molecule. Further, buildups of the bond densities illustrate rather nicely the descent of symmetry of an atom in a chemical environment. Atomic density distributions are anisotropic and their finer description requires the use of higher multipoles, as discussed earlier. We shall illustrate this assertion now by the X-ray deformation density map of 2-cyanoguanidine $(\text{NH}_2)_2\text{C}=\text{N}-\text{C}\equiv\text{N}$ in the mean molecular plane²²⁵ (Figure 3). One can easily recognize the σ - sp^2 moiety of the central carbon atom. Nitrogen deformation density distribution in NH_2 group reveals the approximate sp^2 hybridization. Significant distortion of the sp^2 (D_{3h}) local symmetry is observed at the nitrogen of the $\text{C}=\text{N}-\text{C}$ group where the lone pair in the simplest description assumes hybridization somewhere between sp^2 and sp^3 . The cyano group exhibits some interesting features. The hybrid orbital occupied by a lone pair can be characterized roughly by the sp^1 composition. The deformation isopycnic lines of the triple bond have a pronounced ellipticity, showing that the bent bond picture of multiple bonds has a sound basis. Interestingly, these contours are shifted toward the carbon atom apparently due to the strong Pauli and Coulomb repulsion between the lone pair and three bond pair electrons of the triple bond. This observation is in accord with the effect

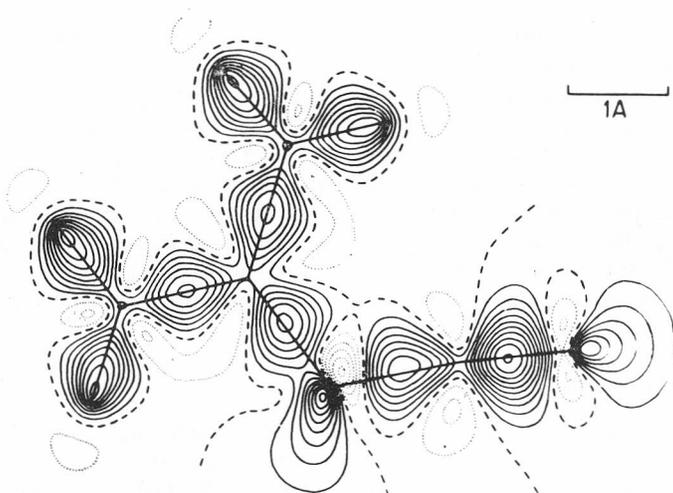


Figure 3. Isopycnic deformation maps in 2-cyanoguanidine (Courtesy of the Israel Journal of Chemistry).

which is sometimes called the π -back donation. Similar deformation isopycnic contours of the CN group are found¹⁴ in $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ by using the McLean-Yoshimine wavefunctions¹³¹ (Figure 4). The C—H and C—C single bonds could be approximately described by the sp^1 hybrids. The $\text{C}\equiv\text{C}$ triple bond has a bent-bond character as expected. These two examples conclusively show the flexibility of the hybrid AOs to conform to the lower symmetry of the local field experienced by atoms in molecular and crystal environments. A word of caution is, however, necessary here. The isopycnic maps displayed in Figures 3 and 4 do not prove the «existence» of hybrids. The latter are, just like pure AOs* or more generally-MOs, one-electron wavefunctions whilst the exact physical meaning has only the total electron density. However, Figures 3 and 4 provide pictorial evidence that hybrid AOs are well adapted

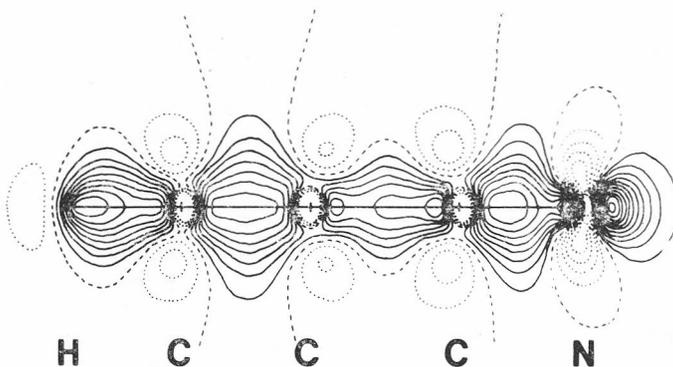


Figure 4. Isopycnic deformation maps in $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ (Courtesy of the Israel Journal of Chemistry).

* Hydrogen orbital in H atom is an exception because it is a true eigenvector of the corresponding H hamiltonian.

for a description of atomic charge anisotropy and reinforcement of densities in the covalent bonding regions.

Charge distribution in highly strained rings calls for particular attention due to the appearance of bent bonds. There are numerous studies, both experimental^{21b,6,216,217,226} and theoretical^{2b,227}, on small ring compounds. Their presentation is beyond the scope of this paper. It should be mentioned, however, that the local hybrid AOs produced by the IMO method give a fair description of the charge distribution in three-, four- and five-membered carbocycles²²⁸. Interestingly, bent bonds are more a rule than an exception even in acyclic molecules²²⁹. However, bending of electron density in this case is very small (a few degrees).

II.5. Molecular Shapes and Size

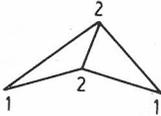
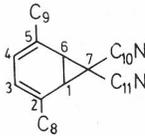
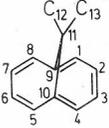
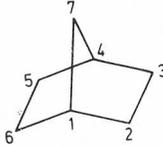
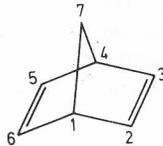
Hybrid orbitals were designed to rationalize molecular geometry, or more specifically, to describe bond angles. The key relations are provided by the orthogonality conditions yielding the formula (24). Other useful expressions are readily obtained. For instance, interhybrid angles of the four-coordinated central atom of the C_{2v} symmetry are related by the identity

$$\cos \vartheta_{34} = (\cos \vartheta_{12} + 1)/(3 \cos \vartheta_{12} - 1) \quad (26)$$

Here ϑ_{12} and ϑ_{34} are the interhybrid angles of two pairs of hybrid orbitals which are placed in mutually perpendicular planes. If the bond bending is absent, the formula (25) establishes a connection between bond angles which are unrelated otherwise. It is, therefore, of some importance to have an experimental test of the equation (26). One easily finds out that the increase in one angle leads to a decrease of the other. This is exactly an empirical observation formulated as the Thorpe-Ingold effect²³⁰. Hence the relation (25) has a practical value. However, it holds only approximately²³¹ due to the neglect of steric effects, incomplete orthogonality of hybrids, influence of higher AOs disregarded in the formula (21) *etc.* Nevertheless, it explains nicely the increase in the CH_2 bond angles of the CH_2 groups attached to the small carbocycles^{194,232}. This is a consequence of the gain in *s*-character in C—H hybrids, since the C—C hybrids prefer high *p*-character in order to decrease angular strain. The same holds for the SiH_2 groups of the silacarbo-cycles²²³. The opposite tendency was found in CH_2 group of the ethylene moiety. Namely, the multiple bond is stronger in a competition for the *s*-content. Consequently, the C—H hybrids assume a higher *p*-character leading to the smaller HCH angle of 117.5° in agreement with experimental value. The relations between bond angles and hybridization indices in AX_2YZ and AX_2Y local environments were discussed by Gilli and Bertolasi²³³. It should be mentioned that local hybrid orbitals and the principle of maximum overlapping provide fair estimates of dihedral angles in polycyclic systems and offer simple interpretations of puckering in some 6—8 membered carbocycles^{195,234}. This is exemplified by the comparison of the estimated angular structural parameters for some bicyclic systems with the measured values in Table VIII. A selection of molecules embraces bicyclo(1.1.0)butane, 2,5-dimethyl-7,7-dicyanonorcaradiene, 11,11-dimethyl-9,10-methano[10]annulene, norbornane and norbornadiene. The dihedral angles are well reproduced although the errors in bicyclo(1.1.0)butane and 11,11-dimethyl-9,10-methano[10]-

TABLE VIII

Comparison of the Angular Structural Parameters as Obtained by the Maximum Overlap Criterion with the Experimental Data for Some Bicyclic Compounds

Molecule	Angle/degrees		
	Calc.	Exp.	
	$C_1C_2C_2C_1$	131 ^a	126 ^b
	$C_1C_2C_3$	118.6 ^c	121.8 ^d
	$C_1C_2C_8$	117.2	117.5
	$C_2C_3C_4$	122.3	119.2
	C_7C_1H	111.0	110.2
	$C_{10}C_7C_{11}$	115.2	114.9
	$C_2C_1C_6C_7$	107.1	108.1
	$C_9C_1C_2$	121 ^e	124 ^f
	$C_1C_2C_3$	125.2	123
	$C_{12}C_{11}C_{13}$	111.6	109
	$C_1C_9C_{10}C_5$	143.4	136
	$C_1C_7C_4$	92 ^g	$93.2 \pm 1.5^{h,1}$
	$C_2C_1C_4C_5$	111.5	113.0 ± 1.5
	$C_1C_7C_4$	90 ^g	92.0 ± 0.8^h
	$C_2C_1C_4C_5$	112.5	115.0 ± 0.8

^aRef. 235; ^bRef. 236; ^cRef. 237; ^dRef. 216; ^eRef. 238; ^fRef. 239; ^gRef. 240; ^hRef. 241; ¹Ref. 242.

-annulene are 5° and 7° , respectively. Nevertheless, the results give some insight into the unusual values of dihedral angles providing their simple and pictorial rationalization, being particularly satisfactory for norcaradiene, norbornane and norbornadiene skeletons. The deviation in 9,10-methano[10]annulene should be ascribed to the neglect of the π -electron delocalization which certainly affects geometry of this molecule. Bicyclo(1.1.0)butane is an interesting system with a highly distorted charge distribution. This is exactly the structure where the so called *twisted* bonds were found for the first time²³⁵. It seems that highly strained and particularly twisted bonds are less well described by hybrid AOs spanned by only *s* and *p* AOs. It would be interesting to examine the influence of atomic orbitals possessing higher angular moments.

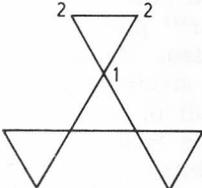
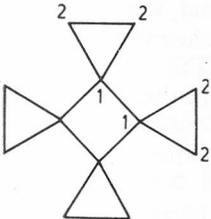
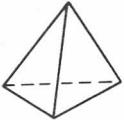
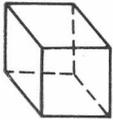
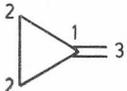
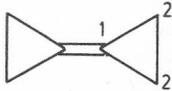
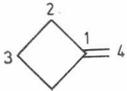
The principle of maximum overlapping and hybrid AOs are an especially convenient means for the examination of very large compounds where more sophisticated methods are not feasible. As two examples of the use of the hybridization concept in interpreting bond angles in polymethin chains we shall mention the work of Radeaglia²⁴³ and Kulpe *et al.*²⁴⁴. Special attention deserves Pauling's model based on the maximum HAO strength. It is very attractive and simple, being free of parameters. Consequently, the calculated bond angles are obtained by pure theoretical considerations. Its strength lies in the fact that the stereochemistry is determined purely by the properties of the central atom, offering perfectly general conclusions regarding a large number of various substituents. The weakness of the model, on the other hand, is in the neglect of the influence of ligands, leading to a loss of finer details of molecular structures. Hence, a price is paid for generality and simplicity of the model as usual. Pauling's hybridization model was used recently for the prediction and interpretation of structural properties of inorganic compounds, in particular transition metal complexes²⁴⁵⁻²⁴⁸ employing *spd* and *spdf* basis sets. The fundamental importance of enneacovalence in determining structures of transition metal compounds was discovered. Analysis of the sp^3d^5 hybridization led to the following remarkable conclusions: (a) there are two nodal cones of an sp^3d^5 hybrid which form angles of 73.2° and 133.6° , respectively, with the symmetry axis of the HAO. These angles determine orientations of symmetry axes of other hybrids orthogonal to the first one. Namely, it can be shown that the nodal cone is exactly the place where other hybrids achieve maxima of their bonding strength, (b) Two optimal polyhedra for enneacovalent transition metal atoms were found. They correspond to hybrids with maximum bonding power and have the form of a trigonal prism with equatorial caps on the three rectangular faces and a tetragonal antiprism with a polar cap on one of the two bases. These polyhedra seem to play the same crucial role in transition metal chemistry as that of tetrahedron in organic chemistry. A large number of transition metal structures was analysed along these lines and reasonable agreement with available experimental data was obtained. More experimental work is needed to assess these remarkable predictions. Pentacovalent bonding situations were described too.²⁴⁹

Hybridization is capable of giving useful information on molecular sizes as well as on molecular shapes. This is not unexpected because the bonding radius is directly dependent on a hybrid's composition as pointed out by Coulson²⁵⁰. Dewar and Schmeising²⁵¹ have shown that the characteristic CC and CH bond lengths could be classified by the canonical hybridization states of the constituent carbon atoms, thus implying an intimate relation between the hybridization indices and interatomic distances. This assertion was supported by the analyses of other researchers.²⁵²⁻²⁵⁵ The hybrid orbitals in the IMO framework are not restricted to the canonical phenotypes since the hybridization indices can vary freely, thus gaining in flexibility. Hence, they are better adapted to describe changes of bond distances in various environments. It should be recalled that hybrids are constrained in the IMO approach to follow the empirical bond distance — bond overlap linear relationships. Therefore, good estimates of the molecular size are to be expected. Still, the extent of agreement with the experimental data^{194,195,256,257} and more sophisticated *ab initio* calculations²³² is somewhat surprising. A *posteriori* one can

say that the hybridization concept, accompanied by the criteria of maximum overlapping or bond strength, provides one of the very few fundamental principles of stereochemistry. Indeed, they reproduce, albeit approximately, the salient features of molecular structures. Although the hybrids were designed mainly to follow and rationalize molecular geometries, the IMO method has a considerable predictive power. We shall substantiate this statement by a couple of characteristic examples (Table IX) involving small strained rings, because this kind of compounds exhibits unusual features. The cyclopropane cycle has a paradoxically short C—C distance of 1.510 Å as compared with the corresponding value in ethane (1.534 Å). Coulson and Moffitt²¹⁵ argued that hybrids of a bent bond have poor overlapping which can be increased only by the approaching of C atoms to each other even at the expense of the increased repulsions of the nuclei. Dewar²⁷⁴ pointed out that cyclopropane has all characteristics of a σ aromatic system. Hence, the CC bonds are shrunk in order to increase the delocalization stabilization. It is beyond doubt that the geometry of cyclopropane is a result of a delicate balance of these effects. Two points are of importance regarding cyclopropane. Firstly, we shall resolve a dilemma concerning the simple orbital description of the cyclopropyl ring. There are two hybrid basis sets designed for this purpose: Förster-Coulson-Moffitt (FCM) or bent bond (BB) and Walsh²⁷⁵ (W) schemes (Figure 5). The latter is extensively used in organic chemistry, particularly in the interpretation of the photoelectron spectra (PES). It appears, however, that the BB set is not only more intuitively appealing but has also conceptual and computational advantages (*vide infra*). Consequently, we are using the BB picture of strained rings throughout this paper. Secondly, we should probably distinguish between the bond length and bond distance. Bond length should be defined as a segment of the curve passing through the points of the maxima of the electron density along the bond.^{276,277} This distinction resolves the paradox that the highly strained CC bond in cyclopropyl ring is shorter than the axially symmetric one (*e. g.* in C₂H₆). It should be pointed out that this shortening of the angularly strained CC bonds in cyclopropane was used for calibration in the IMO procedure. Hence, the good agreement obtained for this compound with the experimental measurements and *ab initio* calculations is a result of an adjustment. However, all other results displayed in Table IX follow directly from the IMO scheme. They exhibit several interesting features. The bond distances in the central carbocycles of [*n*]-rotanes are appreciably shorter than in the parent molecules.²⁵⁷ This finding was confirmed by later X-ray and ED measurements.²⁶¹ Similar results are obtained by the consistent force-field method of Rasmussen.²⁷⁸ Notice that the X-ray results of Conia *et al.*²⁶⁰ for [4]-rotane are in error. Tetrahedrane is a very interesting molecule which still represents a challenge to synthetic organic chemists. However, tetra-tert.-butyltetrahedrane is synthesized and measured by the X-ray technique.²⁶² The experimental central CC distance is essentially in agreement with our estimate¹⁹⁴ and subsequent *ab initio* result of Schulman and Venanzi.²⁶³ The geometry of cubane has an interesting history. Our results¹⁹⁴ were in excellent agreement with the early X-ray measurements²⁶⁵, except for CH bonds. The latter was not unexpected because the proton is a notoriously poor scatterer of X-rays. The most recent ED measurements²⁶⁴ and *ab initio* results²⁶⁶ show that the CC distance is about 1.57 Å. Therefore, the X-ray and IMO estimates are off by 0.02 Å. The

TABLE IX

Comparison of the IMO Bond Distances with the Corresponding Values Obtained by the Electron Diffraction, X-Ray and Ab Initio Techniques for Some Hydrocarbons

Molecule	Bond	Bond distance/Å		
		El. diffraction	X-Ray (or <i>ab initio</i>)	IMO
	C—C C—H	1.510 ^a 1.089	(1.513) ^b (1.08 ass.)	1.516 ^c 1.088
	C ₁ —C ₁ C ₁ —C ₂ C ₂ —C ₂	— — —	1.465 ^d 1.500 1.496	1.468 1.494 1.520
	C ₁ —C ₁ C ₁ —C ₂ C ₂ —C ₂ C—H	1.534 ^f 1.491 1.528 1.103	1.525 ^f 1.468—1.477 ^d 1.502 ^f , 1.518 ^d 1.521 ^f , 1.505 ^d 1.05	1.516 ^e 1.503 1.519
	C—C C—H	— —	1.485 ^g , (1.482) ^h —, (1.054)	1.491 ^e 1.065
	C—C C—H	1.575 ⁱ 1.100	1.55 ^j , (1.570) ^k 1.0—1.1, (1.081)	1.552 ^e 1.089
	C ₁ =C ₃ C ₁ —C ₂ C ₂ —C ₂	1.317 ^l 1.457 1.541	— — —	1.316 ^m 1.475 1.522
	C ₁ =C ₁ C ₁ —C ₂ C ₂ —C ₂ C—H	1.309 ⁿ 1.469 1.544 1.099	1.304 ⁿ , 1.305 ^o 1.442, 1.467 1.504, 1.539 —	1.298 ^p 1.475 1.522 1.089
	C ₁ =C ₄ C ₁ —C ₂ C ₂ —C ₃	1.331 ^r 1.517 1.565	(1.309) ^r (1.529) (1.573)	1.321 ^m 1.522 1.556

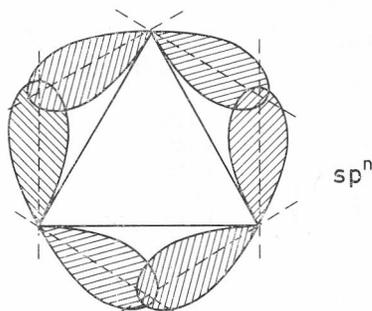
Molecule	Bond	Bond distance/Å		
		El. diffraction	X-Ray (or <i>ab initio</i>)	IMO
	C=C	1.340 ^s	(1.322) ^t	1.339 ^u
	C ₂ -C ₃	1.463	(1.470)	1.467
	C ₂ -C ₅	1.512	(1.509)	1.512
	C (sp ²)-H	1.076	(1.070)	1.081
	C (sp ³)-H	1.110	(1.083)	1.100
	C=C	1.349 ^t	(1.344) ^t	1.339 ^u
	C ₂ -C ₃	1.491	(1.477)	1.466
	C ₂ -C ₅	1.511	(1.505)	1.512
	C (sp ²)-H	1.093	(1.073)	1.081
	C (sp ³)-H	1.123	(1.085)	1.100

* *Ab initio* values are given in parenthesis;

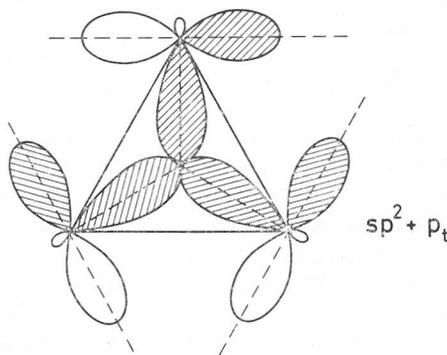
^aRef. 258; ^bRef. 259; ^cRef. 194; ^dRef. 260; ^eRef. 257; ^fRef. 261; ^gX-ray data of tetra-tert.-butyltetrahedrane, Ref. 262; ^h*Ab initio* 4-31G results, Ref. 263; ⁱRef. 264; ^jRef. 265; ^k*Ab initio* DZ+d results, Ref. 266; ^lRef. 267; ^mRef. 256; ⁿRef. 268; ^oRef. 269; ^pRef. 270; ^qRef. 271; ^rRef. 272, ^sCorrected *ab initio* DZ results, Ref. 273; ^tRef. 195.

moral of the story is very interesting. If theory and experiment are in perfect accordance, then they might be both wrong. Another interesting structural feature predicted by the IMO method is a shortening of the C=C double bond emanating from the small carbocycle. Three examples are given: methylenecyclopropane, methylenecyclobutane and bicyclopropylidene (Table IX). The subsequent X-ray, ED and *ab initio* results confirmed that the C=C exo-bond is considerably shrunk relative to the free ethylene bond. A simple explanation is offered by the hybridization picture since the *s*-character is always shifted from the strained ring to the exo-bond(s). Finally, our geometries¹⁹⁵ for isoprene and 2,3-dimethyl-1,3-butadiene are in good agreement with the most recent ED measurements^{272,273} and *ab initio* calculations.²⁷³ This is of some importance regarding the long standing controversy about the origin of the bond distances variation in π -delocalized systems. The idea that bond distances are mostly affected by the bonding hybrid orbitals and that the σ -skeleton is then perturbed by the mobile π -electrons is built in the very basis of the IMO method. It is, therefore, not surprising that our results indicate that the influence of π -electrons is small, even in delocalized molecules *par excellence* like 1,3-butadiene or isoprene. It is gratifying that a similar conclusion is drawn by the analysis of the *ab initio* wavefunctions, which are not based on hybrid orbitals.²⁷³

The good performance and predictive power of the simple IMO approach is encouraging because it is easily applied to large molecules. The significance of this finding lies in the fact that accurate prediction of molecular geometries requires the split-valence + polarization basis sets, including the Moller-Plesset perturbation theory to the third order, to take into account the correlation effects.²⁷⁹ The amount of computational effort is so large that the formalism is feasible in small molecules only.



Förster - Coulson - Moffitt picture



Walsh picture

Figure 5. Bent bond (BB) and Walsh (W) basis sets in cyclopropane ring.

The hybrid orbitals in the IMO method are used as the best basis set within the adopted theoretical (semiempirical) framework. Generally they serve, however, as an important tool in interpreting structural data extracted from the *ab initio* wavefunctions^{259,280} or experimental measurements.^{281,282}

The concept of molecular structure, as an intrinsic property of molecules, is of central importance for chemistry²⁸³ so that a few words on the difficulties in reconciling the classical notion of molecular geometry with the rigorous quantum theory are fully justified. It was pointed out by Wooley that the nuclei are delocalized, just like the electrons.²⁸⁴ Indeed, if there are equivalent nuclei in a molecule (*i. e.* occupying positions related by symmetry operations) they cannot be identified in a particular region of space due to their fundamental property of identity. Hence, they are inherently delocalized even if the geometric structure and its spatial symmetry is tacitly

assumed. The concept of molecular structure is based on the Born-Oppenheimer²⁸⁵ or clamped nuclei approximation and the concomitant idea of potential energy surface which determine the motion of the (classical) nuclei. It is generally physically reasonable and has proved useful in explaining myriads of experimental data, to mention only the ED, X-ray results and powerful conclusions obtained by symmetry arguments in molecular spectroscopy. However, this is not a proof of the existence of molecular geometries because the hypothesis of molecular structure is used in the process of extracting information from measured data. Therefore, agreement between the theoretical Born-Oppenheimer results and molecular properties obtained by experiments shows that they are consistent — but within the same conceptual framework. It can be argued that a molecule exhibits properties compatible with the geometric structure hypothesis only in interaction with other molecules and electromagnetic radiation.²⁸⁶ Another principal problem not yet solved is the question of the »classical limit« of the quantum theory.²⁸⁷ Discussion whether classical theory is derivable from quantum theory or not²⁸⁸ is far beyond the scope of this paper. Our adopted philosophy is a pragmatic one. We consider the concept of molecular structure as a useful model which helps to understand the behaviour of molecules and to rationalize a large body of empirical knowledge. The structural properties are then approximately interpreted by a simple quantum model of polarized (hybridized) orbitals compatible with the idea of deformed atoms in molecules. This type of approach has its merits and validity *per se* regardless of thegnoseological problems outlined above.

II.6. Energetic Properties

If the concept of the localized bonds is accepted, then it is obvious that their spatial arrangement will minimize the interbond repulsion yielding thus the most stable structure. Hence, the relation between the directional properties of localized bonds and total molecular energy is intuitively clear. Although the maximum overlapping principle was questioned as a good criterion for total molecular energies¹⁷⁴, we found satisfactory linear correlations between the CH bond overlaps and the corresponding dissociation energies.²⁸⁹ A very good linear relation was obtained for overlaps and the instantaneous bond dissociation energies (IBDE) of the CC bonds.²⁸⁷ IBDE is defined as the energy necessary for bond rupture, leaving the unrelaxed fragment radicals. By using the additivity property of bond energies good estimates of heats of formation (ΔH_f) of hydrocarbons were obtained by appropriate scaling of overlap integrals.²⁹⁰ It is interesting to mention that zero-point energies are not explicitly considered in the ΔH_f formula, but they are certainly absorbed in empirical parameters. This conclusion is substantiated by the finding of Schulman and Disch²⁹¹ that zero-point energies in hydrocarbons linearly depend on the number of carbon and hydrogen atoms. It was shown that the angular strain is closely related to hybrid bending and the concomitant defect in overlapping.²⁹⁴ By reversing the argument given above, one can say that hybridization and its transferrability between similar molecular fragments offers the simplest explanation of the ΔH_f additivity property.

II.7. Spectroscopic Properties

Spectroscopy is the traditional playground of the MO theory. For example, simple MO schemes are very effective in interpreting the PES spectra. Nevertheless, the hybrid orbital basis set can give additional insight into the origin of particular PE lines and into intramolecular interactions between molecular fragments. It should be mentioned that hybridization is completely unnecessary in highly symmetrical environments like CH_4 but its role becomes more and more important with a decrease in local symmetry.²⁹⁵ Hybrid AOs can be used either within a particular semiempirical method²⁹⁶ or by employing the bond orbital approach.²⁹⁷ The latter is particularly convenient for interpretational purposes. Although the many-body effects play a significant role in the PE spectroscopy of the inner valence shell electrons, the one-electron picture of the outer valence region usually works pretty well. For a discussion of non-Koopmans contributions the reader is referred to a paper of Spanget-Larsen²⁹⁸. A couple of first ionization potentials in strained cyclic and polycyclic systems contains information about the angularly deformed covalent bonds. As mentioned earlier, bond bending can be described by the FCM or W basis sets (Figure 5). They are related by an orthogonal transformation, being thus equivalent in any complete calculation. However, as in any model approach, the question arises which of the two sets leads more directly to the final result. Careful analysis of cyclopropane by Heilbronner *et al.*²⁹⁹ has shown that the bent bond (FCM) set is a much better starting point for a simple interpretation of the PE spectrum. The Walsh basis set yields the same result only after heavy CI mixing. Exactly the same conclusion holds for bicyclo(1.1.0)butane.³⁰⁰ The simple mixing of FCM hybrids in this molecule, which corresponds to the formation of the symmetry adapted linear combinations (SALCs), seems to provide a qualitative insight into the semilocalized MO scheme of the carbon skeleton, yielding a proper ordering of levels. Additional parametrization in the spirit of the simple Hückel theory gives semiquantitative agreement with the PE spectrum. The CI treatment is hardly necessary in the bent bond picture. On the contrary, the occupied W-SLMO combinations belonging to B irreducible representations have too high orbital energies, whilst their virtual counterparts are too low.³⁰⁰ Hence, W-SLMOs have a wrong ordering and only strong CI mixing gives acceptable results. The reason behind it is the presence of appreciable s-character in unoccupied W-SLMOs shifted from the occupied ones and resulting in a wrong ordering of levels. It turns out that the CI interaction is the crucial step in the W-model³⁰¹ which is usually skipped in most calculations employing the Walsh bases. There are numerous examples of improper use of the W-model in the literature without admixture of virtual orbitals. These results should be considered with due caution. The outcome of this discussion is not unexpected. A glance at the Scheme 1 of Ref. 300 reveals that the bent bond (FCM) picture has appreciable bond overlapping evenly distributed over all perimeter bonds. This is not the case of the W-basis involving cumbersome tangential p_t -orbitals (Scheme 2 of Ref. 300) leading to unfavourable overlapping. Detailed analysis shows that p_t -orbitals are not flexible enough in the process of forming semilocalized symmetry orbitals (SLMOs).²⁹⁵ Therefore, the BB orbitals consisting of bent bond hybrids represent the most natural choice of the basis set for simple MO schemes in strained

systems. It is important to stress that by using the transferrability property of hybrids, one obtains a qualitative picture of MO levels without any calculation.

Indirect spin-spin coupling constants across one-bond are ubiquitous and sensitive probes of the electron density in the immediate vicinity of the nuclei. It is intuitively clear that they should be proportional to the *s*-characters in the hybridization picture.³⁰² The early work of Muller and Pritchard³⁰³ on CH couplings and of Frei and Bernstein³⁰⁴ on CC constants confirmed these expectations. Comprehensive maximum overlap calculations provided conclusive evidence that there is intimate relation between the spin-spin coupling constants and hybridization ratios.^{223,305} Although the role of hybridization in determining CC and CH coupling constants was questioned by Gil and Geraldese³⁰⁶, subsequent theoretical analyses³⁰⁷⁻³⁰⁹ have convincingly shown that their criticism was unjustified. Some caution has to be exercised, however, since terms other than the Fermi contact contribution might be of importance, particularly in the presence of multiple bonds.^{310,311} Dependence of the coupling constants on hybridization helps to rationalize various empirical observations, like the relations between the *J*(CH) coupling and *d*(CH) distances.³¹² *J*(CH) and *J*(CC) coupling constants and CCC bond angles in cyclic compounds.³¹³ Finally, the interrelation between the *J*(CH) and *J*(CC) couplings involving the same carbon atom^{314a} and between the Si chemical shifts and SiOSi angles^{314b} can be interpreted by the distribution of *s*-characters which plays a role of the unifying concept.

The connection of the spin-spin coupling constants with other experimentally determined entities is of some importance. We have shown that symmetric and asymmetric stretching frequencies of CH bonds are linearly related to the *s*-character of the corresponding carbon hybrid orbital.³¹⁵ On the basis of this observation we proposed a linear relation between ν (CH) stretching frequencies and *J*(CH) couplings.³¹⁵ Similarly, a linear relation between the experimental CC stretching force constants and the corresponding *J*(CC) coupling constants was recently found by Kamienska-Trela.³¹⁶

The isotropic hyperfine constant a_H of a proton bonded to a trigonal carbon atom, which is a part of the planar radical, is a function of hybridization. We found that the so called Mc Connell's »constant« Q_{CH} is a quadratic function of the *s*-character³¹⁷. Unfortunately, our empirical correlation was based on the wrong experimental isotropic hyperfine constant of cyclopropenyl radical³¹⁸ as pointed out by Ingold *et al.*³¹⁹ Nevertheless, we feel that a proper a_H value for this elusive compound will alter only the empirical weighting factors, but not the final conclusions. Theoretical *ab initio* work would be desirable here. The hybrid AO basis seems to be also useful in discussing anisotropic coupling between a carbon *2p* orbital and a β -proton³²⁰.

Hybrid orbitals provide a natural choice of a basis set in various molecular force field methods³²¹ but care must be exercised regarding the incomplete orbital following of the nuclear motions.^{322,323} Analysis of the force constants in C_2H_6 , C_2H_4 and C_2H_2 has shown that the hybrid orbital force field is in qualitative agreement with the *ab initio* data³²⁴. Changes of dipole moments during normal vibrations caused by rehybridization have a decisive influence on intensities of the IR bands³²⁵. One should probably try to

reconcile here the hybridization idea with the atomic (or bond and atom) multipole model (*vide supra*).

Compton profiles, which depend on the momentum distribution in a molecule³²⁶, should be mentioned. They exhibit, in well localized systems, a characteristic additivity which can be rationalized in terms of localized MOs and their building blocks — hybrid orbitals^{327,328}. It can be shown that the average momentum in, *e. g.*, CH bond increases with the *p*-content of the corresponding hybrid^{326,327}.

To conclude, one can say that a good choice of the hybrid basis set armed with symmetry arguments and accompanied by transferrability of the hybrid AOs saves a lot of computational effort in revealing some of the qualitative features of the spectroscopic phenomena. Appropriate parametrization can considerably enhance the strength of the hybridization model, sometimes yielding semiquantitative information.

II.8. Miscellaneous Molecular Properties

We shall mention several molecular properties which depend only partially on hybridization. In other words, plain mixing of AOs does not suffice in describing the studied features even at the simplest level of sophistication. Nevertheless, the influence of hybridization is significant and must be explicitly taken into account. For example, the total molecular dipole moment and its bond dipole components depend rather strongly on hybridization in the simple picture^{133,164,329,330,331}. However, charge migration (atomic monopoles) contribution is very important, too. The same conclusion holds for the electric field gradients at the nuclei and the corresponding asymmetry parameters^{332,333}. Magnetic properties like diamagnetic shielding σ_A^d and diamagnetic susceptibility of molecules χ^d depend on hybridization only indirectly, *i. e.*, via molecular geometry. The results of the IMO method for hydrocarbons are in good accordance with the observed values and/or *ab initio* data³³⁴. Complementary discussion on the relation between the physico-chemical properties and hybridization can be found in two recent review articles^{335,336}.

II.9. Hybrid AOs and More Sophisticated Calculations

The first use of the hybrid AOs in nonempirical calculations was made in the early thirties. Dickinson³³⁷ and Rosen³³⁸ employed polarized functions of the type $(1s_H + 2p_H)$ for the calculation of the ground states of H_2^+ and H_2 , respectively. The *ab initio* MO studies based on hybrid orbitals are not abundant. The work of Hoyland³³⁹ on hydrocarbons and of Petke and Whitten³⁴⁰ on small heteroatomic molecules should be pointed out in this connection. Simulated (*i. e.* approximate) *ab initio* scheme³⁴¹ (SAMO) relies heavily on the transferrability of the HF matrix-elements from smaller fragment molecules to larger molecular and polymer systems³⁴¹. Although the use of hybrids is not a necessary prerequisite for the SAMO formalism, it certainly helps in the book-keeping procedure and has definite interpretational advantages. As to the conceptual and computational convenience, we would like to mention that hybrid AOs centered on the same atomic core can assume different screening constants in different spatial directions³⁴². Therefore, they

are more flexible in describing anisotropy of the atomic environment than a pure AO basis set. The self-consistent group function method of Klessinger and McWeeny^{343,344} employs the antisymmetrized product of pair functions describing the inner core, bond and lone pairs of electrons. The full CI within the limited basis set of two local hybrid AOs, belonging to a given bond geminal, is exercised. This approach was applied only to several small molecules, which is a pity in view of the simple physical interpretation of the results. The hybridization concept is the best possible description of a couple of perfectly paired electrons of opposite spins. Hence, the HAOs offer the most natural basis for VB and generalized valence bond (GVB) methods. The number of the GVB computations is steadily increasing. The reader is referred to several reviews on that important topic³⁴⁵. It is noteworthy that the use of hybrid orbitals within the VB function gives a fair approximation to the linear combination of several VB configurations³⁴⁶.

An important field of applications of the hybrid AOs might be the calculation of short-range correlation energies in solids. Fulde *et al.*³⁴⁷ have shown in an elegant manner that a versatile use of the hybrid basis sets enables local description of angular and in-out correlations. Furthermore, the different contributions to the correlation energy can be easily visualized and understood. For example, it is easy to distinguish between spin and density correlations. The method was developed on atoms and molecules and by relatively little computational effort usually about 95% of the correlation energy is recovered. We note in passing that the shape of Fermi holes resembles very much the conventional local hybrid functions³⁴⁸.

The hybridization concept is very important in interpreting the properties of metal clusters. Bauschlicher *et al.*³⁴⁹ found by the *ab initio* DZ + CI calculations that the dissociation energies of tetrahedral Be₄, Mg₄ and Ca₄ are closely related to the degree of *sp* hybridization. Additionally, they showed, by making use of a central atom as a model of a bulk atom in Be₁₃ and Mg₁₃, that the heats of sublimation are dependent on the degree of hybridization of the metal. It was concluded that similarities and differences between the alkaline earth compounds can be rationalized in terms of hybridization and bond strengths. This finding was supported by the studies of Koutecký *et al.*³⁵⁰, which conclusively show that the *sp* hybridization is of crucial importance for the stability of higher alkaline earth metal clusters. The role of the *p*-polarization is less decisive in determining the shape and attractive interactions of alkali metal clusters. The extent of hybridization depends, *inter alia*, on the *s-p* energy gap.

Properly adjusted hybrid orbitals can be characterized as local wavefunctions of the zeroth order. Notwithstanding their conceptual and concomitant computational advantage, the use of HAOs in semiempirical MO theories of chemical bonding is rather sparse and it is extremely rare that the semiempirical methods employ the local symmetry adapted basis sets. On the contrary, unitary (*i. e.* including hybridization) invariance of the final wavefunction is the central dogma in the CNDO and related schemes, which should be considered as an unfortunate *lapsus*. The basic problem in any approximate method is, namely, the choice of the most appropriate basis set which gives the best results within the adopted theoretical framework. Hence, the unitary transformations of the basis functions should be determined so

that the integral approximations introduce the least possible error. This was recognized a long time ago by McWeeny and coworkers^{351,352}. It was shown that the matrix elements, which are neglected in the ZDO approximation, are usually very small if a basis set of symmetrically orthogonalized hybrid orbitals is employed. Consequences of the uniform orthogonalization of the local HAOs were discussed in depth by Cook^{353,354}. This freedom in selection of the local (symmetry adapted) basis sets and their subsequent (full or partial) plain or weighted orthogonalization should be better exploited in semiempirical work.

The hybrid AOs were used by Fukui *et al.*³⁵⁶ in an elementary MO scheme developed for a discussion of molecular properties and reactivities. An attempt to implement hybridization within the strictly localized two-center MOs in conjunction with the ZDO approximation between SLMOs was made by Papas³⁵⁷. The use of SLMOs in quantum chemistry and their extension to include delocalization corrections was recently thoroughly discussed and reviewed by Surjan³⁵⁸. A conceptually important semiempirical method based on localized MOs formed by hybrid orbitals (PCILO) was devised by French researchers^{359,360}. The configuration mixing is introduced via the perturbation technique. Concomitant with the basic assumptions, PCILO is effective in treating well localized systems. Its performance however is certainly affected by the adopted ZDO integrals approximation. Hybrid orbitals should be particularly useful in approximate description of electronic properties of systems involving a very large number of sub-units, *i. e.*, atoms. Consequently, they are pivotal in the treatment of covalent solids³⁶¹⁻³⁶³. Hybridization proved useful in discussing surface properties and reaction sites of crystals^{364,365}.

The single determinant wavefunction built from MOs is invariant to hybridization. Thus, directional properties of chemical bonds are hidden. Nevertheless, they can be extracted from the bond-order charge-density matrix by using several recipes^{162,366-369}. Hence the mono-determinant wavefunction does not contradict the hybridization concept and spatial distribution of covalent bonds. This is remarkable and fortunate at the same time, because a single determinant would otherwise not be an acceptable form of the wavefunction for the description of chemical bonding.

Another way of retrieving hybridization from the intricate wavefunctions is by making use of one of the numerous localization procedures. The most popular ones are those of Edmiston-Ruedenberg³⁷⁰ and Boys³⁷¹. The resulting localized MOs are equivalent to the initial canonical MOs, but in addition, they are, spatially localized, corresponding to the chemical idea of the electron pair bond. Analysis of localized MOs yields the component hybrid orbitals and their occupation numbers which determine the bond polarity. The problem of defining the best hybrids which approach a given total wavefunction as close as possible was considered by McWeeny and Del Re³⁷². The localized MOs can be determined at two different degrees of sophistication: the *ab initio*^{227,373-375} and semiempirical^{367,376} levels. An interesting alternative to LMOs is offered by localized atomic orbitals (LAO) developed by Aufderheide³⁷⁷. It is of some importance that the hybridization indices obtained by LMOs are comparable to parameters calculated by the IMO method. There are, however, differences which show that hybridization can not be defined in a unique way. Nevertheless, if the hybridization indices are used within the same theoretical frame, then they give a consistent picture of local

molecular properties. It appears that each theoretical procedure defines its own hybridization scale which should be strictly obeyed, if the properties of the related molecules are to be considered and compared.

II.10. *General Remarks on Hybridization*

There is a number of astonishing misconceptions regarding the concept of hybridization. They originate from the invariance of the Hartree-Fock wavefunction against unitary (orthogonal) transformations.* Since hybridization is an orthogonal transformation of free atom orbitals, they do not change the final Hartree-Fock function. Consequently, some researchers infer that hybridization is merely a mathematical operation, being thus an artefact. This type of reckoning is not quite correct for several reasons. Firstly, the HF functions are also able to reproduce the directional properties of chemical bond and this type of information is deposited in the density matrix. Special techniques are required to extract this information (*vide supra*). Hybridization does the same in an approximate but-simpler and more transparent way being a model on its own. Secondly, it is frequently overlooked that localized and delocalized pictures are equivalent. This is just one more example of quantum dichotomy. Indeed, »*contraria sunt complementa*« in the microworld of atomic and sub-atomic units, as Niels Bohr put it lapidarily. Electrons sometimes behave as if they were localized, whilst in some other phenomena they exhibit their delocalized nature. An electron has two faces just like the ancient deity Janus. Hybridization is the essential ingredient of the localized electron picture. Approximate Hartree-Fock theories deserve a separate comment. The approximate HF functions are spanned by (very) incomplete basis sets which often consist of a minimal number of elementary functions. It is, therefore, of paramount importance to take the best basis set functions within a given subspace. These are obviously provided by atomic orbitals which are very well adapted to describe the local charge anisotropies because they are adjusted to conform to the low local symmetries. This also provides the reason for the high interpretative power of hybridization. Hence, the high information content stored in local hybrid orbitals has a simple physical basis.

Hybridization is not only a heuristic tool for extraction of chemically meaningful information from intricate molecular wavefunctions. It is a simple but chemistry rich model of covalent bonding on its own. In conjunction with the maximum overlapping principle, hybridization offers a transparent and conceptually appealing description of the Lewis electron pair bond. The level of this model is very elementary but nonetheless it provides an important-bridge between the rich chemical experience and the more rigorous theory of molecules.

The hybridization was introduced in chemistry by Pauling in 1928. The idea of creating new quality by mixing completely different subunits is much older. The Egyptian mythology offers a large number of unusual hybrid creatures. They involve the largest hybrid in the world — the sphynx (Figure 6). The hybridization concept probably reflectes the perennial human

* Exact wavefunctions possess, of course, the same invariance property but unfortunately they are not very abundant. HF functions are discussed because of their simplicity.

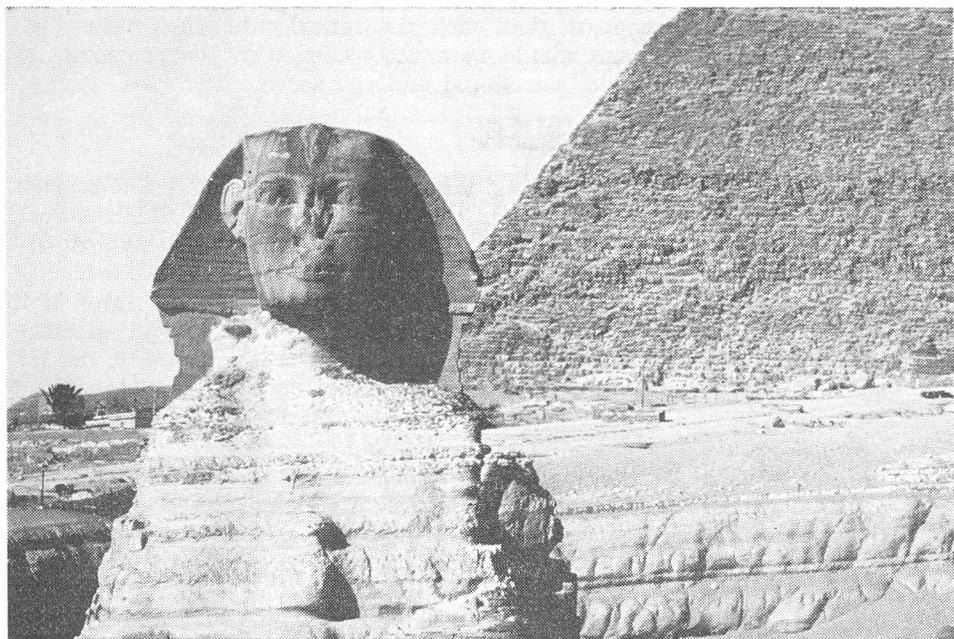


Figure 6. Sphynx in Giza (2550—2500 B. C.).

desire to extend and enrich the notional world by combining known entities in a new way. To conclude, we shall mention an interesting and important example of hybridization in biology. This is provided by the hybridoma-cells which are obtained by fusion of the lymphocyte with plasma-cytoma cells. The former produce a specific antibody, whilst the latter are immortal. Their hybrids are capable of producing monoclonal antibodies *ad infinitum*.

III. CONCLUSION

An abundant and conclusive evidence is presented which strongly supports Moffitt's idea of modified atoms in molecules (MAM). One of the salient features of MAM are their effective charges or electric monopoles. A number of electric and magnetic properties of molecules can be rationalized by the monopole model which is easily extended by higher local multipoles, if necessary. This simple and enlightening model has sometimes an intriguing performance. The promolecule picture is also useful indicating that bonding effects and the accompanying charge migrations might be very small except in cases of large differences in (atomic) electronegativities. This is exemplified by alkali-halides, where the ionic $X^{+1}Y^{-1}$ model is very successful. A conceptually more satisfying model is perhaps given by the idea of charged atoms immersed in a »sea« of the mixed electron density distribution. Then purely atomic and mixed (interatomic or bond) densities could be separately treated by local multipole expansions. This approach is in principle free of any arbitrary dissection of the total molecular density distribution. Local multipole expansions offer a classical (or better to say pseudoclassical) description of atoms in molecules, thus being close to chemical intuition and old structural mole-

cular formulas specifying the types and numbers of atoms. It should be kept in mind, however, that local atomic and mixed densities were obtained quantum mechanically by means of wavefunctions.

Description of directional properties requires a qualitatively new concept of polarized atomic orbitals. The hybridization and the concomitant maximum overlapping principle rationalize not only the spatial arrangement of bonds but also the appearance of the increased mixed density in regions between linked atoms. The latter seems to be an indicator of chemical bonding. It is interesting that directional features are closely related to other local bond properties like the spin-spin coupling constants, stretching frequencies, bond energies, *etc.*, the unifying principle being hybridization. One should point out that the model of local hybrid AOs is more general in the sense that it can, if properly adjusted, reproduce local multipoles discussed earlier. The surprisingly good performance of the hybridization model can be traced to the fact that the HAOs are symmetry adapted local atomic orbitals, being thus wavefunctions of the zeroth order. They correspond to the picture of perturbed or deformed atoms providing the simplest rationalization of the chemical bond concept which is a corner stone of chemistry.

The rigorous quantum theory has some difficulties in describing molecular geometric structure. Consequently, it also denies the existence of atoms in a molecule. Indeed, strictly speaking, an atom cannot be defined within a molecule in a unique manner because any spatial division of the molecular volume or partitioning of the mixed electron charge is always more or less arbitrary. Nevertheless, the MAM hypothesis should not be abandoned because difficulties encountered by the rigorous quantum mechanics will be resolved in the course of time, one way or another. At any rate, the MAM approach has merits on its own because it is so close to chemical phenomenology and common sense. Although approximate, the MAM model has high interpretational power. Consequently, our present task is to use our imagination and efforts to find the most reasonable (*i. e.* the least arbitrary) definition of modified atoms in a molecule providing the best description of those molecular properties which are »atomic« in nature. A picture of atoms which carry some electric charge, imbedded in the mixed electron density distribution deserves a closer scrutiny, because it is free of the objections mentioned above. The concept of modified atoms surpasses the field of chemistry by being extremely useful in describing the solid state properties. According to Harisson, one of the more interesting advances in solid state physics has been the development of atomic pseudopotentials and the discovery that they could be applied directly to atoms in crystals^{363,379}. The use of local hybrid orbitals in covalent crystals is worth mentioning.³⁶³

According to the basic principles of quantum mechanics, systems can be characterized by numerical data which correspond to physical observables. They can be, at least in principle, uniquely determined (measured) by suitable experimental arrangements. What can be measured and how this can be done is decided by rigorous theory combined with experience. Physical meaning have observables and everything else is physically irrelevant³⁸⁰. We would like to point out that there are parameters which cannot be attached to experiment via exact theory and yet have a certain physical meaning. They are built in models which only approximately, sometimes very crudely,

approach true situations. In spite of that, intrinsic parameters can quite successfully follow (correlate) the observed data, establishing connections between experimental findings which are not directly related otherwise. This type of parameters could be termed pseudo-observables. This name is coined to indicate the close relation to measurements and simultaneously the approximate (limited) meaning of the entity in question. The crucial point is that a pseudo-observable belongs to a model which is not designed to reproduce only a single molecular property. On the contrary, a model should be useful in rationalizing several unrelated phenomena. For example, atomic monopoles satisfactorily describe σ_A^d , χ^d and ΔBE_A shifts in inner-shell energy levels. Hybridization relates various local bond properties to the spatial arrangement of covalent bonds. Therefore we feel that atomic monopoles and hybridization indices have a semblance to truth and represent pseudo-observables *par excellence*. It goes without saying that each pseudo-observable is defined only within a specific model, which in turn has to be carefully examined regarding its scope of application and performance in reproducing accurate data.

Acknowledgement. — This work has been partly financed by the Self-managing Authority for Scientific Research of the SR of Croatia (SIZ II). The financial support through the International Office of »Kernforschungsanlage Jülich« is gratefully acknowledged. We are indebted to the Alexander von Humboldt Stiftung for the generous support in scientific books. Thanks are due to Professors R. Gleiter, G. G. Hall, R. Janoschek, P. N. Skancke and J. Tomasi for critical reading of the manuscript and a number of useful comments.

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SAŽETAK

Opis molekulskih svojstava s pomoću modela modificiranih atoma (MAM)

Zvonimir B. Maksić, Mirjana Eckert-Maksić i Krešimir Rupnik

Opsežni i iskustveni podaci pokazuju da model modificiranih atoma u molekula (MAM) vrlo dobro opisuje brojna molekulska svojstva. Promjene koje atom doživljava u kemijskoj okolini mogu se rastaviti na izotropnu i anizotropnu komponentu. Izotropna je komponenta električni monopol koji se javlja uslijed migracije elektronskog naboja. Atomički monopoli vrlo dobro reproduciraju σ_A^d , χ^d i ESCA pomake. Anizotropnu komponentu predstavljaju viši lokalni monopoli koji se mogu lako uključiti kada to opis električnih i magnetskih svojstava zahtijeva. Oni su npr. potrebni pri računu molekulskih elektrostatskih potencijala. Opis usmjerenosti kovalentnih veza također se dobiva jedino uzimanjem u obzir anizotropije atomske gustoće. To se postiže upotrebom polariziranih atomskih orbitala ili hibrida. S pomoću hibridizacije možemo objasniti i relacije koje postoje između oblika molekula i lokaliziranih svojstava veze. Nadalje, hibridizacija na jednostavan način interpretira koncept veze ostvarene parom elektrona, što je kamen temeljac čitave kemije. Iako se atom ne može egzaktno definirati u molekuli na temelju stroge kvantne teorije, MAM model ipak ima vrlo visoku interpretacijsku moć. Na kraju, dana je definicija pseudo-opservable i pokazano je da su atomski monopoli i parametri hibridizacije pseudo-opservable par excellence.