# A Semiempirical Treatment of Molecular Structures.
# III. Equipotential Orbitals for Polyatomic Systems

### G. Klopman

*Contribution from the Cyanamid European Research Institute, Cologny, Geneva, Switzerland. Received January 8, 1965*

*The self-consistent treatment based on a new theoretical definition of electronegativity, described previously for the calculation of the physical properties of diatomic molecules, is now being extended to a completely general form. Preliminary calculations of heats of formation, ionization potentials, and charge distributions have been performed for several hydroxylic derivatives. The analogy with existing SCF theories has been demonstrated for conjugated molecules.*

## I. Introduction

Although the success of so-called "semiempirical methods" has been widely recognized for conjugated molecules,[1] it is surprising to find that no systematic attempts have been made to describe such a theory for other types of compounds. At first sight, the problem seems to be much more difficult, in view of the various heteroatoms which would have to be considered in such a treatment and the various interaction terms which would have to be evaluated.

Consequently, only empirical attempts[2] have been made to calculate the properties of such compounds except for some simple molecules where *ab initio* procedures have been applied with varying success.[3]

A detailed analysis, however, has revealed that many of the difficulties can be overcome by means of a few hypotheses, analogous to those which have been made in the semiempirical methods for conjugated molecules. In the previous two papers, hereafter referred to as parts I[4] and II,[5] the main elements of such a theory were presented for the calculation of molecular as well as atomic properties.

In paper I, atomic terms were defined for an atom X as the sum of those integrals which represent the mutual interaction between the core of X and the electrons belonging to atomic orbitals of X. The relationship between this term and the "neutral electronegativity" is shown by the analogy which exists between the diagonal term of an LCAO-type matrix and the empirical definition of electronegativity. On this basis, the principle of electronegativity equalization was discussed, and it was recognized that, although the concept seems to be correct, it would be completely rational if this equalization also included the molecular terms[6] as required by the variational procedure.

A molecule will thus reach its maximum stability when the potentials around each atom in each orbital are equalized; *i.e.*

$$\frac{\partial E_{\text{total}}}{\partial q_x{}^i} = \frac{\partial E_{\text{total}}}{\partial q_y{}^i}$$

where $q_x{}^i$ and $q_y{}^i$ are the charge densities due to electron $i$ in atomic orbitals $x$ and $y$. In other words, this means that the tendency to modify the population in each atomic orbital is zero in the stable molecule.

This aspect of bonding which characterizes all self-consistent orbitals through the procedure of minimization and which agrees with the generalized principle of molecular electronegativity equalization, has led us to call such orbitals, equipotential orbitals.

In order to build such equipotential orbitals and to calculate the resulting binding energy, molecular terms have to be introduced into the calculations. This has been realized for diatomic molecules with the help of an LCAO–MO approximation based on a SCF procedure in part II. The practical application to the calculation of bond energies and charge densities in these molecules gave most encouraging results.

The complete general formulation of the theory will now be described and applied to a preliminary study of a few inorganic polyatomic molecules. The case of conjugated molecules will also be examined, thus providing a basis for comparison with existing theories.

## II. Theory

According to the variational principle, the total energy of a polyelectronic molecule is given by $E = \int \Psi H \Psi \, d\tau$, where $\Psi$ is an antisymmetrized product of monoelectronic molecular orbitals. This procedure can be simplified by introducing barycenters of states which then allow the sets of electrons with positive and negative spins[5] to be treated separately.

In order to determine the total wave functions $\Psi$ and $\bar{\Psi}$,[7] the best possible molecular orbitals $\varphi_P$ have to be found. This is usually achieved by writing these molecular orbitals as linear combinations of atomic orbitals.

$$\varphi_P(i) = \sum_A C_A{}^P \Phi_A \qquad \bar{\varphi}_P(i) = \sum_A \bar{C}_A{}^P \bar{\Phi}_A$$

This treatment, which requires a procedure similar to that developed by Roothaan for the most general case,[8] can be simplified by making the following two assumptions: (1) all Coulomb interactions between two orbitals, say $k$ and $l$ (core$_k$–core$_l$, core$_k$–electron$_l$, core$_l$–electron$_k$, electron$_k$–electron$_l$) are equated to a unique function (central field approximation)

(1) R. G. Parr, "The Quantum Theory of Molecular Electronic Structures," W. A. Benjamin, Inc., New York, N. Y., 1963.

(2) J. R. Arnold, *J. Chem. Phys.*, 24, 181 (1956); R. Ferreira, *Trans. Faraday Soc.*, 59, 1064, 1075 (1963); L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960; R. G. Pearson and H. B. Gray, *Inorg. Chem.*, 2, 358 (1963).

(3) L. C. Allen and A. M. Karo, *Rev. Mod. Phys.*, 32, 275 (1960).

(4) G. Klopman, *J. Am. Chem. Soc.*, 86, 1463 (1964).

(5) G. Klopman, *ibid.*, 86, 4550 (1964).

(6) This has since been recognized also by Ferreira who improved very much his empirical theory of bonding in diatomic molecules by

including this correction into his calculation: R. Ferreira, *J. Phys. Chem.*, 68, 2240 (1964).

(7) A bar will be used throughout this paper to characterize quantities related to electrons with spin $\beta$.

(8) C. C. J. Roothaan, *J. Chem. Phys.*, 19, 1445 (1951).

$$\Gamma_{kl} = (kk/ll)$$

(The advantages and limitations of this approximation have been discussed in a previous communication and will not be dealt with further here.); (2) the differential overlap between orbitals of different atoms is neglected.

Concerning this assumption which has been fully discussed in the case of conjugated molecules, it is necessary to make the following comments. In polyatomic nonconjugated molecules, the atoms usually bring more than one atomic orbital into the molecular orbital; integrals of the type $[ab/ab]$ (where $a$ and $b$ are atomic orbitals belonging to the same atom) thus appear in the treatment. These should, according to the above hypothesis, be equated to zero, but the interaction between two electrons with the same or with opposite spin would then become equal. This is contrary to the conclusions drawn in part I from a study of the ultraviolet spectra of the atoms, where these integrals were found to differ significantly from zero. For this reason the use of the zero differential overlap approximation will be restricted to orbitals belonging to different atoms.

Another difficulty may arise from the fact that the overlap is usually not negligible for $\sigma$-bonds. This will not at first sight modify significantly the results for ground-state species, but might possibly introduce important discrepancies in some excited species.

With these two hypotheses, the treatment is much simpler, but the complete solution of the problem still requires the evaluation of some polycentric integrals. These were classified into two useful groups, atomic and molecular terms, which can be evaluated empirically according to the procedure described in the next section.

## III. Procedure

The general name "atomic terms" includes the following interactions: $B_k{}^X$ is the interaction between the core of X and the electrons belonging to an atomic orbital $k$ of atom X. $A^+_{kj}$ and $A^-_{kj}$ are the interactions between two electrons with the same and opposite spin, respectively, and belonging to atomic orbitals $k$ and $j$ of the atom X. Only electrons belonging to the valence shell are taken into account; other electrons are included in the core.

The values of $B$, $A^-$, and $A^+$ can be calculated from a comparison between the spectroscopically determined values of the energies of the barycenters of atomic states and those calculated from eq. 1.[4]

$$E = \sum_i B_k{}^X + \frac{1}{2}\sum_i \sum_{j \neq i} A^+_{ij}\,\delta_{ij} + \frac{1}{2}\sum_i \sum_{j \neq i} A^-_{ij}(1 - \delta_{ij}) \quad (1)$$

where $\delta_{ij}$ is the Kronecker symbol, equal to 1 if electrons $i$ and $j$ have the same spin, and equal to zero otherwise.

The introduction of these atomic terms into the procedure described in section II leads to an equation (eq. 2) which allows the calculation of the energy of any molecular state to be performed

$$E = \sum_k [(q_k + \bar{q}_k)(B_k - \sum_{l \neq k}\Gamma_{kl}N_l) + q_k\bar{q}_k A^-_{kk}] +$$
$$\sum_k \sum_{l > k} [\Gamma_{kl}N_k N_l + 2(p_{kl} + \bar{p}_{kl})B_{kl} +$$
$$(q_k q_l - p^2_{kl} + \bar{q}_k\bar{q}_l - \bar{p}^2_{kl})(A^+_{kl} + \Gamma_{kl}) +$$
$$(q_k\bar{q}_l + \bar{q}_k q_l)(A^-_{kl} + \Gamma_{kl})] \quad (2)$$

where $N_k = 2, 1$, or 0 depending on whether orbital $k$ is occupied by 2, 1, or 0 electrons in the valence state of the isolated atom; $q_k$ and $\bar{q}_k$ are the total charge densities $(= \sum_i C_k{}^{i2})$ of $\alpha$ and $\beta$ spinned electrons, respectively, in the orbital $k$; $p_{kl}$ and $\bar{p}_{kl}$ are the $kl$ bond indices $(= \sum C_k{}^i C_l{}^i)$ due to $\alpha$ and $\beta$ spinned electrons, respectively; $\Gamma_{kl}$ and $B_{kl}$ represent, respectively, the bicentric Coulomb integral (see hypothesis 1) and the resonance integral between orbitals $k$ and $l$.

Minimization of this equation with respect to $\sum C_k{}^i$ leads to the following equations for the diagonal and nondiagonal terms of the resultant secular equation.

$$\alpha_{kk} = B_k - \sum_{l \neq k}\Gamma_{kl}N_l + \bar{q}_k A^-_{kk} +$$
$$\sum_{l \neq k}[q_l A^+_{kl} + \bar{q}_l A^-_{kl} + (q_l + \bar{q}_l)\Gamma_{kl}]$$
$$\alpha_{kl} = B_{kl} - p_{kl}A^+_{kl} - p_{kl}\Gamma_{kl} \quad (3)$$

The resulting procedure which has been programmed in our laboratories in Algol 803 consists in solving the $\alpha$-matrix. The eigenvectors obtained in this way are used to build a new $\alpha$-matrix, and this process is repeated until self-consistency is reached.

Although this calculation gives equipotential orbitals whose electronic distribution represents the actual distribution in the molecules, it leads to calculated energies which measure the ease of removal of electrons from the equipotential orbitals (or energy of adding an electron in the case of an empty orbital) without perturbing the remaining polyelectronic systems. Therefore the total energy is not the sum of the various orbital energies, since electronic repulsions would be counted twice, but is obtained by replacing the charges in eq. 2 by their calculated values for the occupied equipotential orbitals.

It is interesting to note that eq. 2 and 3 should be as valid for open shells or ionized species as for closed shells. In order to proceed with the calculations, it is necessary to attribute values to the two molecular terms $\Gamma_{kl}$ and $B_{kl}$. This may be done with the help of the hypothesis and formulas already described in part II

$$\Gamma_{kl} = \frac{-14.388}{\sqrt{r^2 + (\rho_k + \rho_l)^2}}$$

where $\rho_k = 0$ for $p_\sigma$-orbitals and $-14.388/2A^-_{kk}$ for s- and $p_\pi$-orbitals and for nonbonded orbitals. $B_{kl}$ is the geometric mean of $B_{kk}$ and $B_{ll}$, which have been determined[5] from a suitably chosen reference compound for each atom. Only those values of $B_{kl}$ which characterize the orbitals responsible for the bonding are taken into account, but possibly better results can be obtained by introducing all of them. The $B_{kl}$ values are assumed to be effectively independent of neighbors and of small changes in bond length.

It is important to point out, however, that the determination of $B_{kl}$ and $\Gamma_{kl}$ is not really critical to the theory, and better formulas may possibly be found. Nevertheless, the simple equations proposed here are sufficiently accurate for the present purpose.

## IV. Application to Nonconjugated Molecules

In part II, the general approach described in the previous section has been applied successfully to the cal-

**Table I.** Ionization Potential of Diatomic Molecules

| Molecules | Ionization potential, e.v. Calcd. | Obsd.[a] |
|---|---|---|
| H | 15.3 | 15.4 |
| Li₂ | 5.6 | ... |
| Na₂ | 5.2 | ... |
| K₂ | 4.3 | ... |
| Rb₂ | 4.1 | ... |
| Cs₂ | 3.9 | ... |
| HI | 10.9 | 10.4 |
| HBr | 12.0 | 11.6 |
| HCl | 12.9 | 12.7 |
| HF | 15.1 | 15.8 |
| KI | 7.0 | 8.3 |
| HCl → HCl²⁺ | 34.7 | (36)[b] |

[a] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer,* **2,** 369 (1962). [b] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.

The charge distributions and orbital energies for the various compounds are not reported in detail, but are illustrated for one case only, *i.e.,* ionized water; for an OH distance of 0.958 Å. and an H–H separation of 1.52 A., the orbital energies and charge densities recorded in Table III are obtained assuming that the ionized electron is removed from the $2p_\pi$-orbital of oxygen.

A direct comparison with experiment is provided by the results obtained for the calculations of thermochemical quantities.

The calculated and observed heats of formation and ionization energies for several oxygen derivatives are compared in Table IV.

The agreement here also is good enough to provide interesting observations; for example, we find in complete agreement with experiment that the OH bond energy in $H_2O$ is 109.5 kcal., although the bond dissocia-

**Table II.** Charge Distribution and OH Bond Index in Hydroxylic Derivatives

| Compound H–O–X–Y | Charges on atom H | O | X | Y | OH bond index[a] |
|---|---|---|---|---|---|
| H–O | +0.3229 | −0.3228 | ... | ... | 0.9314 |
| [H–O]⁺ | +0.6311 | +0.3689 | ... | ... | 0.7510 |
| [H–O]⁻ | −0.1912 | −0.8088 | ... | ... | 0.9815 |
| H–O–H | +0.3179 | −0.6358 | +0.3179 | ... | 0.9482 |
| [H–O–H]⁺ | +0.6207 | −0.2414 | +0.6207 | ... | 0.7767 |
| H–O–O–H | +0.2633 | −0.2632 | −0.2632 | +0.2633 | 0.9647 |
| H–O–Cl | +0.3252 | −0.3110 | −0.0150 | ... | 0.9456 |
| H–O–Na | +0.0374 | −0.8112 | +0.7739 | ... | 0.9993 |

[a] The bond index as reported here is equal to $p_{OH} + \bar{p}_{OH}$ and refers to the bond between the $2p_\sigma$-orbital of oxygen and the 1s-orbital of hydrogen.

culation of bond energies and charge distribution in the simple case of $\sigma$-bonded diatomic molecules.

It has now been extended to the calculation of the energy of core electrons in these systems, thus providing a basis for the calculation of ionization potentials. The results, reported in the second column of Table I are in fair agreement with the observed values of column 3.

In a preliminary study of polyatomic molecules, the physical properties of oxygen and several of its hydrogenated derivatives have been investigated.

The atomic terms of oxygen and hydrogen have been calculated previously[4]; they are (in e.v.): $B_p^{ox} = 80.591$, $B_s^{hydr} = 13.595$, $A^+_{ox} = -12.149$, $A^-_{ox} = -13.707$, $A^-_{hydr} = -12.845$.

The molecule OH has been chosen as the reference compound to determine the resonance integral of oxygen. With a bond distance of 0.9706 Å., the calculated bond energy is in agreement with the experimental value of 101 kcal., when the parameter $B_{OH}$ between the $2p_\sigma$-orbital of oxygen and the 1s-orbital of hydrogen has the value of 2.498 e.v., all the values of $B_{OH}$ between other orbitals of oxygen and hydrogen being neglected. Since $B_{HH}$ (for a 1s–1s bond) was previously found to be equal to 2.771 e.v.,[5] we find that $B_{OO} = B^2_{HH}/B_{OH} = 2.252$ e.v. (for a $2p_\sigma$–$2p_\sigma$ oxygen–oxygen bond).

The introduction of these values and the experimental bond distances[9] into the previously described procedure has allowed us to calculate the thermochemical quantities and charge distribution (Table II) of several oxygen derivatives.

(9) L. E. Sutton, "Tables of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

**Table III.** Charge Densities and Vertical Ionization Energies of $H_2O$ ⁺

| Vertical ionization energies, e.v.[a] | Charge densities in orbital H₁ₛ¹ | O⁺ₓ₂pσ | Oʸ₂pπ | O²₂pσ | H₁ₛ² |
|---|---|---|---|---|---|
| *Occupied Orbitals* | | | | | |
| 28.35 | 0.148 | 0.852 | 0 | 0 | 0 |
| 28.35 | 0 | 0 | 0 | 0.852 | 0.148 |
| 26.88 | 0.232 | 9.768 | 0 | 0 | 0 |
| 26.88 | 0 | 0 | 0 | 0.768 | 0.232 |
| 25.38 | 0 | 0 | 1 | 0 | 0 |
| *Nonoccupied Orbitals* | | | | | |
| 11.37 | 0 | 0 | 1 | 0 | 0 |
| 8.18 | 0 | 0 | 0 | 0.148 | 0.852 |
| 8.18 | 0.852 | 0.148 | 0 | 0 | 0 |
| 7.85 | 0 | 0 | 0 | 0.232 | 0.768 |
| 7.85 | 0.768 | 0.232 | 0 | 0 | 0 |

[a] The vertical ionization energies obtained here are the energies required to remove electrons without involving a change in either the distance or the charge distribution in the remaining ion.

tions are

$$HO\text{-}H \longrightarrow HO + H \qquad 118 \text{ kcal.}$$

$$O\text{-}H \longrightarrow O + H \qquad 101 \text{ kcal.}$$
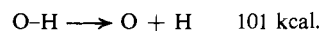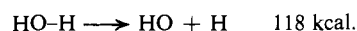
Similarly, we find that the dissociation energy of the O–O bond in $H_2O_2$

$$HO\text{-}OH \longrightarrow 2OH \qquad 53 \text{ kcal.}$$

is in good agreement with experiment (experimental value 50 kcal.).

**Table IV.** Thermochemical Properties of Oxygen Derivatives

| Compound | Calcd. | Obsd. |
|---|---|---|
| Heats of Formation (kcal.)[a] | | |
| OH | 101 | 101 |
| $H_2O$ | 219 | 219 |
| NaOH | 168 | 188 |
| HOCl | 157 | 160 |
| $H_2O_2$ | 255 | 252 |
| Ionization Potentials (e.v.)[b] | | |
| $OH \rightarrow OH^+$ | 12.8 | 13.2 |
| $H_2O \rightarrow H_2O^+$ | 12.2 | 12.6 |
| Electron Affinity (e.v.)[c] | | |
| $OH \rightarrow OH^-$ | 1.95 | 2.11 |

[a] "JANAL Thermochemical Tables," Dow Chemical Co., Midland, Mich. [b] See footnote a, Table I. [c] See footnote b, Table I.

These calculations may be extended to the field of heteroatomic saturated compounds and might be of great interest, not only in the calculation of heats of formation and ionization potentials, but also charge densities by means of which the chemical properties can be interpreted.

## V. Application to Conjugated Organic Molecules

The general procedure described in the preceding sections can be applied directly to the calculation of the molecular properties of conjugated molecules. The $\sigma$-core can be included in a self-consistent way, but in this case matrices of high degree have to be solved.

However, an approximation can be made by first assuming an equal distribution of $\pi$-electrons in the molecule, then calculating the $\sigma$-bonds in a self-consistent way and finally building on this rigid nonpolarizable $\sigma$-core a new $\pi$-electronic distribution. To do this, a well-defined arrangement of $\sigma$- and $\pi$-orbitals in space has to be chosen in advance by assuming the $\sigma$-orbitals to be pure coplanar $sp_2$ hybridized orbitals pointing in the direction of the bonded atoms, the $p\pi$-orbital being perpendicular to this plane.

A further simplification can be made by considering the framework to be a constant, uniform, and nonpolarizable system, and by building the $\pi$-system on it. In such a case, each carbon atom contributes one orbital to the $\pi$-system, and all the values of $N$ are equal to 1. In this way, terms such as $A^+_{kl}$ and $A^-_{kl}$ need not be considered.

On the other hand, if closed shell molecules only are considered, the charges due to $\alpha$ and $\beta$ electrons of opposite spin are identical, i.e.

$$q_k = \bar{q}_k = {}^1/_2 P_{kk} \quad p_{kl} = \bar{p}_{kl} = {}^1/_2 P_{kl}$$

where $P_{kk}$ is the charge index and $P_{kl}$ is the bond index.

Let $B_k = H_{kk}$, $B_{kl} = H_{kl}$, $A^-_{kk} = \langle kk|G|kk \rangle$, $\Gamma_{kl} = \langle kl|G|kl \rangle$. Introduction of these new approximations and the above symbolism into eq. 3 leads to the following expressions for the matrix elements (eq. 4).

$$\alpha_{kk} = H_{kk} + {}^1/_2 P_{kk}\langle kk|G|kk \rangle + \sum_{l \neq k}(P_{ll} - 1)\langle kl|G|kl \rangle \tag{4}$$

$$\alpha_{kl} = H_{kl} - {}^1/_2 P_{kl}\langle kl|G|kl \rangle$$

These expressions are equivalent to those proposed by Pople[10] in his SCF treatment of conjugated mole-

cules, which thus appears to be a particular case of our general treatment. Within the above approximations, both treatments are equivalent and all the results obtained by the Pariser and Parr[11] and Pople treatments could be obtained by our method, provided that the parameters used by these authors and in this method (that is, the resonance integral and the Coulomb integrals) can be shown to be identical.

In both methods the resonance integral is determined from the best fit with experimental values: i.e., $\beta \sim 2.4$ e.v. The Coulomb integrals between $\pi$-orbitals are obtained by our procedure, from the following equation

$$\Gamma_{AB} = -\frac{14.388}{\sqrt{r^2_{AB} + (\rho_A + \rho_B)^2}} \text{ e.v.} \tag{5}$$

where $\rho_A = \rho_B = -{}^1/_2(14.388/A^-_{carbon}) = 0.645$ Å. and $A^-_{carbon} = -11.144$. In the Pariser–Parr and Pople procedure, many approximations have been suggested for the evaluation of $\Gamma$, all of these leading to values lower than that obtained by using Slater orbitals.

Apart from the purely empirically determined value, it is worthwhile mentioning other methods, such as the uniformly charged sphere approximation[12]; the methods proposed by Kolos[13] and Julg[14]; the split $\pi$-orbital approximation[15]; and finally the equation proposed by Mataga,[16] i.e., $\Gamma = e^2/R$, where $R = a + r_{AB}$ and $a = e^2/(I - A)$, and by Ohno,[17] $\Gamma = e^2/R$, where $R = \sqrt{a^2 + r_{AB}^2}$ and $a = e^2/(I - A)$, which are actually analogous to eq. 5.

In Table V the values of the Coulomb integral obtained from the various methods are compared.

**Table V.** Calculation of Coulomb Interactions

| Method | Distance, Å. | | | |
|---|---|---|---|---|
| | 0 | 1.397 | 2.420 | 2.794 |
| Slater[11] | 16.93 | 9.027 | 5.668 | 4.968 |
| Pariser–Parr[11] | 10.53–11.1 | 7.30 | 5.46 | 4.90 |
| Julg[14] | 9.8 | 7.45 | ... | ... |
| Dewar[15] | 10.02 | 7.61 | ... | ... |
| Kolos[13] | 10.1 | 7.78 | ... | ... |
| This work | 11.144 | 7.56 | 5.25 | 4.68 |

They appear to be consistent with those from our simplified treatment, and therefore one may consider that the results from both methods are similar. It would be interesting, however, to test the other proposed approximations, i.e., modified $\sigma$-core values and the complete SCF treatment, and this will be done in a forthcoming publication.

(10) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
(11) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).
(12) R. G. Parr, *ibid.*, **20**, 1499 (1952).
(13) W. Kolos, *Acta Physiol. Polon.*, **16**, 257, 267, 299 (1957).
(14) A. Julg, *Tetrahedron Suppl.*, **2**, 25 (1963).
(15) M. J. S. Dewar and C. E. Wulfman, *J. Chem. Phys.*, **29**, 158 (1958).
(16) N. Mataga, *Bull. Chem. Soc. Japan*, **31**, 453 (1958).
(17) K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).