Theoret. chim. Acta (Berl.) 14, 91—135 (1969)

Indagationum conspectus

On the Development of Semiempirical Methods in the MO Formalism

KARL JUG

Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616, USA

Received December 6, 1968

Reviews on semiempirical methods treating chemical bonding in the framework of quantum mechanics have been a favored subject for a long time. Recent tendencies have been described by Y. I'Haya [92], P. G. Lykos [132], R. McWeeny [140], I. Fischer-Hjalmars [48–51], K. Ohno [154]. The author will follow along these lines with no intention to be complete: *e.g.* ligand field theory will not be a topic of this paper.

Instead, the author will try to give a more systematic way for a comparison of different π-electron theories and the recent extensions to σ-electrons than has been done before. For more than one reason, the year 1963 has brought a significant change. The π-electron theories had reached a culmination point with Berthier's complete explanation of the Pariser-Parr approximation. Parr and Del Re showed a way towards an improved π-electron theory. Correction effects like π-electron polarization in the effective Hamiltonian, inclusion of $3p\pi$- and $3d\pi$-orbitals and π-electron correlation had become familiar extensions. According to Orloff and Fitts larger molecules should be attacked by an Aufbau principle. This situation was well represented in Parr's well known book. At the same time doubts were expressed that some basic assumptions of the π-electron approximation were not valid. This led to an extension of the Hückel scheme by Hoffmann. Since then inclusion of all valence electrons or even "non-bonding" $1s$-electrons has become a definitive necessity. Recently some contribution on the questions involved has been given by ab-initio calculations (Preuss [180]; Clementi [24, 25]).

The following introductory remarks on the LCAO formalism may be regarded as a guide-line for comparison and discussion of π-electron and all valence electron theories. Basic assumptions, matrix elements of the SCF operator, expressions for the total electronic energy, and the remaining basic quantities are presented for easy comparison. Tables on the various choices of parameters are included as they have been proposed or used.

This representation is by no means complete. So far there is little insight how to integrate properly configuration interaction or, more general, correlation in a semiempirical scheme. Yet, the author hopes that this systematic way of representation may clarify what kind of restrictions are involved in the present theories and may be helpful to support studies in the directions shown below.

I. Introductory Remarks

1. The Total Energy of an Electronic State

Neglecting spin-orbit, spin-spin and relativistic effects the Hamiltonian for n electrons in a molecule is defined in the Born-Oppenheimer approximation as

$$H = H_{\text{core}} + \frac{1}{2} \sum_{i,j}^{n} \frac{1}{r_{ij}} \tag{1.1}$$

where H_{core} is the sum of the kinetic and potential energies of all electrons in the field of the core

$$H_{\text{core}} = \sum_{i}^{n} [T(i) + U_{\text{core}}(i)]\,. \tag{1.2}$$

In order to get the electronic energy of the system, we have to find a solution of the relevant eigenvalue equation

$$H\Psi = E\Psi\,. \tag{1.3}$$

As in most cases the eigenvalue problem (1,3) is too complicated to yield directly analytical expressions as solutions, we have to restrict ourselves to approximations. Among those, one of the best-known is the ASMO CI (antisymmetric molecular orbital configuration interaction) approximation which represents the total wavefunction Ψ as a finite linear combination of antisymmetrized product functions Φ consisting of molecular orbitals ϕ. The Φ's may be taken in the form of determinants:

$$\Psi = \sum_{i}^{K} A_i \Phi_i \tag{1.4}$$

with $\Phi_i = \det|\phi_{i_1} \phi_{i_2} \ldots \phi_{i_n}|$.

The coefficients A_i are regarded as variation parameters and determined by the application of the variation principle to the total energy expression

$$E = \frac{\langle \Psi | H\Psi \rangle}{\langle \Psi | \Psi \rangle}\,. \tag{1.5}$$

This yields a set of linear equations for the A_i

$$\sum_m^K A_m(H_{mn}-S_{mn}E)=0, \qquad n=1\ldots K \tag{1.6}$$

and a secular equation for E

$$\det|H_{mn}-S_{mn}E|=0 \tag{1.7}$$

where S_{mn} and H_{mn} are integrals over Φ functions:

$$S_{mn}=\int \Phi_m^*\Phi_n d\tau\,, \tag{1.8a}$$

$$H_{mn}=\int \Phi_m^* H \Phi_n d\tau\,. \tag{1.8b}$$

With increasing number K of *configurations* Φ_i the total wavefunction can be approximated to any desired degree if the Φ_i form a complete set of functions.

In order to be able to calculate the values of the integrals S_{mn} and H_{mn} in special cases one has to have a method to get the necessary information about the ϕ's which build up the Φ's. The idea behind the concept of molecular orbitals is the *independent particle* picture. It is assumed that each electron moves independent from the other electrons in an *effective* field arising from the nuclei and the other electrons.

$$H=H_0+H_1 \tag{1.9}$$

$$\text{with } H_0=\sum_i^n H_{\text{eff}}(i).$$

With the assumption $H=H_0$, regarding H_1 as a small perturbation, one is able to separate the Schrödinger Eq. (1.3) and to solve the equation for each electron separately. It is advantageous to use the same form of H_{eff} for all electrons because in this case one has only one representative eigenvalue problem to solve, the eigenfunctions of which can easily be obtained as an orthogonal set:

$$H_{\text{eff}}\phi_i=\varepsilon_i\phi_i\,. \tag{1.10}$$

The energy integrals over antisymmetrized product functions built up from an orthogonal set of MO's can be simplified to a high degree (Parr [166]).

H_{eff} may be chosen as $H_{\text{core}}(i)$ or as the self-consistent field operator $F=H_{\text{core}}(i)+G(i)$, where the last operator represents an average electronic repulsion field. The self-consistent field approximation can be adopted only if the total energy can be expressed in a special form (Roothaan [184, 185]). In this case, the assumption that H_{eff} is equal for all electrons cannot be preserved in general, especially if the molecule contains an odd number of electrons. Besides, one has to have a certain knowledge of all orbitals ϕ_i which are used to describe electrons, in order to have a starting point for an effective field resulting from the core and averaged electronic repulsion.

Once the ϕ_i are known the integrals S_{mn} and H_{mn} are expressible in terms of the following integrals

$$S_{ij}=\int \phi_i^*\phi_j d\tau\,, \tag{1.11a}$$

$$I_{ij}=\int \phi_i^* H_{\text{core}}\phi_j d\tau\,, \tag{1.11b}$$

$$J_{ijkl}=\int \phi_i^*(1)\phi_k^*(2)\frac{1}{r_{12}}\phi_j(1)\phi_l(2)d\tau_1 d\tau_2\,. \tag{1.11c}$$

2. *Closed and Open Shell Systems*

In many molecules with an even number $2n$ of electrons the most important contribution to the ground state wavefunction Ψ_N arises from one determinant Φ_N only. In this case the electrons can be grouped in pairs where each pair is described by molecular orbitals with the same space part differing only by the spin part α or β.

$$\begin{aligned} \phi_1 &= \psi_1\alpha\,, & \phi_2 &= \psi_1\beta\,, \\ \phi_{2n-1} &= \psi_n\alpha\,, & \phi_{2n} &= \psi_n\beta\,. \end{aligned} \tag{2.1}$$

The ϕ_i resp. ψ_i are solutions of (1.10). The eigenvalues ε_i of (1.10) are ordered according to increasing values and the $2n$ electrons are described to "occupy" the n lowest energy levels, two in each level. As according to the Pauli principle the maximum number of electrons in a non-degenerate level is two, this case is called a "closed-shell" case.

Molecules with an odd number of electrons cannot be described in such a simple way because the resulting spin is different from zero. How to choose an effective Hamiltonian operator $H_{\text{eff}}(i)$ and to obey spin restrictions is reviewed elsewhere (Berthier [8]). Furthermore one cannot distribute all electrons in such a way that each occupied orbital is fully occupied. As there remains at least one "singly occupied" orbital, we call it an "open-shell" case. In the simplest form of an excitation where one assumes that one electron has moved from an occupied to an unoccupied level, we have an open-shell case, too. But we must not forget that our model, where excitation takes place from and to *one-electron* levels, has involved as basis the independent-particle picture.

3. LCAO *Formalism*

Unfortunately there is no easy approach for molecules to solve Eq. (1.10) directly. It was a gratifying idea (Lennard-Jones [115]; Coulson and Longuet-Higgins [28]) to start with a set of atomic orbitals χ_i from which linear combinations are built to approximate the molecular orbitals ψ_i

$$\psi_i = \sum_{\nu}^{A} c_{i\nu}\chi_\nu \tag{3.1}$$

and to determine the coefficients $c_{i\nu}$ by the variation principle. This leads to equations for $c_{i\nu}$ and ε_i similar to (1.6) and (1.7).

$$\sum_{\mu}^{A} c_{i\mu}(H_{\mu\nu}^{\text{eff}} - S_{\mu\nu}\varepsilon_i) = 0\,, \qquad \nu = 1 \ldots A\,, \tag{3.2}$$

$$\det|H_{\mu\nu}^{\text{eff}} - S_{\mu\nu}\varepsilon_i| = 0 \tag{3.3}$$

where $H_{\mu\nu}^{\text{eff}}$ and $S_{\mu\nu}$ are defined as integrals over atomic orbitals

$$S_{\mu\nu} = \int \chi_\mu^*\chi_\nu d\tau\,, \tag{3.4a}$$

$$H_{\mu\nu}^{\text{eff}} = \int \chi_\mu^* H_{\text{eff}}\chi_\nu d\tau\,. \tag{3.4b}$$

The molecular orbitals ψ_i can be approximated to any desired degree and the solutions of Eqs. (3.2) and (3.3) are unique if the atomic basic set is complete. Taking a complete atomic set on each center would lead to an over-complete set. As one uses in practice a rather limited number of functions on each center this difficulty will be in general avoided.

Let us consider the closed-shell case with $2n$ electrons and let us use for H_{eff} the self-consistent field operator (Roothaan [184]; Hall [63])

$$F = H_{\text{core}} + \sum_i^n (2J_i - K_i) \tag{3.5}$$

with

$$J_i(1)\chi_\mu(1) = \int \psi_i^*(2)\psi_i(2)\frac{1}{r_{12}}\,d\tau_2\,\chi_\mu(1)\,,$$

$$K_i(1)\chi_\mu(1) = \int \psi_i^*(2)\chi_\mu(2)\frac{1}{r_{12}}\,d\tau_2\,\psi_i(1)\,.$$

If we take only one configuration as an approximation for the total wavefunction Ψ the total energy can be written as

$$E = \frac{1}{2}\sum_{\mu,\nu}^n P_{\mu\nu}(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \tag{3.6}$$

where the density matrix $P_{\mu\nu}$, the core matrix $H_{\mu\nu}^{\text{core}}$ and the self-consistent-field matrix $F_{\mu\nu}$ have the following meaning.

$$\begin{aligned} P_{\mu\nu} &= 2\sum_i^{\text{occ}} c_{i\mu}^* c_{i\nu} \\ H_{\mu\nu}^{\text{core}} &= \int \chi_\mu^* H_{\text{core}}\chi_\nu\, dv \\ F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + \sum_{\varrho,\sigma} P_{\varrho\sigma}\left[(\mu\nu|\varrho\sigma) - \frac{1}{2}(\mu\sigma|\varrho\nu)\right] \end{aligned} \tag{3.7}$$

with

$$(\mu\nu|\varrho\sigma) = \int \chi_\mu^*(1)\chi_\varrho^*(2)\frac{1}{r_{12}}\chi_\nu(1)\chi_\sigma(2)\,d\tau_1\,d\tau_2\,.$$

In addition, it proves useful later to use the following notation for the elements of the core matrix and the penetration integrals.

$$\begin{aligned} \alpha_\mu &= H_{\mu\mu}^{\text{core}}, \\ \beta_{\mu\nu} &= H_{\mu\nu}^{\text{core}}, \qquad \mu \neq \nu\,, \\ (\nu:\mu\mu) &= -\int \chi_\mu^* U_\nu^* \chi_\mu\, d\tau\,, \end{aligned} \tag{3.8}$$

U_ν^* neutral atom potential.

II. The π-Electron Approximation

1. Pariser-Parr's Method [161]

Basic Assumptions

A. The method is designed for planar unsaturated hydrocarbons and their derivatives. Only the π-electrons of carbon (or hetero) atoms are explicitly taken into consideration. The original version of the theory assumes that each center contributes one π-electron only.

B. The overlap integral is neglected for orbitals on different centers

$$S_{\mu\nu} = \delta_{\mu\nu} \,. \tag{1.1}$$

C. The σ-system is treated as a non-polarizable core and its effect is included in H_{core}

$$H_{\text{core}} = T + U_\mu + \sum_{\sigma \neq \mu} U_\sigma + \sum_{\varrho} U_\varrho^* \,. \tag{1.2}$$

U_μ or U_σ is the potential of a carbon (or hetero) atom deprived of its π-electron described by the atomic orbital χ_μ or χ_σ, U_ϱ^* is the potential of a neutral atom without π-electrons, *e.g.* an H-atom.

D. The potential of an atom contributing one π-electron to the system is replaced by the potential of a neutral atom and an average electronic potential (Goeppert-Mayer and Sklar [60])

$$U_\sigma = U_\sigma^* - \int \chi_\sigma^*(2)\chi_\sigma(2)\frac{1}{r_{12}}\,d\tau_2 \,. \tag{1.3}$$

E. The atomic orbitals are assumed to be eigenfunctions of an appropriate one-electron Hamiltonian (Goeppert-Mayer and Sklar [60])

$$(T + U_\mu)\chi_\mu = W_\mu \chi_\mu \tag{1.4}$$

where W_μ is considered as an atomic valence state potential.

F. The resonance integral is zero for μ, ν non-nearest neighbours

$$\beta_{\mu\nu} = \begin{cases} \beta \text{ for } \mu, \nu \text{ nearest neighbours}, \\ 0 \text{ in any other case}. \end{cases} \tag{1.5}$$

G. Zero differential overlap assumption for electronic repulsion integrals

$$(\mu\nu|\varrho\sigma) = (\mu\mu|\varrho\varrho)\delta_{\mu\nu}\delta_{\varrho\sigma} \,. \tag{1.6}$$

Matrix Elements

With assumptions 1D and 1E we can rewrite α_μ as

$$\alpha_\mu = W_\mu - \sum_{\sigma \neq \mu} [(\sigma\sigma|\mu\mu) + (\sigma : \mu\mu)] - \sum_{\varrho} (\varrho : \mu\mu) \tag{1.7}$$

and furthermore H_{eff} which is taken as the self-consistent field operator F

$$F_{\mu\mu} = W_\mu + \frac{1}{2} P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - 1)(\sigma\sigma|\mu\mu) - \sum_{\sigma \neq \mu} (\sigma : \mu\mu) - \sum_{\varrho} (\varrho : \mu\mu)\,, \tag{1.8a}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu}(\mu\mu|\nu\nu)\,. \tag{1.8b}$$

The total electronic energy may then be formulated as

$$\begin{aligned} E = {} & \sum_{\mu} P_{\mu\mu}\left[W_\mu + \frac{1}{4} P_{\mu\mu}(\mu\mu|\mu\mu)\right] + \sum_{\substack{\mu,\nu \\ \mu \neq \nu}} P_{\mu\nu}\beta_{\mu\nu} - \sum_{\mu}\sum_{\sigma \neq \mu} P_{\mu\mu}(\sigma : \mu\mu) \\ & - \sum_{\mu}\sum_{\varrho} P_{\varrho\varrho}(\varrho : \mu\mu) + \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu \neq \nu}}\left[(P_{\mu\mu} - 1)(P_{\nu\nu} - 1) - \frac{1}{2} P_{\mu\nu}^2 - 1\right](\mu\mu|\nu\nu) \end{aligned} \tag{1.9}$$

Basic Quantities

The remaining quantities to be determined are:

$-W_\mu$ is taken as atomic valence state ionization potential of a $2pz$-electron.

β is chosen to adjust the theoretical value for the first excited singlet state to the empirical value; it depends on the choice of the repulsion integrals; for cases with heteroatoms more than one β-value is necessary.

$(\mu\mu|\mu\mu)$ 1. is calculated theoretically by taking Slater type orbitals for χ, using Slaters shielding exponents.

2. is set equal to the difference of ionization potential I and electron affinity A of a carbon atom $I - A$.

$(\mu\mu|\nu\nu)$ 1. is calculated theoretically like $(\mu\mu|\mu\mu)$.

2. is calculated by the uniformly charged sphere approximation; the diameter of the two tangent spheres $R_\mu = R_\nu = (4.597/Z_\mu)\,10^{-8}$ cm, Z_μ Slater's effective nuclear charge is calculated by fitting the theoretical value of $(\mu\mu|\mu\mu)$ to the classical electrostatic self-energy of a sphere.

3. is calculated by using an approximation formula with a quadratic dependency on the distance R for distances less or equal to 2.8 Å

$$aR + bR^2 = \tfrac{1}{2}[(\mu\mu|\mu\mu) + (\nu\nu|\nu\nu)] - (\mu\mu|\nu\nu), \qquad R \leqq 2.8\,\text{Å}\,.$$

a and b are fitted for 2.8 Å and 3.7 Å by the uniformly charged sphere model which is generally used for distances larger than 2.8 Å.

$(\nu : \mu\mu)$ 1. is calculated theoretically like $(\mu\mu|\mu\mu)$.

2. is calculated by an approximation formula which has a quadratic dependency for distances up to 2.8 Å and is set equal to zero for larger distances

$$\left.\begin{aligned} a'R + b'R^2 &= W_\mu - W_\nu + (\mu : \nu\nu) - (\nu : \mu\mu) + (\mu\mu|\mu\mu) - (\mu\mu|\nu\nu)\,, \\ a''R + b''R^2 &= W_\nu - W_\mu + (\nu : \mu\mu) - (\mu : \nu\nu) + (\nu\nu|\nu\nu) - (\nu\nu|\mu\mu) \end{aligned}\right. \quad R \leqq 2.8\,\text{Å}$$

is equal to zero for $R > 2.8$ Å.

a', b', a'', b'' are fitted for 2.8 Å and 3.7 Å.

The formula is good only for the calculation of differences of penetration integrals; this is sufficient for the calculation of excitation energies.

Comments

The above described method is distinguished by a remarkable simplicity which was the reason for innumerable applications. Although improvements have been made in the meantime, one should not forget the courage which was necessary to establish the ZDO assumptions (1.1) and (1.6) which are essentially the reason for its applicability. Those were by no means easily justified. They were even used in *differential* form, instead of the less strong, but sufficient *integral* one. Also assumption (1.4) has been proved to be rather a weak point. Here again the integral form as used by Berthier is less restrictive. On the other hand, the adjustment of β in connection with the choice of electronic repulsion integrals made the scheme superior to Hückel's method. A better understanding was given later by Berthier [9] and Fischer-Hjalmars [49, 50]. The Pariser-Parr method has been reinterpreted recently by Koutecký [112]. Also a representation in the second quantization formalism has been attempted (Linderberg and Öhrn [120]).

2. *Pople's Method* [171]

Basic Assumptions

A. Essentially 1A. An extension to hetero atoms with more than one π-electron is included.

B. The same as 1B.

C. The σ-system is treated as a non-polarizable core and its effect is included in H_{core}. Neutral atom potentials are not explicitly considered.

$$H_{\text{core}} = T + U_\mu + \sum_{\sigma \neq \mu} U_\sigma . \tag{2.1}$$

D. The interaction integrals between electrons and different cores are expressed by the interaction of point charges; Z is an effective core charge.

$$\int \chi_\mu^* U_\sigma \chi_\mu d\tau = -Z_\sigma R_{\mu\sigma}^{-1} . \tag{2.2}$$

E. Essentially the same as 1E.

F. The same as 1F.

G. The same as 1G.

H. The remaining interaction integrals between electrons on different centers are expressed by the interaction of point charges

$$(\mu\mu|\nu\nu) = R_{\mu\nu}^{-1} . \tag{2.3}$$

Matrix Elements

With these assumptions the diagonal core element takes the form

$$\alpha_\mu = W_\mu - \sum_{\sigma \neq \mu} Z_\sigma R_{\mu\sigma}^{-1} \tag{2.4}$$

and the elements of the Hartree-Fock operator may be rewritten as

$$F_{\mu\mu} = W_\mu + \frac{1}{2} P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - Z_\sigma) R_{\mu\sigma}^{-1} , \tag{2.5a}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu} R_{\mu\nu}^{-1} . \tag{2.5b}$$

The total electronic energy expression takes the form

$$E=\sum_{\mu} P_{\mu\mu}\left[W_{\mu}+\frac{1}{4} P_{\mu\mu}(\mu\mu|\mu\mu)\right]+\sum_{\substack{\mu,\nu \\ \mu\neq\nu}} P_{\mu\nu}\beta_{\mu\nu}$$
$$+\frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}\left[(P_{\mu\mu}-Z_{\mu})(P_{\nu\nu}-Z_{\nu})-\frac{1}{2}P_{\mu\nu}-Z_{\mu}Z_{\nu}\right]R_{\mu\nu}^{-1}. \tag{2.6}$$

Basic Quantities

W_{μ} is unspecified, should be the same for all molecules.
$\beta_{\mu\nu}$ is calculated through the resonance energy of benzene

$$\varepsilon_{\pi}(\text{benzene})-3\varepsilon_{\pi}(\text{ethylene})=2\beta-\tfrac{1}{12}R^{-1}.$$

$(\mu\mu|\mu\mu)$ is unspecified.
Z_{σ} is taken equal to unity for carbon atoms, unspecified for hetero atoms.
$R_{\mu\sigma}$ molecular distance.

Comments

Basically different from the Pariser-Parr treatment is the neglect of penetration integrals and the assumption of point charge interactions. Both contributed to a further simplification of the scheme and made the effect of net charges on atoms more visible. It may be added that Pople liked to define the π-electron energy by adding the nuclear core repulsion which cancels the last term in the bracket of (2.6). Unfortunately some parameters remained unspecified. In later papers (Brickstock and Pople [15]; Hush and Pople [90]) assumptions 2D and 2H were dropped. β, $(\mu\mu|\mu\mu)$ and $(\mu\mu|\nu\nu)$ were calculated according to Pariser-Parr's method; W_{μ} shall fit the ionization potential of benzene and is assumed to include the neutral atom effect.

3. *Ruedenberg's Method* [187]

Basic Assumptions

A. Essentially the same as 1A.
B. The overlap integral is taken into account if μ,ν are nearest neighbours

$$S_{\mu\nu}=\delta_{\mu\nu}+SM_{\mu\nu} \quad \text{with} \quad M_{\mu\nu}=\begin{cases}1 \text{ for } \mu,\ \nu \text{ nearest neighbours},\\ 0 \text{ otherwise}.\end{cases} \tag{3.1}$$

C. The σ-system is treated as a non-polarizable core and its effect is included in H_{core}

$$H_{\text{core}}=T+\sum_{\mu\in \text{C}} U_{\mu}+\sum_{\nu\in \text{H}} U_{\nu} \tag{3.2}$$

where U_{μ} and U_{ν} are the potentials of the framework without the π-electrons.

D. Essentially the same as 1D.

$$U_\mu = U_\mu^* - \int \chi_\mu^*(2)\chi_\mu(2)\frac{1}{r_{12}}\,d\tau_2\,, \tag{3.3a}$$

$$U_\nu = U_\nu^*\,, \tag{3.3b}$$

E. The neutral atom potentials U_μ^* and U_ν^* are further specified as point charge potentials, which include nuclei and non-valence electrons, and average electronic potentials[1]

$$U_\mu^* = -\frac{4}{r_1} + \int [(2s)^2 + (2px)^2 + (2py)^2 + (2pz)^2]\frac{1}{r_{12}}\,d\tau_2\,, \tag{3.4a}$$

$$U_\nu^* = -\frac{1}{r_1} + \int (1s)^2\frac{1}{r_{12}}\,d\tau_2\,. \tag{3.4b}$$

The effect of the carbon 1*s*-electrons is included in the point charge potential. The orbital exponents for χ_μ in (3.3a) and the four orbitals in (3.4a) may have different values.

F. Penetration integrals and kinetic energy integrals are neglected for μ, ν non-nearest neighbors. This is based on the reasonable assumption that these quantities decrease exponentially, similar to the overlap integral

$$(\varrho:\mu\nu) = (\varrho:\mu\mu)\delta_{\mu\nu} + (\varrho:\mu\nu)M_{\mu\nu} \quad \text{with} \quad (\varrho:\mu\nu) = -\int \chi_\mu^* U_\varrho^* \chi_\nu d\tau \tag{3.5a}$$

$\varrho = \mu, \nu$ or nearest neighbours of μ or ν

$$T_{\mu\nu} = T_{\mu\mu}\delta_{\mu\nu} + T_{\mu\nu}M_{\mu\nu}\,. \tag{3.5b}$$

The original definition is over sums $\sum\limits_\varrho (\varrho:\mu\nu)$.

G. Electronic interaction integrals are simplified according to Mulliken's approximation (Mulliken [142], p. 500, 521)

$$(\mu\nu|\varrho\sigma) = \tfrac{1}{4}S_{\mu\nu}S_{\varrho\sigma}[(\mu\mu|\varrho\varrho) + (\mu\mu|\sigma\sigma) + (\nu\nu|\varrho\varrho) + (\nu\nu|\sigma\sigma)]\,. \tag{3.6}$$

Matrix Elements

Ruedenberg does not take the self-consistent field operator F as H_{eff}, but a neutral core operator H_{neutr}, because the cores are shielded by the other π-electrons

$$H_{\text{neutr}} = T + \sum_{\sigma\in\text{C}} U_\varrho^* + \sum_{\varrho\in\text{H}} U_\varrho^*\,. \tag{3.7}$$

The matrix elements of this operator are used only for the calculation of the MO's

$$H_{\mu\nu}^{\text{neutr}} = T_{\mu\nu} - \sum_{\sigma\in\text{C}} (\sigma:\mu\nu) - \sum_{\varrho\in\text{H}} (\varrho:\mu\nu)\,. \tag{3.8}$$

Using (3.5a) and (3.5b) $H_{\mu\nu}^{\text{neutr}}$ can be represented as

$$H_{\mu\nu}^{\text{neutr}} = (\alpha + \delta\alpha_\mu)\delta_{\mu\nu} + \beta M_{\mu\nu} \tag{3.9}$$

with α mean value of all α_μ.

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[1] Compare Eq. (3.4a) with Eq. (34) of the Goeppert-Mayer-Sklar paper.

$\delta\alpha_\mu$ deviation from α in a special case

$$\beta = \int \chi_1^*(T + 2U_1^*)\chi_2 d\tau .$$

If one considers that the eigenvectors of H_{neutr} are at the same time eigenvectors of S because both operators commute one gets a final form for the energy

$$\begin{aligned} E = \sum_{\mu} P_{\mu\mu}(\alpha + \delta\alpha_\mu) + \sum_{\substack{\mu,\nu \\ \mu \neq \nu}} P_{\mu\nu}\beta M_{\mu\nu} \\ + \frac{1}{2}\sum_{\mu,\nu}\left[(P_{\mu\mu} - 1)(P_{\nu\nu} - 1) - \frac{1}{4}(P_{\mu\nu}^2 + P'_{\mu\nu}P''_{\mu\nu}) - 1\right](\mu\mu|\nu\nu) \end{aligned} \tag{3.10}$$

with

$$P'_{\mu\nu} = 2\sum_i c_{\mu i}^* c_{\nu i}/s_i ,$$

$$P''_{\mu\nu} = 2\sum_i c_{\mu i}^* c_{\nu i} s_i .$$

Basic Quantities

The remaining quantities to be calculated are:

$S_{\mu\nu} = S$ is calculated theoretically as two-center integral over Slater orbitals in elliptic coordinates.

$T_{\mu\mu} = T_{11}$ in the same way as S.

$T_{\mu\nu} = T_{12}$ in the same way as S.

A simple relation is found between T_{12}, T_{11} and S.

$(1_C:11)$, $(2_C:11)$, $(2_C:12)$, $(1_H:11)$ are calculated in a similar way to S.

$(\mu\mu|\nu\nu)$ 1. is calculated theoretically in elliptic coordinates. 2. is calculated by an approximation formula which is fitted by the spectrum of benzene, because the transition energies are dependent only on the differences of interaction integrals

$$(\mu\mu|\nu\nu) = A/R\left(1 - e^{-\alpha R}\sum_{k=1}^{5}\gamma_k R^k\right).$$

The orbital exponents ζ of (3.3a) and the shielding exponents ζ_C of (3.4a) are determined by setting the orbital energy of a neutral carbon atom equal to the carbon electron affinity and minimizing this quantity with respect to ζ

$$\begin{aligned} (\chi(\zeta)|T + U_C^*(\zeta_C)|\chi(\zeta)) = -A_C , \\ \frac{d}{d\zeta}(\chi(\zeta)|T + U_C^*(\zeta_C)|\chi(\zeta)) = 0 . \end{aligned} \tag{3.11}$$

Comments

Ruedenberg's approach is essentially a topological approach. The effective Hamiltonian which is used for the calculation of the orbitals is determined by the topological structure of the molecule, which means that one has to know only whether an atom is a nearest neighbour to another atom, not where it is located geometrically. The model has the advantage of strong relationship between energy and overlap eigenvalues. A similar, but purely analytical approach to this problem has been proposed by Lykos and Schmeising [134] and Gilbert and Lykos [58].

The two kinds of energy terms can be distinguished as due to short range forces [T and U] and long range forces [$(\mu\mu|\nu\nu)$]; the former are essentially determined by the *topology* of the molecule (matrix M), the latter are depending on the *geometry*. The energy expression (3.10) gives an interesting aspect. The second term in the brackets is a generalization of Pople's result. It suggests that the latter is valid only if the eigenvalues s_i of the overlap matrix are all approximately equal to unity.

There seems to be only one inconsistency in Ruedenberg's method. He allows the $2pz$-orbital in the neutral atom potential to be different from the $2pz-\pi$-orbital. In fact, assumption (3.11) might be the reason for the unexpected result that the σ-orbitals ($2s$-, $2px$- and $2y$-orbitals in the neutral atom potential) have a smaller shielding exponent than the π-orbital $(2pz)$[2]. This means that in $\sigma-\pi$-systems the σ-orbitals should be more expanded than the π-orbitals. Ab-initio calculations on C_2 suggest the opposite (Ransil [182]).

4. *Berthier's Method* [9]

Basic Assumptions[3]

A. The method is designed for π-electron systems. It is flexible enough to include hetero atoms with two or zero π-electrons.

B. The atomic orbitals are considered as Löwdin orthogonalized orbitals.

$$S_{ij}^{\lambda} = \delta_{ij} \,. \tag{4.1}$$

The transformation is given by

$$\boldsymbol{\lambda} = \boldsymbol{\chi} \boldsymbol{S}^{-1/2}$$

or

$$\lambda_i = \sum_{\mu} (S^{-1/2})_{\mu i} \chi_\mu \,. \tag{4.2}$$

C. The Hamiltonian for the core is written as

$$H_{\text{core}} = T + U_\mu + \sum_{\sigma \neq \mu} U_\sigma \tag{4.3}$$

where U_μ and U_σ are effective potentials of the atoms deprived of their π-electrons.

D. According to the number n_μ of π-electrons on atom μ the integral W_μ has different values

$$W_\mu = \int \chi_\mu^* (T + U_\mu) \chi_\mu d\tau = \begin{cases} -A_\mu \\ -I_\mu \\ -I'_\mu - (\mu\mu|\mu\mu) \end{cases} \quad \text{for} \quad n_\mu = \begin{cases} 0 \\ 1 \\ 2 \end{cases} \tag{4.4}$$

where A_μ is the electron affinity and I_μ an appropriate ionization potential of carbon (Berthier *et al.* [10]).

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[2] Some comment on this point in terms of penetration integrals has already been given (Gladney [59]).

[3] An essential part of the method has been described earlier by Suard *et al.* [202].

E. The potentials U_σ are expressed by neutral atom potentials and average electronic potentials

$$U_\sigma = U_\sigma^* - n_\sigma (J_z - \tfrac{1}{2} K_z)_\sigma \,. \tag{4.5}$$

F. For the resonance integral the "Mulliken approximation" is adopted and a correction term $\varepsilon_{\mu\nu}$ added

$$\beta_{\mu\nu} = \tfrac{1}{2} S_{\mu\nu}^\chi (\alpha_\mu + \alpha_\nu) + \varepsilon_{\mu\nu} \tag{4.6}$$

where α_μ and $\varepsilon_{\mu\nu}$ are given as

$$\alpha_\mu = W_\mu - \sum_{\sigma \neq \mu} \left\{ (\sigma : \mu\mu) + n_\sigma \left[(\sigma\sigma | \mu\mu)^\chi - \frac{1}{2} (\sigma\mu | \sigma\mu)^\chi \right] \right\} \tag{4.7}$$

$$\varepsilon_{\mu\nu} = -k S_{\mu\nu}^\chi \text{ (Berthier [8])} \,. \tag{4.8}$$

G. The core integrals in the λ-basis may now be written as

$$\alpha_\mu^\lambda = \sum_\varrho (S^{-1/2})_{\mu\varrho} \alpha_\varrho (S^{1/2})_{\varrho\mu} \,, \tag{4.9}$$

$$\begin{aligned} \beta_{\mu\nu}^\lambda = {} & \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} \varepsilon_{\varrho\sigma} (S^{-1/2})_{\sigma\nu} \\ & + \frac{1}{2} \sum_\varrho [(S^{-1/2})_{\mu\varrho} \alpha_\varrho (S^{1/2})_{\varrho\nu} + (S^{1/2})_{\mu\varrho} \alpha_\varrho (S^{-1/2})_{\varrho\nu}] \,. \end{aligned} \tag{4.10}$$

H. Zero differential overlap assumption is taken for the electronic interaction integrals in the λ-basis

$$(\mu\nu | \varrho\sigma)^\lambda = (\mu\mu | \varrho\varrho)^\lambda \delta_{\mu\nu} \delta_{\varrho\sigma} \,. \tag{4.11}$$

I. The remaining Coulomb integrals are transformed to integrals in the χ-basis for which Mulliken's approximation (Mulliken [142]) is adopted

$$(\mu\nu | \varrho\sigma)^\chi = \tfrac{1}{4} S_{\mu\nu} S_{\varrho\sigma} [(\mu\mu | \varrho\varrho)^\chi + (\mu\mu | \sigma\sigma)^\chi + (\nu\nu | \varrho\varrho)^\chi + (\nu\nu | \sigma\sigma)^\chi] \,. \tag{4.12}$$

The $(\mu\mu | \nu\nu)^\lambda$ may finally be written as

$$(\mu\mu | \nu\nu)^\lambda = \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} (S^{1/2})_{\mu\varrho} (\varrho\varrho | \sigma\sigma)^\chi (S^{-1/2})_{\sigma\nu} (S^{1/2})_{\sigma\nu} \,. \tag{4.13}$$

Matrix Elements

The elements of the SCF matrix may be written as

$$\begin{aligned} F_{\mu\mu}^\lambda = {} & \sum_\varrho (S^{-1/2})_{\mu\varrho} \left[W_\varrho - \sum_{\sigma \neq \varrho} n_\sigma \left\{ (\sigma\sigma | \varrho\varrho)^\chi - \frac{1}{8} S_{\varrho\sigma}^2 [(\varrho\varrho | \varrho\varrho)^\chi + (\sigma\sigma | \sigma\sigma)^\chi \right.\right. \\ & \left.\left. + 2 (\varrho\varrho | \sigma\sigma)^\chi] \right\} \right] (S^{1/2})_{\varrho\mu} + \frac{1}{2} P_{\mu\mu}^\lambda \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} (S^{1/2})_{\mu\varrho} (\varrho\varrho | \sigma\sigma)^\chi (S^{-1/2})_{\sigma\mu} (S^{1/2})_{\sigma\mu} \\ & + \sum_{\omega \neq \mu} P_{\omega\omega}^\lambda \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} (S^{+1/2})_{\mu\varrho} (\varrho\varrho | \sigma\sigma)^\chi (S^{-1/2})_{\sigma\omega} (S^{1/2})_{\sigma\omega} \,, \end{aligned} \tag{4.14a}$$

$$\begin{aligned} F^{\lambda}_{\mu\nu} = \frac{1}{2} \sum_{\varrho} (S^{-1/2})_{\mu\varrho} \alpha_{\varrho} (S^{1/2})_{\varrho\nu} + (S^{1/2})_{\mu\varrho} \alpha_{\varrho} (S^{-1/2})_{\varrho\nu} \\ + \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} \varepsilon_{\varrho\sigma} (S^{-1/2})_{\sigma\nu} \\ - \frac{1}{2} P^{\lambda}_{\mu\nu} \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} (S^{1/2})_{\mu\varrho} (\varrho\varrho | \sigma\sigma)^{\chi} (S^{-1/2})_{\sigma\nu} (S^{1/2}) . \end{aligned} \tag{4.14b}$$

If one expands $S^{-1/2}$ and $S^{+1/2}$ in a series and restricts oneself to first-order terms, the simple relations result

$$F_{\mu\mu} = W_{\mu} + \frac{1}{2} P^{\lambda}_{\mu\mu} (\mu\mu | \mu\mu)^{\chi} + \sum_{\sigma \neq \mu} (P^{\lambda}_{\sigma\sigma} - n_{\sigma}) (\sigma\sigma | \mu\mu)^{\chi} , \tag{4.15a}$$

$$F_{\mu\nu} = \varepsilon_{\mu\nu} - \frac{1}{2} P^{\lambda}_{\mu\nu} (\mu\mu | \nu\nu)^{\chi} . \tag{4.15b}$$

$\boldsymbol{P}^{\lambda}$ is the gross atomic population (Mulliken [143]) if $\boldsymbol{P}^{\lambda}$ and $\boldsymbol{S}$ commute. It has been shown (Fischer-Hjalmars [50]) that this interpretation is correct to the first order even if $\boldsymbol{P}^{\lambda}$ and $\boldsymbol{S}$ do not commute[4].

The total electronic energy may be written as

$$\begin{aligned} E = \frac{1}{2} \sum_{\mu,\nu} P^{\lambda}_{\mu\nu} \Big[\sum_{\varrho} (S^{-1/2})_{\mu\varrho} \alpha_{\varrho} (S^{1/2})_{\varrho\nu} + (S^{1/2})_{\mu\varrho} \alpha_{\varrho} (S^{-1/2})_{\varrho\nu} \\ + \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} \varepsilon_{\varrho\sigma} (S^{-1/2})_{\sigma\nu} \Big] \\ + \left(P^{\lambda}_{\mu\mu} P^{\lambda}_{\nu\nu} - \frac{1}{2} P^{\lambda^2}_{\mu\nu} \right) \sum_{\varrho,\sigma} (S^{-1/2})_{\mu\varrho} (S^{1/2})_{\mu\varrho} (\varrho\varrho | \sigma\sigma)^{\chi} (S^{-1/2})_{\sigma\nu} (S^{1/2})_{\sigma\nu} . \end{aligned} \tag{4.16}$$

Collecting first order terms from an expansion of $S^{-1/2}$ and $S^{1/2}$ yields

$$\begin{aligned} E = \sum_{\mu} P_{\mu\mu} \left(W_{\mu} + \frac{1}{4} P^{\lambda}_{\mu\mu} (\mu\mu | \mu\mu)^{\chi} \right) + \sum_{\substack{\mu,\nu \\ \mu \neq \gamma}} P^{\lambda}_{\mu\nu} \varepsilon_{\mu\nu} \\ + \frac{1}{2} \sum_{\mu,\nu} \left[(P^{\lambda}_{\mu\mu} - n_{\mu}) (P^{\lambda}_{\nu\nu} - n_{\nu}) - \frac{1}{2} P^{\lambda^2}_{\mu\nu} - n_{\mu} n_{\nu} \right] (\mu\mu | \nu\nu)^{\chi} . \end{aligned} \tag{4.17}$$

Basic Quantities

$S_{\mu\nu}$ 1. is calculated theoretically using Slater shielding exponents.

2. is calculated theoretically by taking the same exponent as for T_{2p}; this quantity and T_{2s} are calculated by applying the virial theorem to the $(V_4, sxyz)$ and (V_2, s^2xz) valence states of carbon; T_{1s} has to be known and is assumed to be equal to the conventionally calculated value.

$-W_{\mu}$ is taken as an appropriate ionization potential or electron affinity of carbon.

k shall fit the benzene spectrum.

$(\sigma : \mu\mu)$ is neglected.

$(\mu\mu | \mu\mu)^{\chi}$ shall fit the experimental value; this yields an appropriate shielding exponent.

$(\mu\mu | \nu\nu)^{\chi}$ is calculated theoretically using the exponent which was yielded for $(\mu\mu | \mu\mu)^{\chi}$.

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[4] For a recent discussion on atomic populations in molecules see Cusachs and Politzer [32].

Comments

Berthier's scheme was the first complete approach to give a satisfactory explanation of the earlier Pariser-Parr method. Although it had become clear in the meantime that the orbitals used in connection with the ZDO assumptions have to be considered as Löwdin orthogonalized, only the fortunate connection with the Mulliken approximation for the original atomic set[5] and the idea of expanding the overlap matrix to first order terms has led to this result. The inclusion of exchange potential terms, as well as a more general interpretation of the integral W_μ, which takes care of the fact that the atomic valence orbitals are influenced by the molecular environment (pyrrole or pyridine) gives semiempirical methods a better basis. Perhaps relationship (4.8) remains unsatisfactory, because k is of the same order of magnitude as α_μ and α_ν in (4.6). The first term is neglected in an expansion, whereas the second, although of the same order of magnitude, is not.

5. Other Developments

Since the scheme for effective Hamiltonian and energy expression has been outlined by Pariser-Parr and Pople, it has been essentially changed or generalized only a few times. Shortly after those above-described methods had been elaborated for unsaturated hydrocarbons, an extension to radicals and ions with an unpaired electron was attempted (Longuet-Higgins and Pople [124]). A formalism for open-shell systems had been briefly outlined (Pople and Nesbet [173]). The Hamiltonian

$$H = H_{\text{core}} + \sum_{\varrho \neq \sigma}^{\text{paired}} (2J_\varrho - K_\varrho) + J_\sigma - \frac{1}{2} K_\sigma \tag{5.1}$$

which the authors (Longuet-Higgins and Pople) used even for the unpaired electron is in fact the Hamiltonian for the closed-shell part in the restricted Hartree-Fock form. Calculations were made independently at the same time by Berthier [6, 7]. Nevertheless there was much detailed work left to evaluate the basic parameters: Z_μ, W_μ, β, $(\mu\mu|\mu\mu)$, $(\mu\mu|\nu\nu)$.

It was realized that in case of net charges in heteroatomatic systems, especially ions, parameters become dependent on the electronic charge distribution. A *variable electronegativity* method was developed (Brown and Heffernan [18]) where the exponent Z_μ is a function of the density at atom μ:

$$Z_\mu = n_\mu - 1.35 - 0.35(N_\mu^\sigma + P_{\mu\mu}^\pi)\,. \tag{5.2}$$

The basic integrals, especially W_μ and $(\mu\mu|\mu\mu)$, become, as functions of the orbitals, functions of the electronic distribution.

Recently there was proposed as alternative a *variable core* method (Nishimoto [150]) which together with the earlier *variable β* method (Nishimoto and Forster [152]) and the improved method for the calculation of electronic repulsion integrals (Nishimoto [148, 149]) completes a new scheme. The latter method distinguishes between upper-upper and upper-lower interaction in molecules.

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[5] The equivalence of Mulliken approximation for AO's and ZDO for OAO's has been pointed out first by Löwdin [126].

For many purposes the older version (Nishimoto and Mataga [151]) which generalizes Pople's idea (2.3) seems to be sufficient.

$$(\mu\mu|\nu\nu)=\frac{1}{a+R_{\mu\nu}}, \tag{5.3a}$$

$$(\mu\mu|\mu\mu)=\frac{1}{a}=I-A. \tag{5.3b}$$

The results reported for many cases are satisfactory, and the formula is perhaps better than Pariser-Parr's quadratic formula. This might be due to the fact that in configuration interaction calculations the steeper decrease of the two-center integral in the Nishimoto-Mataga form gives a larger expression of correlation effects (Koutecký [111]).

Another explanation has been given by Little [121] who shows that the Nishimoto-Mataga formula works well for π-electrons because it represents quite well the Coulomb interaction which is partially screened by the *collective* motion of the π-electrons. The author describes a procedure for a better approximation.

A method where deviations from reference values for W_μ, $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ are measured by changes of a reference bond distance has been proposed by Roos and Skancke [183]. The bond distances are related linearly to bond orders $P_{\mu\nu}$.

About the one-center electronic repulsion integral $(\mu\mu|\mu\mu)$ there has been much discussion. The theoretical value calculated by using Slater's shielding exponents (16.93 eV) deviated considerably from the "experimental" value (10.53 eV) calculated by the difference of ionization potential and electron affinity $I-A$. This formula was derived by a $2C \rightarrow C^+ + C^-$ type reaction (Pariser [159]). A generalization has been given for other reaction types (Paoloni [158]). Many explanations have been given in the meantime based on correlation considerations (*e.g.* Kolos [108], Arai and Lykos [4]). More recently it has been pointed out that the integral $(\mu\mu|\mu\mu)$ which is involved in the above mentioned reaction type has to be ascribed to the negative ion C^- (Hermann [79]; Orloff and Sinanoğlu [157]; Anno [3]). In consequence it has to be compared with the theoretical value derived from C^- (12.72 eV). The occurance of a C^--type one-center repulsion integral may be explained by assuming that it accounts for ionic structures.

Whereas all these explanations are based on atomic definitions of a "valence state", this is not the case for another approach (Silverstone *et al.* [192]). The authors define valence state in a molecular environment by collecting terms which belong to *one atom only* from a *molecular* expression. This procedure yields an electronic repulsion term involving a $2p\pi$-orbital which did not occur in the earlier version (van Vleck [205]). Minimization of the valence state energy yields shielding exponents strikingly different from the Zener-Slater values (Zener [213], Slater [197]) and allowing the $2p\sigma$- and $2p\pi$-orbital exponents to be different. Considerations have been made for ground and excited states and ions of carbon in π-electron systems (Silverstone and Joy [193]; Joy and Silverstone [95]). The authors hope that considerations based on a minimization of the total energy expression of the molecule may later justify their procedure.

The difficult choice of parameters has led some authors to investigations how certain parameters affect the values of molecular quantities (Chiorboli *et al.* [20]; Flurry and Bell [52]). In heteroatomic systems charge densities and orbital energies may vary considerably dependent on the choice of W_μ and $\beta_{\mu\nu}$ values. Even term crossings may occur.

In spite of the success of the π-electron approximation in many cases, there remains the question whether the $\sigma-\pi$ separability conditions (Lykos and Parr [133]) are actually fulfilled. Recently some doubt was raised in connection with this question (Moskowitz and Barnett [141]; Schulman and Moskowitz [190]). It has become obvious that σ-orbital terms are embedded between π-orbital terms in ring systems. In addition, it seems unlikely now that charge distributions and dipole moments calculated in the π-electron approximation may be interpreted as due to π-electrons only. Calculations indicate that there is implicitly an influence of the σ-electrons involved (Veillard and Berthier [204]). This is substantiated by some ab-initio calculations (Diercksen and Preuss [42]; Preuss and Diercksen [180]; Clementi *et al.* [24, 25]). Sometimes the influence of the σ-electrons is difficult to predict; *e.g.* in pyridine the dipole moment seems to be primarily due to the σ-electrons, not to the π-electrons as has been assumed earlier. Despite the limitations of the π-electron approximation, some justification can be given for the above described methods, which is done more in detail in the following chapter.

III. Justification of the Zero Differential Overlap Assumptions

1. The Zero Differential Overlap Assumptions

$$S^{\lambda}_{\mu\nu} = \delta_{\mu\nu}\,, \tag{1.1}$$

$$H^{\text{core},\lambda}_{\mu\mu} \neq 0\,, \tag{1.2}$$

$$H^{\text{core},\lambda}_{\mu\nu} \neq 0\,, \quad \text{for } \mu,\, \nu \text{ nearest neighbours} \tag{1.3}$$

$$H^{\text{core},\lambda}_{\mu\nu} = 0\,, \quad \textit{otherwise} \tag{1.4}$$

$$(\mu\nu|\varrho\sigma)^{\lambda} = (\mu\mu|\varrho\varrho)^{\lambda}\,\delta_{\mu\nu}\delta_{\varrho\sigma}\,. \tag{1.5}$$

In Eqs. (1.1)–(1.5) the superscript λ indicates that the basis for the matrix elements is supposed to be different from the usual atomic orbital basis $\{\chi\}$. Sometimes this difference has been overlooked and in consequence the ZDO assumptions were found to be unreliable (Coulson and Schaad [29]). Note that the ZDO assumptions were originally given in the *differential* form (*e.g.* Parr [164]; Pariser and Parr [161]). The differential form is not only mathematically inexact for the conventional AO's but completely unnecessary in a theory where only integrals are required.

Recently, however, there has been drawn attention to the fact that orthogonality alone, *e.g.* between 2*s*- and 2*p*-orbitals, might not be a sufficient basis for the introduction of ZDO in electronic repulsion integrals, but the orbitals have to be localized and non-overlapping like the four sp^3-hybrids (Cook *et al.* [26]). This gives support to the old idea of zero *differential* overlap.

A completely new interpretation of ZDO is suggested by Weare and Parr [207]. This interesting method is based on cut-off orbitals and would allow an unapproximated application of ZDO in the differential form. The method might become attractive if a recipe for the difficult boundary conditions can be found. The cusps have to yield non-vanishing β-values (see *e.g.* Ohno [153]).

2. *Orthogonalized Atomic Orbitals*

After the introduction of the ZDO assumptions into the MO formalism many authors (Fumi and Parr [56]; Löwdin [126–128, 130]; McWeeny [138, 139]; Parr [165]; Lykos [131]) have pointed out that it might be preferable to use symmetrically orthogonalized atomic orbitals (Löwdin [125]) instead of the purely atomic basis set[6]:

$$\boldsymbol{\lambda} = \boldsymbol{\chi} \boldsymbol{S}^{-1/2} \tag{2.1}$$

or

$$\lambda_i = \sum_{\mu} (S^{-1/2})_{\mu i} \chi_\mu \,.$$

The notation implies that $\boldsymbol{\lambda}$ and $\boldsymbol{\chi}$ are row vectors. Although some of the above-mentioned authors have given reason for the justification of the ZDO assumptions when using an orthogonalized basis set, only recently a systematic treatment has been carried out (Fischer-Hjalmars [49, 50]) and more general applications have been performed (Adams and Miller [1]). When the orbital basis is subjected to the transformation (2.1) the matrices of one-electron operators will be transformed as follows

$$\boldsymbol{M}^{\lambda} = \boldsymbol{S}^{-1/2} \boldsymbol{M} \boldsymbol{S}^{-1/2} \tag{2.2}$$

or

$$M^{\lambda}_{\mu\nu} = \sum_{i,j} (S^{-1/2})_{\mu i} (S^{-1/2})_{\nu j} M_{ij} \,.$$

The matrices of two-electron operators can be transformed easily if one considers the electronic interaction as an interaction between two one-electron charge clouds which are transformed according to (2.2)

$$\boldsymbol{\Omega}^{\lambda} = \boldsymbol{\lambda}^{\dagger}\, \boldsymbol{\lambda} = \boldsymbol{S}^{-1/2} \boldsymbol{\Omega} \boldsymbol{S}^{-1/2} \quad \text{with} \quad \Omega_{ij} = \chi_i^* \chi_j \,.$$

Introducing a matrix $(\boldsymbol{\Omega} | \boldsymbol{\Omega})$ with double indices

$$(\boldsymbol{\Omega} | \boldsymbol{\Omega})_{ij,kl} = (\Omega_{ij} | \Omega_{kl}) \tag{2.3}$$

the transformation of the matrix elements yields

$$(\boldsymbol{\Omega}^{\lambda} | \boldsymbol{\Omega}^{\lambda}) = (\boldsymbol{S}^{-1/2} \boldsymbol{\Omega} \boldsymbol{S}^{-1/2} | \boldsymbol{S}^{-1/2} \boldsymbol{\Omega} \boldsymbol{S}^{-1/2}) \tag{2.4}$$

or

$$(\mu\nu | \varrho\sigma)^{\lambda} = \sum_{i,j,k,l} (S^{-1/2})_{\mu i} (S^{-1/2})_{\nu j} (S^{-1/2})_{\varrho k} (S^{-1/2})_{\sigma l} (ij/kl) \,.$$

The overlap matrix $\boldsymbol{S}^{-1/2}$, and as sometimes needed $\boldsymbol{S}^{+1/2}$, may be expanded in terms of S as

$$\boldsymbol{S}^{-1/2} = \boldsymbol{1} + \tfrac{1}{2}(\boldsymbol{1} - \boldsymbol{S}) + \tfrac{3}{8}(\boldsymbol{1} - \boldsymbol{S})^2 \ldots, \tag{2.5a}$$

$$\boldsymbol{S}^{+1/2} = \boldsymbol{1} - \tfrac{1}{2}(\boldsymbol{1} - \boldsymbol{S}) - \tfrac{1}{8}(\boldsymbol{1} - \boldsymbol{S})^2 \ldots\,. \tag{2.5b}$$

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[6] It is interesting to notice that OAO's have been used first in the valence bond method (McWeeny [136, 137]). Also a kind of equivalent orbitals with localization properties have been used (Hall [64]).

It might be worthwhile to remember that the expansion is obvious only in the Löwdin definition of the overlap integral (Löwdin [125]), but looks somewhat artificial in Eqs. (2.5a, b) where the generally adopted form of S is used.

Following the pattern of a recent review (Fischer-Hjalmars [49, 50]), let us consider the case of hydrocarbons with approximately equidistant atoms and let us use the notation

$$\begin{aligned} S_{\mu,\mu+1} &= S_1 && \text{for } \mu, \mu+1 \text{ nearest neighbours,} \\ S_{\mu,\mu+2} &= S_2 = O(S_1^2) && \text{for } \mu, \mu+2 \text{ next nearest neighbours,} \\ S_{\mu,\mu+3} &= S_3 = O(S_1^3) && \text{for } \mu, \mu+3 \text{ non-next nearest neighbours.} \end{aligned} \tag{2.6}$$

In this special case and under the neglection of third order terms $O(S_1^3)$ the matrices of the one-electron operators may be written as

$$S_{\mu\nu} = \delta_{\mu\nu} + S_1(\delta_{\mu,\nu-1} + \delta_{\mu,\nu+1}) + S_2(\delta_{\mu,\nu-2} + \delta_{\mu,\nu+2}) + O(S_1^3), \tag{2.7}$$

$$\begin{aligned} (S^{-1/2})_{\mu\nu} = {} & (1 + \tfrac{3}{4}S_1^2)\delta_{\mu\nu} - \tfrac{1}{2}S_1(\delta_{\mu,\nu-1} + \delta_{\mu,\nu+1}) + (\tfrac{3}{8}S_1^2 - \tfrac{1}{2}S_2) \\ & \times (\delta_{\mu,\nu-2} + \delta_{\mu,\nu+2}) + O(S_1^3), \end{aligned} \tag{2.8a}$$

$$\begin{aligned} (S^{1/2})_{\mu\nu} = {} & (1 - \tfrac{1}{4}S_1^2)\delta_{\mu\nu} + \tfrac{1}{2}S_1(\delta_{\mu,\nu-1} + \delta_{\mu,\nu+1}) \\ & + (-\tfrac{1}{8}S_1^2 + \tfrac{1}{2}S_2)(\delta_{\mu,\nu-2} + \delta_{\mu,\nu+2}) + O(S_1^3), \end{aligned} \tag{2.8b}$$

$$\begin{aligned} M^{\lambda}_{\mu\nu} = {} & (1 + \tfrac{3}{2}S_1^2)M_{\mu\nu} - \tfrac{1}{2}S_1(M_{\mu-1,\nu} + M_{\mu+1,\nu} + M_{\mu,\nu-1} + M_{\mu,\nu+1}) \\ & + \tfrac{1}{4}S_1^2(M_{\mu-1,\nu-1} + M_{\mu-1,\nu+1} + M_{\mu+1,\nu-1} + M_{\mu+1,\nu+1}) \\ & + (\tfrac{3}{8}S_1^2 - \tfrac{1}{2}S_2)(M_{\mu-2,\nu} + M_{\mu,\nu-2} + M_{\mu,\nu+2} + M_{\mu+2,\nu}) + O(S_1^3). \end{aligned} \tag{2.9}$$

The matrices $(\Omega^{\lambda}|\Omega^{\lambda})$ are not given here because the formulas are much more complicated and they are needed only in special cases. The reader may derive them by inserting (2.9) into (2.3) and neglecting terms of higher than second order.

By inserting (2.8a) into (2.1) we can make an interesting statement about the new basis $\boldsymbol{\lambda}$:

$$\lambda_i = (1 + \tfrac{3}{4}S_1^2)\chi_i - \tfrac{1}{2}S_1(\chi_{i-1} + \chi_{i+1}) + (\tfrac{3}{8}S_1^2 - \tfrac{1}{2}S_2)(\chi_{i-2} + \chi_{i+2}) \cdots \tag{2.10}$$

The local character of the AO basis set $\boldsymbol{\chi}$ is preserved in the OAO basis set $\boldsymbol{\lambda}$ (McWeeny [140], Fischer-Hjalmars [49, 50]).

3. *Construction of the* SCF *Matrix*

Let us use the following notation

$$H^{\text{core}} = T + \sum_{\mu} (U_{\mu}^{*} - n_{\mu}J_{\mu\mu}) \tag{3.1}$$

where U_{μ}^{*} is a neutral atom potential, n_{μ} the number of π-electrons contributed by atom μ and $J_{\mu\mu}$ the Coulomb operator. Application of Eqs. (2.7)–(2.9) yields in connection with Ruedenberg's approximation $T_{\mu\nu} = S_{\mu\nu}^2 T_{\mu\mu}$ the matrix elements which enter the SCF matrix in the second order approximation as follows

$$T^{\lambda}_{\mu\mu} = (1+2S_1^2)\,T_{\mu\mu} + O(S_1^3)\,, \tag{3.2}$$

$$T^{\lambda}_{\mu,\mu+1} = T_{\mu,\mu+1} - S_1 T_{\mu\mu} + O(S_1^3)\,, \tag{3.3}$$

$$(\mu:\mu\mu)^{\lambda} = (1+\tfrac{3}{2}S_1^2)\,(\mu:\mu\mu) - 2S_1(\mu:\mu,\mu+1) + O(S_1^3)\,, \tag{3.4}$$

$$(\mu+1:\mu\mu)^{\lambda} = (\mu+1:\mu\mu) - S_1(\mu:\mu,\mu+1) + \tfrac{1}{4}S_1^2(\mu:\mu\mu) + O(S_1^3)\,, \tag{3.5}$$

$$(\mu_{\mathrm{H}}:\mu\mu)^{\lambda} = (\mu_{\mathrm{H}}:\mu\mu) + O(S_1^3)\,, \tag{3.6}$$

$$(\mu:\mu,\mu+1)^{\lambda} = (\mu:\mu,\mu+1) - \tfrac{1}{2}S_1(\mu:\mu\mu) + O(S_1^3)\,, \tag{3.7}$$

$$(\mu\mu|\nu\nu)^{\lambda} = (\mu\mu|\nu\nu) + S_1^2[(\mu\mu|\nu\nu) - (\mu\mu|\nu+1,\nu+1)] + O(S_1^3)\,. \tag{3.8}$$

Integrals which are not among those in (3.2)–(3.8) vanish in the second order approximation.

Now we are able to write down the expansion of the various integrals (1.1)–(1.5) in terms of S_1 and S_2.

Eq. (1.1) must be obviously fulfilled in the $\{\lambda\}$-basis to any order of S_1.

Eq. (1.2) becomes

$$H^{\mathrm{core},\lambda}_{\mu\mu} = W^{\lambda}_{\mu} - (n_\mu - 1)\,(\mu\mu|\mu\mu)^{\lambda} - \sum_{\nu\neq\mu} n_\nu(\mu\mu|\nu\nu)^{\lambda} + O(S_1^3) \tag{3.9}$$

where

$$W^{\lambda}_{\mu} = T^{\lambda}_{\mu\mu} - (\mu:\mu\mu)^{\lambda} - (\mu\mu|\mu\mu)^{\lambda} - (\mu-1:\mu\mu)^{\lambda} - (\mu+1:\mu\mu)^{\lambda} - (\mu_{\mathrm{H}}:\mu\mu)^{\lambda}. \tag{3.10}$$

Expression (3.10) differs from the usual expression for W_μ by the inclusion of the three nearest neighbour penetration terms (Fischer-Hjalmars [50]). The notation has the advantage that no penetration integrals are explicitly needed in calculations. In addition, it shows strikingly that there is no essential difference between semiempirical methods which neglect penetration terms in $\mathrm{H}^{\mathrm{core},\lambda}_{\mu\mu}$ or keep them. It is just a matter of different parameter values for W_μ. The same idea was expressed earlier without specifying a value for W_μ (Brickstock and Pople [15]).

If we define W_μ accordingly

$$W_\mu = T_{\mu\mu} - (\mu:\mu\mu) - (\mu\mu|\mu\mu) - (\mu-1:\mu\mu) - (\mu+1:\mu\mu) - (\mu_{\mathrm{H}}:\mu\mu) \tag{3.11}$$

then W_μ may be expressed as

$$\begin{aligned} W^{\lambda}_{\mu} = W_\mu &+ nS_1^2[T_{\mu\mu} - (\mu:\mu\mu) - \tfrac{1}{2}(\mu\mu|\mu\mu) + \tfrac{1}{2}(\mu\mu|\mu+1,\mu+1)] \\ &+ 2nS_1(\mu:\mu,\mu+1)\,. \end{aligned} \tag{3.12}$$

Here the generalization has been used that atom μ has n instead of two nearest neighbours with π-electrons. Formula (3.12) reduces to Fischer-Hjalmars Eq. (39) if we assume $(\mu:\mu,\mu+1)$ is a term of second order in comparison to $(\mu:\mu\mu)$.

Sometimes the expression $T_{\mu\mu} - (\mu:\mu\mu)$ is considered as the electron affinity of atom μ (Ruedenberg [187]; Fischer-Hjalmars [50]).

That this is not justified is shown in a table[7] of one of the authors (Fischer-Hjalmars [49]) and may lead to irrelevant results for the σ-electrons (Ruedenberg [187]). Whereas Fischer-Hjalmars formula (40) suggests that $|W^{\lambda}_{\mu}| > |W_{\mu}|$, formula (3.12) might rather yield $|W^{\lambda}_{\mu}| < |W_{\mu}|$. This is substantiated by calculation using values for the various parts of W^{λ}_{μ} and W_{μ} from a table of Fischer-Hjalmars [49]. Eq. (1.3) becomes

$$H^{\text{core},\lambda}_{\mu,\mu+1} = T^{\lambda}_{\mu,\mu+1} - (\mu:\mu,\mu+1)^{\lambda} - (\mu+1:\mu,\mu+1)^{\lambda}\,. \tag{3.13}$$

This equation emphasizes the importance of penetration terms in theoretical calculations being by no means negligeable but of the same order of magnitude as $T^{\lambda}_{\mu,\mu+1}$. The matrix elements $H^{\text{core},\lambda}_{\mu\nu}$ where μ, ν arenon-neighbours only contain terms of third and higher order. Thus (1.4) is fulfilled to the second order.

In conclusion we may say that to the first order in S_1 all remaining basic quantities are independent of the surroundings. If we include second order terms all integrals except W_{μ}, because of the flexible number n of neighbours with π-electrons, remain transferable. To a large extent, the success of the Pariser-Parr-Pople theory is due to the local character of the basic quantities in the OAO basis.

For the homonuclear case it has been demonstrated (Fischer-Hjalmars [50]), that Eq. (3.13) may be reformulated to reproduce to the first order the "Mulliken" and to the second order the Ruedenberg approximation for β (see Parr [166], p. 100). But in any case, one has to be careful, because the matrix elements $T_{\mu,\mu+1}$ as well as $(\mu:\mu,\mu+1)$ have opposite sign in the $\{\lambda\}$- and $\{\chi\}$-basis. Only the sign of the quantity $H_{\mu,\mu+1} = T_{\mu,\mu+1} + 2(\mu:\mu,\mu+1)$ remains unchanged under a transformation from one basis to the other.

Finally we are able to write down the matrix elements of the Fock operator as

$$F_{\mu\mu} = W^{\lambda}_{\mu} + \left(1 - \frac{1}{2} n_{\mu}\right)(\mu\mu|\mu\mu)^{\lambda} - \frac{1}{2} Q^{\lambda}_{\mu}(\mu\mu|\mu\mu)^{\lambda} - \sum_{\nu\neq\mu} Q^{\lambda}_{\nu}(\mu\mu|\nu\nu)^{\lambda}, \tag{3.14a}$$

$$F^{\lambda}_{\mu\nu} = H^{\text{core},\lambda}_{\mu\nu} - \frac{1}{2} P^{\lambda}_{\mu\nu}(\mu\mu|\nu\nu)^{\lambda} \tag{3.14b}$$

where the definition of the atomic net charge has been used

$$Q^{\lambda}_{\mu} = n_{\mu} - P^{\lambda}_{\mu\mu}\,. \tag{3.15}$$

In (3.14b) the first term on the right hand side will vanish if

$$\nu \neq \mu+1, \mu-1\,.$$

4. *The Hückel Method*

The Hückel method which is nowadays a familiar tool for every spectroscopist, has been developed at an early stage of MO theory (Hückel [87–89]). Its simple form has significant features which are based much more on intuition than on

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[7] The author appreciates a remark by Prof. Fischer-Hjalmars that the resulting large difference of 10 eV is decreased by the inclusion of one-center exchange integrals. It remains, however, by an order of magnitude larger than the experimental electron affinity of carbon. With respect to the relationship between W^{λ} and W it has to be added that in this case also other third order terms have to be included.

mathematical justification. With increasing popularity, explanations have been given for its success. As the electronic repulsion is not explicitly taken into account, the simplest assumption would be that H_{eff} [(3.2), chapter I] might be identified with H_{core}. But as soon as one realizes the importance of electronic repulsion for orbital energies and spectra, one is forced to assume that some average electronic repulsion is involved in the choice of parameter values.

As the one-electron model yields the SCF operator as optimal for the solution of the Schrödinger equation, an interpretation of H_{eff} in the Hückel theory as the SCF operator presents itself as an obvious choice.

If we compare the Hückel equations

$$(\alpha_\mu - \varepsilon_i) c_{\mu i} + \sum_{\nu \neq \mu}^{\text{neighbours}} \beta_{\mu\nu} c_{\nu i} = 0, \qquad \mu = 1 \dots n \tag{4.1}$$

with Eq. (3.2) of chapter I and take $H_{\mathrm{eff}} = F$, we have to put

$$\alpha_\mu^{\mathrm{spectr}} = F_{\mu\mu}^\lambda, \tag{4.2a}$$

$$\beta_{\mu\nu}^{\mathrm{spectr}} = F_{\mu\nu}^\lambda \qquad \text{if } \mu, \nu \text{ nearest neighbours}, \tag{4.2b}$$

$$\beta_{\mu\nu}^{\mathrm{spectr}} = 0 \qquad \text{otherwise}. \tag{4.2c}$$

If we have reason to assume that semiempirical α- and β-values for nearest neighbours are close to the values of $F_{\mu\mu}^\lambda$ and $F_{\mu\nu}^\lambda$, the results for physical quantities which depend on eigenvalues and eigenvectors of the SCF operator should be sufficiently good. Some explanation is needed for Eq. (4.2c). From the previous chapter we know that for non-nearest neighbours the core part of $F_{\mu\nu}^\lambda$ in (3.14b) vanishes in the second order approximation, but the term $-\frac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu)$ is left[8]. This term is usually assumed to be small.

For alternant hydrocarbons it has been shown (Pople [171]) that the following relation between the Hückel parameter α and various integrals in the ZDO approximation is valid

$$\alpha_\mu^0 = W_\mu + \tfrac{1}{2}(\mu\mu|\mu\mu) \tag{4.3}$$

where the superscript 0 indicates an atom μ with net charge zero. If there is more than one electron on atom μ this can be generalized by using (3.14a)

$$\alpha_\mu^0 = W_\mu + (1 - \tfrac{1}{2}n_\mu)(\mu\mu|\mu\mu). \tag{4.4}$$

If there is a net charge on atom μ this can be taken into account by putting

$$\alpha_\mu = \alpha_\mu^0 - \tfrac{1}{2}Q_\mu(\mu\mu|\mu\mu). \tag{4.5}$$

It has been pointed out (Fischer-Hjalmars [49, 50]) that this equation gives an explanation for the relationship of the ω-technique

$$\alpha_\mu = \alpha_\mu^0 + \omega\beta^0 Q_\mu. \tag{4.6}$$

A comparison of (4.5) and (4.6) yields

$$\omega = -(\mu\mu|\mu\mu)/(2\beta^0). \tag{4.7}$$

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[8] In the following we do not keep the superscript λ, although all quantities are still considered on this basis.

It may be noticed, however, that with increasing net charges on the atoms the method becomes less reliable because the constancy of α is no longer guaranteed.

On the other hand, if one is interested in preserving the additivity of the Hückel energy

$$E_{\text{Hückel}} = 2\sum_i \varepsilon_i \tag{4.8}$$

the parameters have to be chosen differently (Mulliken [142]). They may be taken as (McWeeny [140])

$$\alpha_\mu^{\text{ad}} = \alpha_\mu^{\text{spectr}} - \frac{1}{4} P_{\mu\mu}(\mu\mu|\mu\mu) - \frac{1}{2}\sum_{\nu\neq\mu} P_{\nu\nu}(\mu\mu|\nu\nu)\,, \tag{4.9a}$$

$$\beta_\mu^{\text{ad}} = \beta_{\mu\nu}^{\text{spectr}} + \frac{1}{4} P_{\mu\nu}(\mu\mu|\nu\nu) \tag{4.9b}$$

where $\alpha_\mu^{\text{spectr}}$ and $\beta_\mu^{\text{spectr}}$ are defined by (4.2). Whereas the non-diagonal elements are only slightly different from each other, this is not the case for the diagonal elements.

One can easily understand the different choice of parameters $\alpha_\mu^{\text{spectr}}$ and and $\beta_{\mu\nu}^{\text{spectr}}$ resp. α_μ^{ad} and $\beta_{\mu\nu}^{\text{ad}}$ if one reformulates the energy expression

$$\begin{aligned} E &= \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \\ &= \sum_{\mu,\nu} P_{\mu\nu}\left(F_{\mu\nu} - \frac{1}{2} G_{\mu\nu}\right) \\ &= 2\sum_i^{\text{occ}} \varepsilon_i^{\text{ad}} \end{aligned} \tag{4.10}$$

with

$$\varepsilon_i^{\text{ad}} = \sum_{\mu,\nu} c_{i\mu} c_{i\nu} H_{\mu\nu}^{\text{eff, ad}}\,,$$

$$H_{\mu\nu}^{\text{eff, ad}} = F_{\mu\nu} - \frac{1}{2} G_{\mu\nu}\,.$$

To have a better comparison between molecules with different cores, some authors have preferred to add the repulsion energy between positively charged cores to the total energy (Pople [171]; Del Re and Parr [38]; Fischer-Hjalmars [50, 51]):

$$E_{\text{total}} = E_{\text{electr}} + E_{\text{repuls}}\,.$$

As the cores are not bare nuclei, but consist of nuclei and σ-electrons, it has been proposed to consider the Coulombic part of the core-core interaction as a hole-hole interaction and to write it in the form (Del Re and Parr [38]):

$$E_{\text{repuls}} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}} n_\mu n_\nu (\mu\mu|\nu\nu)\,. \tag{4.11}$$

We may use (4.11) to define a new H_{eff} by the relation

$$E_{\text{total}} = \sum_{\mu,\nu} P_{\mu\nu} H_{\mu\nu}^{\text{eff}}\,. \tag{4.12}$$

It is, however, arbitrary how to divide the various parts of the energy to form matrix elements $H^{\text{eff}}_{\mu\nu}$. An interesting way to do it has been proposed by Fischer-Hjalmars [51]:

$$H^{\text{eff}}_{\mu\mu} = W_\mu + \frac{1}{4} P_{\mu\mu}(\mu\mu|\mu\mu) + \frac{1}{2} Q_\mu/P_{\mu\mu} \sum_{\sigma\neq\mu} Q_\sigma(\sigma\sigma|\mu\mu) \tag{4.13a}$$

$$H^{\text{eff}}_{\mu\nu} = \beta^{\text{spectr}}_{\mu\nu} + \frac{1}{4} P_{\mu\nu}(\mu\mu|\nu\nu)\,. \tag{4.13b}$$

A comparison of (4.9) and (4.13) shows that the non-diagonal elements of H_{eff} with and without core-core repulsion are the same whereas the diagonal part of (4.13a) is much more localized than of (4.9a). This localization effect may justify the procedure. On the other hand, the author wonders, whether the core-core repulsion is not better interpreted as a bonding part and has to be integrated into the non-diagonal part of the effective Hamiltonian. Nevertheless, the discussion about the effective Hamiltonian defined by (4.12) should not be overemphasized, because this Hamiltonian is not the one to determine the molecular orbital coefficients. It has been pointed out (F. Harris [74]) that once an effective Hamiltonian, which is dependent on charge distributions, is given according to (4.12), the eigenvectors for the MO's have to be determined by an operator F which is derived from H_{eff} by

$$F_{\mu\nu} = H^{\text{eff}}_{\mu\nu} + \sum_{\varrho,\sigma} P_{\varrho\sigma} \frac{\partial H^{\text{eff}}_{\varrho\sigma}}{\partial P_{\mu\nu}}\,. \tag{4.14}$$

In the above mentioned case, the proper operator for the MO's is still the SCF operator, whether the effective Hamiltonian contains core-core repulsion or not. The reason is that the core-core repulsion energy does not depend on $P_{\mu\nu}$.

A simpler way to correct the energy expression for Hückel calculations may be derived in the following way. We divide the total energy into

$$E_{\text{total}} = E_{\text{Hückel}} + \Delta E \tag{4.15}$$

where $E_{\text{Hückel}}$ contains the SCF part

$$E_{\text{Hückel}} = \sum_{\mu,\nu} P_{\mu\nu} F_{\mu\nu} \tag{4.16}$$

and ΔE the difference between core-core repulsion and electronic repulsion

$$\Delta E = \frac{1}{2} \sum_{\substack{\mu,\nu \\ \mu\neq\nu}} n_\mu n_\nu (\mu\mu|\nu\nu) - \frac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} G_{\mu\nu}\,. \tag{4.17}$$

Using the ZDO assumption for $G_{\mu\nu}$, E may be reformulated as

$$\begin{aligned} \Delta E = &-\frac{1}{4}\Big[\sum_{\mu} P^2_{\mu\mu}(\mu\mu|\mu\mu) - \sum_{\substack{\mu,\nu \\ \mu\neq\nu}} P^2_{\mu\nu}(\mu\mu|\nu\nu)\Big] \\ &+ \frac{1}{2} \sum_{\substack{\mu,\nu \\ \mu\neq\nu}} (n_\mu n_\nu - P_{\mu\mu} P_{\nu\nu})(\mu\mu|\nu\nu)\,. \end{aligned} \tag{4.18}$$

In many cases, it might be reasonable to assume the last term to be small, so we get

$$\Delta E = -\frac{1}{4}\left[\sum_{\mu} P_{\mu\mu}^2(\mu\mu|\mu\mu) - \sum_{\substack{\mu,\nu \\ \mu\neq\nu}} P_{\mu\nu}^2(\mu\mu|\nu\nu)\right]. \tag{4.19}$$

The first term represents an atomic contribution, the second a bonding part. Presumably the first term is larger. How small ΔE in (4.19) is depends on the special molecule. But anyway, it should be reasonable to compare total energies in classes of molecules where this term is approximately constant.

Another interesting discussion on the total energy expression has been given by Fukui and Fujimoto [55]. The authors apply the Mulliken approximation to the electronic repulsion integrals and collect intra- and inter-atomic terms. Within reasonable approximations they are able to explain that the resulting correction term ΔE is independent of the nuclear configuration. Some remarks have been given on the difficulty of representing H as a sum of one-electron operators.

IV. All-Valence Electron Treatment

1. *Hoffmann's Method* [83]

Basic Assumptions

A. All valence electrons are treated explicitly, only the 1*s*-electrons of carbon (or hetero) atoms are contained in the core.

B. All overlap integrals are calculated.

C. The Hamiltonian remains undefined. Its diagonal matrix elements are considered as semiempirical quantities.

$$H_{\mu\mu}^{\text{eff}} = \alpha_\mu . \tag{1.1}$$

D. The non-diagonal elements are approximated according to a generalized "Mulliken" form (Wolfsberg and Helmholz [209])

$$H_{\mu\nu}^{\text{eff}} = \tfrac{1}{2}K(\alpha_\mu + \alpha_\nu)S_{\mu\nu} . \tag{1.2}$$

The total energy[9] is considered as a sum of the eigenvalues of H_{eff} and can be formulated with assumptions (1.1) and (1.2) as

$$\begin{aligned} E_{\text{total}} &= \sum_i^{\text{occ}} \varepsilon_i \\ &= \sum_\mu N_{\mu\mu} + (K-1)(N_{\mu\mu} - P_{\mu\mu})\alpha_\mu \end{aligned} \tag{1.3}$$

where $N_{\mu\mu} = \sum_\nu P_{\mu\nu}S_{\mu\nu}$ is the gross atomic population (Mulliken [143]).

Basic Quantities

$S_{\mu\nu}$ calculated with Slater orbitals.

α_μ valence state ionization potential.

K is chosen as 1.75.

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[9] For a discussion see Fukui and Fujimoto [55].

Comments

The increasing difficulties in the reliability of improved Hückel theories for π-electron systems has finally led to a scheme which includes all valence electrons. One may wonder why it took so long to free the Hückel scheme from its obvious limitations: the restriction to planar unsaturated hydrocarbons and ZDO assumption for the overlap integral. In spite of many weak points of the extended Hückel theory like different parameter choice for excitation energies and total ground state energy, overemphasis of steric repulsions, or difficulty in predicting polarization effects, one should not forget the tremendous impulse which the work had on ab-initio calculations. The final breakdown of long believed π-electron theory assumptions was the discovery that σ-electron levels are embedded between π-electron levels in benzene. Treating the π-electrons apart was based on the assumption of a considerable energy gap between σ- and π-electrons so that moving of the π-electrons would not influence the σ-electrons very much. From the energy level arrangement of the extended Hückel method, however, one might expect σ-rearrangement effects with $\pi \to \pi^*$ excitation[10].

From the discussion in the previous chapter, it should be possible in extended Hückel theory to compare ground state energies in related molecules.

2. *Pople's Methods* [176–179]

a) Complete Neglect of Differential Overlap (CNDO)

Basic Assumptions

A. The method is designed for first row elements. All valence electrons are treated explicitly, only the 1s-electrons of carbon (or hetero)atoms are contained in the core.

B. The ZDO assumption is adopted for the overlap integrals

$$S_{\mu\nu} = \delta_{\mu\nu} . \tag{2.1}$$

C. The Hamiltonian operator is given as

$$H = T + U_A + \sum_{B \neq A} U_B \tag{2.2}$$

where U_A and U_B are the effective potentials resulting from atoms A and B.

D. The core integrals are divided into two categories given by the condition that μ and ν belong to the same atom A or not. In the first case it is assumed

$$\int \chi_\mu^* (T + U_A) \chi_\nu d\tau = \begin{cases} W_\mu & \text{if} \quad \mu = \nu \\ 0 & \quad\quad \mu \neq \nu . \end{cases} \tag{2.3}$$

The assumption for $\mu \neq \nu$ is justified by symmetry only, if χ_μ and χ_ν are *s*-, *p*- or *d*-orbitals, but not for hybrids. The case where μ and ν are on different atoms is treated under G.

E. The ZDO assumption for the interaction of electronic charge distributions on atom A with the core of atom B is adopted. To preserve invariance of those core integrals under rotations of local axes and hybridization it is assumed that

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[10] A comment by Prof. R. G. Parr has led the author to this more specific formulation.

the integrals are independent of the kind of orbitals, dependent only on the nature of atoms A and B

$$\int \chi_\mu^* U_B \chi_\nu d\tau = - U_{AB} \delta_{\mu\nu}, \qquad \mu \text{ on atom A} . \tag{2.4}$$

F. Under those simplifications α_μ and $\beta_{\mu\nu}$ with μ, ν on the same atom A may be written as

$$\alpha_\mu = W_\mu - \sum_{B \neq A} U_{AB} , \tag{2.5}$$

$$\beta_{\mu\nu} = 0 . \tag{2.6}$$

G. For μ, ν on different atoms A and B it is assumed

$$\beta_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} \tag{2.7}$$

where β^0_{AB} is dependent only on the nature of atoms A and B.

H. The ZDO assumption is adopted for electronic interaction integrals. To preserve invariance of these integrals under rotation of local axes or hybridization it is assumed that they depend only on the nature of the atoms to which the orbitals χ belong. This is important in cases where more than one electron per atom is contributed to the system.

$$(\mu\nu | \varrho\sigma) = \gamma_{AB} \delta_{\mu\nu} \delta_{\varrho\sigma}, \qquad \mu \in A, \ \varrho \in B . \tag{2.8}$$

I. Later (Pople and Segal [178]) the core potential U_{AB} is approximated by

$$U_{AB} = Z_B \gamma_{AB} . \tag{2.9}$$

Matrix Elements

The matrix elements of the SCF operator can be written as

$$F_{\mu\mu} = W_\mu + \left(P_{AA} - \frac{1}{2} P_{\mu\mu} \right) \gamma_{AA} + \sum_{A \neq B} (P_{BB} \gamma_{AB} - U_{AB}) \quad \text{CNDO/1} , \tag{2.10a}$$

$$\begin{aligned} F_{\mu\mu} = & - \frac{1}{2} (I_\mu + A_\mu) + \left\{ (P_{AA} - Z_A) - \frac{1}{2} (P_{\mu\mu} - 1) \right\} \gamma_{AA} \\ & + \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB} , \qquad \text{CNDO/2} \end{aligned} \tag{2.10b}$$

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \tag{2.10c}$$

with $P_{AA} = \sum^A_\nu P_{\nu\nu}$ total valence electron density on atom A. The total energy including nuclear repulsion is given as

$$E = \sum_A E_A + \sum_{A<B} E_{AB} \tag{2.11}$$

with

$$E_A = \sum^A_\mu P_{\mu\mu} W_\mu + \frac{1}{2} \sum^A_{\mu,\nu} \left(P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P^2_{\mu\nu} \right) \gamma_{AA} ,$$

$$\begin{aligned} E_{AB} = & \sum^A_\mu \sum^B_\nu \left(2 P_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} P^2_{\mu\nu} \right) \gamma_{AB} \\ & + (Z_A Z_B R^{-1}_{AB} - P_{AA} U_{AB} - P_{BB} U_{BA} + P_{AA} P_{BB} \gamma_{AB}) . \end{aligned}$$

For large internuclear distances the quantities approximate to R_{AB}^{-1}, so that the last group of terms become

$$Q_{\mathrm{A}} Q_{\mathrm{B}} R_{\mathrm{AB}}^{-1} \quad \text{with} \quad Q_{\mathrm{A}} = Z_{\mathrm{A}} - P_{\mathrm{AA}}\,.$$

Basic Quantities

$S_{\mu\nu}$ calculated theoretically.

$\gamma_{\mathrm{AA}} = \int s_{\mathrm{A}}^2(1) \frac{1}{r_{12}} s_{\mathrm{A}}^2(2) d\tau_1 d\tau_2$, calculated theoretically.

$\gamma_{\mathrm{AB}} = \int s_{\mathrm{A}}^2(1) \frac{1}{r_{12}} s_{\mathrm{B}}^2(2) d\tau_1 d\tau_2$ calculated theoretically.

$U_{\mathrm{AB}} = \int s_{\mathrm{A}}^2(1) \frac{Z_{\mathrm{B}}}{r_{1\mathrm{B}}} d\tau_1$, calculated theoretically.

$W_{\mu\mu}$ is taken from observed atomic energy data

$$-I_\mu = W_\mu + (Z_{\mathrm{A}} - 1)\gamma_{\mathrm{AB}} \quad \text{CNDO/1}$$

$$-(I_\mu + A_\mu) = W_\mu + (Z_{\mathrm{A}} - \tfrac{1}{2})\gamma_{\mathrm{AB}} \quad \text{CNDO/2}$$

$\beta_{\mathrm{AB}}^0 = \frac{1}{2}(\beta_{\mathrm{A}}^0 + \beta_{\mathrm{B}}^0)$; β_{A}^0, β_{B}^0 are chosen empirically to give the best overall fit with accurate LCAO calculations.

b) Neglect of Diatomic Differential Overlap (NDDO)

Basic Assumptions

A. The same as Aa.

B. The same as Ba.

C. The same as Ca.

D. The core integrals are divided into two categories given by the condition that μ and ν belong to the same atom A or not. In the first case all integrals are treated explicitly

$$\int \chi_\mu^* (T + U_{\mathrm{A}}) \chi_\nu d\tau = W_{\mu\nu}\,. \tag{2.12}$$

E. The same assumption is made for the interaction of electronic charge distributions on atom A with the core of atom B

$$\int \chi_\mu^* U_{\mathrm{B}} \chi_\nu d\tau = - U_{\mu\nu,\mathrm{B}}, \qquad \mu, \nu \text{ on A}\,. \tag{2.13}$$

F. Under these assumptions α_μ and $\beta_{\mu\nu}$ with μ, ν on the same atom may be written as

$$\alpha_\mu = W_{\mu\mu} - \sum_{\mathrm{B} \neq \mathrm{A}} U_{\mu\mu,\mathrm{B}}\,, \tag{2.14}$$

$$\beta_{\mu\nu} = W_{\mu\nu} - \sum_{\mathrm{B} \neq \mathrm{A}} U_{\mu\nu,\mathrm{B}}\,. \tag{2.15}$$

G. The same as Ga.

H. All two-electron integrals which depend on the overlapping charge densities of basic orbitals on different atoms are neglected

$$(\mu_{\mathrm{A}} \nu_{\mathrm{B}} | \varrho_{\mathrm{C}} \sigma_{\mathrm{D}}) = (\mu\nu | \varrho\sigma) \delta_{\mathrm{AB}} \delta_{\mathrm{CD}}\,. \tag{2.16}$$

Matrix Elements

In this case the matrix elements of the SCF operator cannot be simplified much

$$F_{\mu\mu} = \alpha_\mu + \sum_{\varrho,\sigma}^{A} P_{\varrho\sigma}\left\{(\mu\mu|\varrho\sigma) - \frac{1}{2}(\mu\sigma|\varrho\mu)\right\} + \sum_{B \neq A} \sum_{\varrho,\sigma}^{B} P_{\varrho\sigma}(\mu\mu|\varrho\sigma), \quad (2.17a)$$

$$F_{\mu\nu} = \beta_{\mu\nu} + \sum_{\varrho,\sigma}^{A} P_{\varrho\sigma}\left\{(\mu\nu|\varrho\sigma) - \frac{1}{2}(\mu\nu|\varrho\nu)\right\} + \sum_{B \neq A} \sum_{\varrho,\sigma}^{B} P_{\varrho\nu}(\mu\nu|\varrho\sigma), \quad (2.17b)$$

μ, ν on A,

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2}\sum_{\sigma}^{A}\sum_{\varrho}^{B} P_{\varrho\sigma}(\mu\sigma|\varrho\nu) \quad \mu \text{ on A}, \nu \text{ on B}. \quad (2.17c)$$

The total energy including nuclear repulsion can be derived from

$$E_{\text{total}} = \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}F_{\mu\nu} + E_{\text{nucl}}.$$

Basic Quantities

There is no discussion how to choose the quantities which occur in this method in addition to those of the CNDO method, especially the most general form of two-center electronic interaction integrals.

c) Intermediate Neglect of Differential Overlap (INDO)

Basic Assumptions

A. The same as Aa.

B. The same as Ba.

C. The same as Ca.

D. The diagonal core matrix elements are calculated by separating the interactions of the χ centered on atom A with the core of A and with the other atomic cores

$$\alpha_\mu = W_{\mu\mu} - \sum_{B \neq A} Z_B \gamma_{AB}. \quad (2.18)$$

E. The non-diagonal elements $\beta_{\mu\nu}$ with μ, ν on the same atom are

$$\beta_{\mu\nu} = W_{\mu\nu}. \quad (2.19)$$

F. The two-center core matrix elements are treated as in the CNDO method

$$\beta_{\mu\nu} = \tfrac{1}{2}(\beta_A^0 + \beta_B^0) S_{\mu\nu}. \quad (2.20)$$

G. The two-, three- and four-center integrals are set equal to zero unless $\mu = \nu$ and $\varrho = \sigma$. All one-center integrals are retained.

$$(\mu_A \nu_C | \varrho_B \sigma_D) = \gamma_{AB}\delta_{AC}\delta_{BD} \quad \text{if} \quad A \neq B. \quad (2.21)$$

Matrix Elements

With these assumptions the matrix elements of the SCF matrix may be written

$$F_{\mu\mu} = W_{\mu\mu} + \sum_{\varrho,\sigma}^{\mathrm{A}} P_{\varrho\sigma}\left\{(\mu\mu|\varrho\sigma) - \frac{1}{2}(\mu\sigma|\varrho\mu)\right\} + \sum_{\mathrm{B}\neq\mathrm{A}} (P_{\mathrm{BB}} - Z_{\mathrm{B}})\gamma_{\mathrm{AB}}, \quad (2.22\mathrm{a})$$

$$F_{\mu\nu} = W_{\mu\nu} + \sum_{\varrho,\sigma}^{\mathrm{A}} P_{\varrho\sigma}\left\{(\mu\nu|\varrho\sigma) - \frac{1}{2}(\mu\sigma|\varrho\nu)\right\}, \quad \mu, \nu \text{ on A}, \quad (2.22\mathrm{b})$$

$$F_{\mu\nu} = \frac{1}{2}(\beta_{\mathrm{A}}^{0} + \beta_{\mathrm{B}}^{0}) S_{\mu\nu} - P_{\mu\nu}\gamma_{\mathrm{AB}}. \quad (2.22\mathrm{c})$$

From these expressions the total energy may be derived according to

$$E_{\mathrm{total}} = \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu} F_{\mu\nu} + E_{\mathrm{nucl}}.$$

Basic Quantities

$$(ss|ss) = (ss|xx) = F^0 = \gamma_{\mathrm{AA}}$$
$$(sx|sx) = \tfrac{1}{3}G^1$$
$$(xy|xy) = \tfrac{3}{25}F^2$$
$$(xx|xx) = F^0 + \tfrac{4}{25}F^2$$
$$(xx|xy) = F^0 - \tfrac{2}{25}F^2$$

F^0 is evaluated from Slater type orbitals as in the CNDO method. F^2 and G^1 are determined semiempirically to fit atomic experimental data.

$W_{\mu\mu}$ is treated semiempirically by subtracting electronic interaction terms from the mean of the ionization potential I and electron affinity A of appropriate atomic states; they are different from those in the CNDO method because of various types of interaction integrals.

$W_{\mu\nu}$ is derived from orbital electronegativities.

Comments

After the obvious failure of the π-electron approximation in many cases, Pople and coworkers have finally offered three choices to overcome this difficulty. The approximations are along the lines of an earlier paper (Pople [171]): the ZDO assumption and the point charge interaction. But a full valence electron treatment causes a serious problem. Approximations for the various electronic interaction integrals and some core integrals have to fulfill certain invariance requirements concerning rotation and hybridization. Pople and coworkers have required that those integrals are dependent only on the atoms A and B, not on the special orbital. This implies the equivalence of all 2s- and 2p-orbitals on one atom in a molecule. CNDO calculations indicate that this might be a serious restriction in aromatic systems (Del Bene and Jaffé [35]). The author has shown that different shielding exponents are compatible with the invariance requirements without introducing stronger postulates than Pople *et al.* did. However ZDO can only be partly preserved, namely for orthogonal hybrids, each of which is composed of 2s- and 2p-orbitals with the same exponent (Jug [96]). Part of these consequences, namely different values for β_σ and β_π have already been used (Del Bene and Jaffé [35, 36]).

The author does not share the pessimism of a recent paper (Cook *et al.* [26, 27]) in which the CNDO method is found to be completely unreliable, and only the NDDO method is considered as a proper choice, because only the latter one has implicitly the features of an OAO basis together with localization properties. A careful parameter choice may reveal some justification for the CNDO method. In any case, there is some hope that the INDO method is sufficiently good to give reliable qualitative results.

The CNDO method has been analyzed recently on the basis of orthogonalized atomic orbitals (Dahl [33]; Dahl and Ballhausen [34]). It has been found to be linear, correct to the first order in the interatomic overlap integrals. The case of more than one orbital per atom was studied and the general applicability of the ZDO assumption to two-center exchange distributions questioned. The authors' argumentation against the NDDO method cannot be followed completely, because they do not distinguish carefully enough between different orders of magnitudes of integrals.

3. *Other Developments*

Calculations on molecules with σ-bonds have been based earlier on a concept by Lennard-Jones [116]. The idea that the energy is invariant under a transformation of the occupied orbitals among themselves has led to a series of papers on equivalent orbitals (Hall and Lennard-Jones [65, 66]; Lennard-Jones and Pople [117]; Hall [62]). Molecular orbitals can be formed from these bond orbitals, each of which is composed of atomic orbitals of two adjacent atoms. This concept of localized σ-bonds seemed to be appropriate for saturated molecules and has been used by Brown [17] and extended later by Del Re [37]. Along these lines are methods in which sp^3-hybrids are used as building units for paraffins (Sandorfy [188]; Yoshizumi [212]). Whereas the C–H bonds are neglected for simplicity, the introduction of response integrals besides the well-known resonance integrals $\beta' = m\beta$ ($m = 0.34$) allows for the consideration of non-bonding interactions. An extension of Yoshizumi's work to include non-linear paraffins which requires additional parameters has been described by Fukui *et al.* [54]. Recently another LCBO method for σ-electron systems has been proposed where the inner shell electrons are represented by AO's and the outer electrons by bond orbitals (Hamano [67]). SCF MO's are associated with lone pairs (one solution) and localized σ-bonds. The overlap between BO's is considered to be smaller as between AO's and therefore neglected[11]. The interaction between different bonds is given through the non-diagonal LCBO SCF elements which are taken as semiempirical parameters. Linear combinations of hybrids have been used in a Hückel-like theory for saturated compounds (Pople and Santry [174, 175]). Three α-values and six β-values have been used and $H_{\mu\nu}$ is neglected if μ, ν are on the same atom, which is valid only in highly symmetrical molecules.

Whereas a strict application to aliphatics caused no problem, molecules involving σ- and π-bonds had to be treated with different methods for the σ- and π-electrons, which sometimes was expressed by the assumption of non-polarized σ-bonds (McEwen [135]). This discrepancy has finally led to extensions which were more consistent. A good reason for the importance of the influence of the

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[11] The same idea has been expressed in another context again by Cook *et al.* [26].

σ-electrons on the π-electrons was given through a re-examination of conventional variational procedures in $\sigma-\pi$-systems where the dependency of π-electron parameters of the σ-electrons and vice versa was studied (Parks and Parr [163]; Stewart [200]). The last author gave a rather pessimistic view on the choice of semiempirical parameters. Non-empirical calculations on benzene with varying scale parameter Z show both state energies, and to a lesser degree excitation energies, as rapidly varying functions of Z. In conclusion any energy calculation with an effective charge Z which is not properly defined for molecules might have little quantitative significance (Stewart [201]).

The above described methods by Hoffmann [83] and Pople [176–179] have been widely used (*e.g.* Hoffmann [84]), occasionally even for second-row elements (Santry and Segal [189]). Another consistent scheme[12] to treat σ- and π-electrons has been developed by Berthier *et al.* [10]. Unfortunately the approximations make the method invalid for strongly polarized molecules. This difficulty may be avoided by introducing two-center repulsion integrals (de Brouckère [16]). Similar to the ω-method in π-electron theory, the extended Hückel scheme has been extended to include net charge effects in the effective Hamiltonian. The net charges are determined by an iterative SCF process, which sometimes leads to convergence problems (Duke [44]). It might be worthwhile to study this question in connection with the recent remark that the operator F which determines the MO coefficients and the operator H_{eff} which determines the total energy are different in cases where net charges are involved (F. Harris [74]).

Some methods have lost equivalence with the SCF method through application of the Wolfsberg-Helmholz approximation for β (Bishop *et al.* [13]) or establishing a linear dependency of W_μ and $(\mu\mu/\nu\nu)$ (Roos and Skancke [183]) or quadratic dependency of β (Nishimoto [149]) on the bond distance $R_{\mu\nu}$ which is taken as linearly dependent on $P_{\mu\nu}$. Nishimoto has argued that the quadratic term in his formula is small, so it might not effect the convergence of the SCF process. It has to be proved that this is valid also for the other methods. It is not quite clear, however, that a variation of E_{total} with respect to $R_{\mu\nu}$ (Skancke [195]; Nishimoto [149]) or with respect to $P_{\mu\nu}$ is equivalent.

An increasing number of semiempirical theories has been offered in recent years, many of them with similar features to those described above. Some remarks will be given on the following ones: A method similar to Pople's all-valence electron treatment has been proposed by Klopman [105, 106], where the one-center terms are determined through transition energies [104] and where the two-center terms are rigorously simplified to two species α_{AB} and β_{AB}, for which further approximations were applied. There is no discussion about the justification of the more severe simplifications. A method similar to the INDO method, where one-center exchange integrals are retained, has been proposed by Dixon [43] and Dewar and Klopman [41]. A simplified method for saturated hydrocarbons which has a close resemblance to a π-electron method (Fischer-Hjalmars [48]) has been proposed by Skancke [196]. Overlap is included and exchange and hybrid type integrals occur. Most interesting to notice is that α- and β-values are strongly dependent on the value of the overlap integral. Comparisons are

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[12] The method has been originally designed for transition metal complexes (Berthier, Millie, and Veillard [11]).

made for Slater's exponents and the optimized exponents for C_2 by Ransil [182]. An iterative SCF procedure for σ-reorganization effects has been used by Jungen *et al.* [103] for a treatment of π-electron transitions in formaldehyde. ZDO is rigorously applied, the remaining Coulombintegrals are multiplied with factors to compensate for correlation. The choice of these correlation factors is not unreasonable, but lacks somewhat quantitative significance. Heteroatomic cases cause a special problem. In a treatment of diatomic hydrides Jenkins and Pedley [94] describe the valence electron pair by an MO, the remaining electrons by AO's. The authors insert correction effects for the non-orthogonality. Because of the involved approximations, the paper is not easy to read. A simplified SCF method for σ-bonded systems is described and applied to hydrogen halides by Pohl *et al.* [170]. The inner shells and subshells are treated as non-polarizable core, only the electron pair in the bonding orbital is considered explicitly. Well-known approximations are used for core and electronic repulsion integrals, a new feature is the core-core repulsion formula, which is mentioned as due to J. Linderberg,

$$E_{\text{core-core}} = (1 + (Z-1)A\exp(-2\varrho R))/R\,, \tag{3.1}$$

Z nuclear charge, ϱ orbital exponent of a subshell,
A characteristic factor for atom involved,

which allows for penetration of the proton into charge clouds of lower subshells. Harris and Pohl [70] have made split-shell calculations for the valence electron pair. The different spatial orbitals for the two considered electrons were found to be complex conjugates in certain cases, which means that the spatial distribution is the same but the phase is different.

This may be the point to make a few remarks about the choice of β in Hückel-like theories, which once again seems to draw attention (Fukui [53]) and leads to discussions (Golebiewski and Taylor [61]), sometimes about facts which are already well-known (Blyholder and Coulson [14]). The series of calculations by Hoffmann [83, 84] has led to increased efforts with the extended Hückel method and the various choices for the evaluation of integral β are sometimes considered specific for the *extended* Hückel formalism, although most of them have their origin in π-electron theory. A survey is given in Table 1.

First one has to distinguish between methods using overlap integrals (χ) or neglecting them (λ). A relationship between $\tilde{\beta}_{\mu\nu}$ in a treatment including overlap integrals and $\beta_{\mu\nu}$ with neglect of overlap had been derived as early as 1941 by Mulliken and coworkers in a remarkably simple way. It has since been proved to be valid to the first order if one considers the basic orbitals for $\beta_{\mu\nu}$ as Löwdin orthogonalized orbitals (Ohno [153]). Methods 2–7 deal with overlap; 8–13 deal with the ZDO assumption. The simplest assumption for the first kind is the proportionality between $\tilde{\beta}_{\mu\nu}$ and $S_{\mu\nu}$ which was proposed first by Wheland and has been used later, *e.g.* in calculations on borides (Longuet-Higgins and Roberts [122, 123]). Methods 3[13] and 4 are different kinds of corrections to the arithmetic mean, which is sometimes called the Mulliken approximation. It may be noticed

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[13] The Wolfsberg-Helmholz approximation has been criticized recently by Berthier *et al.* [12] for lacking covariance under a unitary transformation of the basis.

Table 1. *Various approximations for the β integral*

1. $\beta_{\mu\nu}=\tilde{\beta}_{\mu\nu}-\frac{1}{2}(\tilde{\alpha}_\mu+\tilde{\alpha}_\nu)S_{\mu\nu}$	Mulliken *et al.* [144]; Pariser and Parr [161]
2. $\chi\,\tilde{\beta}_{\mu\nu}=KS_{\mu\nu}$	Wheland [208]; Longuet-Higgins and Roberts [122, 123]
3. $\chi\,\tilde{\beta}_{\mu\nu}=\frac{1}{2}K(\tilde{\alpha}_\mu+\tilde{\alpha}_\nu)S_{\mu\nu}$	Wolfsberg and Helmholz [209]; Hoffmann [83]
4. $\chi\,\tilde{\beta}_{\mu\nu}=\frac{1}{2}\{K+(\tilde{\alpha}_\mu+\tilde{\alpha})\}S_{\mu\nu}$	Berthier [8]
5. $\chi\,\tilde{\beta}_{\mu\nu}=\frac{1}{2}(\tilde{\alpha}_\mu+\tilde{\alpha}_\nu)\,S_{\mu\nu}(2-\lvert S_{\mu\nu}\rvert)$	Cusachs [30][14]
6. $\chi\,\tilde{\beta}_{\mu\nu}=K(\tilde{\alpha}_\mu\tilde{\alpha}_\nu)^{1/2}S_{\mu\nu}$	Ballhausen and Gray [5]
7. $\chi\,\tilde{\beta}_{\mu\nu}=K\dfrac{\tilde{\alpha}_\mu\tilde{\alpha}_\nu}{\frac{1}{2}(\tilde{\alpha}_\mu+\tilde{\alpha}_\nu)}S_{\mu\nu}$	Yeranos [211]
8. $\lambda\,\beta_{\mu\nu}=A\exp(-BR_{\mu\nu})$	Pariser and Parr [161]
9. $\lambda\,\beta_{\mu\nu}=A\exp(-R_{\mu\nu})$	Pritchard and Sumner [181]
10. $\lambda\,\beta_{\mu\nu}=A/R^6$	Kon [109]
11. $\lambda\,\beta_{\mu\nu}=n\left\{-\dfrac{2}{R}+(\mu\mu\vert\nu\nu)\right\}S_{\mu\nu}$	Ohno [153]
12. $\lambda\,\beta_{\mu\nu}=-\{K_1[(\mu\mu/\mu\mu)+(\nu\nu/\nu\nu)]+K_2(\mu\mu/\nu\nu)\}S_{\mu\nu}$	Fischer-Hjalmars [47]
13. $\lambda\,\beta_{\mu\nu}=\dfrac{1}{R_{\mu\nu}}\dfrac{dS_{\mu\nu}}{dR_{\mu\nu}}$	Linderberg [118]

however that Mulliken himself used this kind of approximation very carefully only for the three- and four-center integrals (Mulliken [142], see p. 500, 521). Some remarks on this approximation in terms of a series expansion have been given (Ruedenberg [186]; Parker [162]). Methods 3 and 4 result in connection with approximation 1 in the proportionality between $\beta_{\mu\nu}$ and $S_{\mu\nu}$. This cannot be valid in general because β-values for non-nearest neighbors may have opposite sign to nearest neighbor β-values (Chong [21]). An extension based on the observation that the kinetic energy integral for neighbors is proportional to the square of the overlap integral (Ruedenberg [187]) has led to method 6. Some discussion about failure of the method to be invariant under rotations has been given (Newton [146], Cusachs [31]). Finally there have been proposed geometric (method 7) and reciprocal (method 8) means. The first requires a positive value for $\alpha_\mu\alpha_\nu$. A case has been reported where this product was negative in a calculation on thiosulphate (Bishop *et al.* [13]). The author is inclined to believe that this is due to the way in which Bishop *et al.* assume the diagonal elements are dependent on net charges and iterate them to consistency (see again F. Harris [74]). Methods 8–13 present different choices for β-values in the ZDO assumption. Whereas the exponential dependency (methods 8–9) seems to be a natural choice for a proper distance interval, the inverse sixth power dependency (method 10) and the dependency on distance, two-center repulsion integral and overlap (method 11, 12) are quite unusual. A most interesting relationship has been derived recently between β and the slope of the overlap integral through a consistency requirement in PPP-theory concerning the equivalence dipole length and dipole velocity

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[14] A similar form $\beta\sim S(1-S)$ is mentioned in Parr's book ([166], p. 100) as due to an unpublished work of K. Ruedenberg and E. L. Mehler.

forms of the oscillator strength (method 13). The surprising result has been found that the slope of the overlap integral nearly independent of the choice of the orbital (Slater type and SCF orbitals), although the overlap values may differ by 20%. However, the actual β values have been calculated with Slater's shielding exponents. The formula should be checked with the more recent exponents (Silverstone *et al.* [192], Hermann *et al.* [80]).

Wratten [210] has given some comment on the β_A^0 of Pople's CNDO method under the assumption of exponential dependence of the overlap integral on the distance. A proportionality between β and the shielding exponent is found. To make this method superior to the others it has to be proved, however, that β goes to the proper limit α if $R=0$. This puts some restrictions on the form of S. The exponential form does not converge properly.

The variety of choices for $\tilde{\beta}$ and β parameters seems to suggest that there is no simple approximation for this integral.

V. Choice of Parameters in π-Electron Systems

1. *One-Electron One-Center Integrals*

α_μ	A	B	C	D	E
Carbon, eV	-6.64	-5.92	-12	-11.4	-11.28

A Hückel method; $-I_{\text{Benzene}} = \alpha + \beta$ (Fischer-Hjalmars [47]);
B Orthogonalized orbitals; $\alpha = -\frac{1}{2}(I_C + A_C)$ (Berthier *et al.* [10]);
C Hückel method including overlap; $\alpha = -(I_C + A_C)$ (Giambiagi *et al.* [57]);
D Extended Hückel method including overlap; $\alpha = -I_C$ (Hoffmann [83]);
E SCF method; $\alpha = -I_C$ (Fischer-Hjalmars [47]).

Remarks. Note that $\alpha_\mu^{\text{Hückel}} = \int \chi_\mu^* H_{\text{eff}} \chi_\mu d\tau$ whereas in SCF theory

$$\alpha_\mu = \int \chi_\mu^* H_{\text{core}} \chi_\mu d\tau \,.$$

W_{2p}	A	B	C
Carbon, eV	-11.22	-9.50	-9.59

A Carbon sp^3 valence state potential; $W_{2p} = -I_C$ (Pariser and Parr [161]);
B fits average ionization potential of benzene and ethylene;

$$-\tfrac{1}{2}(I_{\text{Benz}} + I_{\text{Meth}}) = W_{2p} + \tfrac{1}{2}\gamma_{11} - \tfrac{1}{2}\sum_{\mu,\nu} c_{i\mu}^2 c_{i\nu}^2 \gamma_{\mu\nu}$$

(Hush and Pople [90]);
C fits ionization potential of ethylene; $-I_{\text{Eth}} = W_{2p} + \beta_{\mu\nu} + \frac{1}{2}\{(\mu\mu|\mu\mu) - (\mu\mu|\nu\nu)\}$ (Fischer-Hjalmars [48]).

Remarks. Neither α nor W_{2p} are necessary for the calculation of excitation energies in hydrocarbons. Valence state ionization potentials and electron affinities are most often taken from the work of Hinze and Jaffé [81] and Hinze *et al.* [82].

2. *One-Electron Two-Center Integrals*

$\beta_{\mu\nu}$	A	B	C	D	E
Benzene, $R=1.39$ Å eV	-2.6	-2.2^{a} -2.39^{b} -2.79^{c}	-5.19	-5.15	-1.16

A Hückel method without overlap; $\beta_{\mu\nu}^{\text{Hückel}}$ (Fischer-Hjalmars [47]);
B Pariser-Parr method without overlap; $\beta_{\mu\nu}$ (Pariser and Parr [161]); electronic interaction integrals calculated
  a) theoretically, $\zeta=1.59$,
  b) semiempirically, $\gamma_{\mu\mu}=I_{\mathrm{C}}-A_{\mathrm{C}}$,
  c) by uniformly charged sphere model;
C Hückel method including overlap; $\tilde{\beta}_{\mu\nu}=\frac{1}{2}K(\tilde{\alpha}_{\mu}+\tilde{\alpha}_{\nu})S_{\mu\nu}$ (Hoffmann [83]);
D non-orthogonal orbitals; $\tilde{\beta}_{\mu\nu}=\beta_{\mu\nu}+\frac{1}{2}(\tilde{\alpha}_{\mu}+\tilde{\alpha}_{\nu})S_{\mu\nu}$, $\beta_{\mu\nu}=-8.53\,S_{\mu\nu}$ (Berthier [8, 10]);
E Hückel method including overlap; $\tilde{\beta}_{\mu\nu}=-(A_{\mu}+A_{\nu})$ (Giambiagi *et al.* [57]).

Remarks. Dependency of β on the distance R is given in Table 1.

3. *Two-Electron One-Center Integrals*

$(\mu\mu\|\mu\mu)$	A	B	C	D	E	F	G	H	I
Carbon, eV	16.93	17.30	15.71	12.2	11.9	10.53	9.87	12.72	12.38

A theoretical value using Slater type $2p$-orbitals, $\zeta=1.59$ (Parr, Craig and Ross [167]);
B theoretical value using orthogonalized orbitals (Fischer-Hjalmars [49]);
C theoretical value using SCF orbitals (Silverstone *et al.* [192], see also Sponer and Löwdin [199]);
D $(\mu\mu|\mu\mu)_{\text{exact}}=(\mu\mu|\mu\mu)_{\text{HF}}-n\cdot 2\,V_{2p,\text{corr}}$, n number of $2p$-electron pairs (Arai and Lykos [4]);
E $(\mu\mu|\mu\mu)=\frac{501}{9}F_2^{pp}$ (Fischer-Hjalmars [48]);
F semiempirical value, $(\mu\mu|\mu\mu)=I-A$ (Pariser [159]);
G $(\mu\mu|\mu\mu)=I-A+\varepsilon(I+A)$ (Julg [98, 99], Berthier *et al.* [9]);
H derived from reaction $2C\rightarrow C^{-}+C^{+}$ together with correlation considerations (Orloff and Sinanoğlu [157]);
I minimization of newly defined valence state energy, non-integral n^* (Silverstone *et al.* [192]).

4. *Two-Electron Two-Center Integrals*

$(\mu\mu\|\nu\nu)$	A	B	C	D	E	F
Benzene, $R=1.39$ Å eV	9.03	8.71	10.31	5.32	7.3	7.45

A theoretical value using Slater $2p\pi$-orbitals, $\zeta=1.59$ (Parr, Craig and Ross [167]);
B orthogonalized orbitals, (Fischer-Hjalmars [49]);
C $(\mu\mu|\nu\nu)=1/R$ (Pople [171]);
D $(\mu\mu|\nu\nu)=1/(a+R)$, $1/a=(\mu\mu|\mu\mu)=I-A$ (Nishimoto and Mataga [151]);
E $(\mu\mu|\nu\nu)=\frac{1}{2}\{(\mu\mu|\mu\mu)+(\nu\nu|\nu\nu)\}-(aR+bR^2)$, a and b fitted by uniformly charged sphere model for 2.8 Å and 3.7 Å (Pariser and Parr [161]);
F theoretical value using Slater $2p\pi$-orbitals, $\zeta=0.925$ derived by fitting theoretically the value for $(\mu\mu|\mu\mu)$ in 3*F* (Julg [98, 99]; Berthier *et al.* [9]).

5. *Multicenter, Exchange and Penetration Integrals*

Benzene, $R=1.39$ Å eV	A	B	C
(11|12)	3.37	−0.067	
(11|13)	0.403		
(11|23)	1.957		
(12|12)	0.968	0.088	
(1:11)	23.213	24.974	35.77
(1:22)	0.759	0.762	2.42
(1:12)	1.761	−1.641	3.06
(1:13)	0.105	0.083	
$(1_H:11)$	0.645	0.667	0.608
$(1_H:22)$	0.018	0.005	
$(1_H:12)$	0.093	0.004	

A theoretically calculated for Slater $2p\pi$-orbitals (Fischer-Hjalmars [49], see also Parr, Craig and Ross [167]);
B theoretically calculated for orthogonalized orbitals (Fischer-Hjalmars [49]);
C theoretically calculated for Slater $2p\pi$-orbitals, $\zeta_{\text{core}}=1.13$, $\zeta_\pi=1.61$ (Ruedenberg [187]).

Remarks. Values for four-center integrals may be obtained from Harris and Michels [72].

VI. Problem of Overlap

Even if one considers the basic orbitals as Löwdin orthogonalized orbitals $\{\lambda\}$ there remains the problem how to choose the basis $\{\chi\}$ to get the transformation matrix $S^{-1/2}$. Until now many proposals have been made for basis sets $\{\chi\}$. Even a restriction to Slater type orbitals yields a variety of choices which differ in the value for the overlap integral S. Some values for overlap integrals for π-electrons are listed in Table 2.

Table 2

	A	B	C	D
S Benzene, $R=1.4$ Å	0.26	0.33	0.38	0.49

A STO's with $\zeta=1.59$	Parr, Craig and Ross [167]
B Carbon SCF orbitals	Sponer and Löwdin [199]
C CH_3 radical orbitals	Hermann *et al.* [80]
D STO's with $\zeta=1.015$	Giambiagi *et al.* [57]

The Slater type overlap integral is essentially dependent on the choice of the exponent, which is determined by the choice of the effective charge Z_{eff} and the effective quantum number n^*. The larger the shielding by the "inner" electrons the more extended is the charge cloud of an atomic orbital in space. Atomic shielding parameters or effective nuclear charges have been proposed through the variation principle to an appropriate atomic valence state energy (Zener [213], Silverstone *et al.* [192]), atomic energy data (Slater [197]; Kohlrausch [107]), through comparison of the moments with SCF calculations (Burns [19]) and through molecular fragment calculations[15] (Hermann *et al.* [80]).

Tables 3 and 4 show that newer studies suggest different values for the effective charges of σ- and π-orbitals. This conclusion has been reached earlier through exponent optimization of C_2 in an ab-initio calculation (Ransil [182]). Some scale factors yield rather large values for the π-electron overlap integrals. This raises some doubt in the validity of a truncated expansion of integrals in powers of S.

Table 3. *Effective charges Z_{eff} in neutral carbon atoms*

	A	B	C	D
1*s*	5.70	6	5.68	5.38 (0.92); 9.15 (0.08)
1*s*	5.70	5.375	5.68	5.38 (0.92); 9.15 (0.08)
2*s*	3.25	4.37	3.33	3.36 (0.849)
2*px*	3.25	3.78	3.22	1.94 (0.118); 3.36 (0.419); 7.1 (0.087)
2*py*	3.25	2.76	3.22	1.94 (0.118); 3.36 (0.419); 7.1 (0.087)
2*pz*	3.25	2.03	2.58	1.91 (0.435); 2.84 (0.438); 5.18 (0.194)

A Slater [197], B Kohlrausch [107], C Silverstone *et al.* [192], D Hermann *et al.* [80].

Table 4. *Effective charges for 2s- and 2p-orbitals in carbon ions*

Charge	A	B	C	D
+3	4.36	4.30	4.37	
+2	4.02	3.95	3.78; 4.37	
+1	3.63	3.60	2.76; 3.78; 4.37	3.5
0	*3.28*	*3.25*	*2.03*; 2.76; 3.78; 4.37	*3.08*; 3.13; 3.29
−1	*2.93*	*2.90*	*1.28*; *2.03*; 2.76; 3.78; 4.37	*2.3*; 2.98; 3.2

π-orbital effective charges in italics.
A Zener [213], B Slater [197], C Kohlrausch [107], D Joy and Silverstone [95].

Method of Calculation

Zener: Variation method with variation parameters n, γ, δ. $Z_{\text{eff}} = n^*(\Sigma \varepsilon_i / n)^{1/2}$; Z_{eff} eff. charge, n^* eff. quantum number, n number of electrons in L-shell, ε_i ionization potential, γ exponent for 1*s*, δ exponent for 2*s*, 2*p*.

Slater: Rules to get adjustment to stripped atoms, X-ray energy levels, sizes of atoms and ions.

Kohlrausch: Effective charges are calculated by the assumption that the electrons are influenced by inner electrons only (Aufbau principle); $A = \alpha(Z - \sigma)^2 - \gamma$, where A = ionization potential.

Silverstone et al: Minimization of a valence state energy which is defined by keeping only atomic terms in a molecular energy expression.

Hermann et al.: Minimization of the energy of the CH_3 radical with an ab-initio calculation.

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[15] For further data see Sharp-Ritter and Lykos [191].

VII. Possible Extensions

The description along these lines so far is rather limited. We have to remember that we posted severe restrictions on the scheme at the very beginning: We gave a picture of a scheme for a closed-shell molecule where each electron was represented by a single atomic orbital only and the total wavefunction by a single configuration. The molecular orbitals were determined by the independent particle Hartree-Fock formalism.

Extensions of this scheme should consequently include 1) open-shell situations, 2) higher than $2p\pi$-orbitals in the LCAO expansion, 3) configuration interaction and 4) correlation. Although there has been a lot of work in these directions, we are not able yet to integrate these ideas to form a more general scheme similar to what has been outlined in Chapters II and IV.

An open-shell case is given for singly excited states. The reader may have wondered why so far no discussion on this topic was included. Although some regularities for excitation energies have been found which reduce them to differences of a few basic quantities (Lykos [131]; Murrell and Salem [145]; Ruedenberg [187]), progress has been slow for an obvious reason. The singly excited state is not a closed-shell state so that a basic assumption of the treatment in Chapter I is not fulfilled. Furthermore it is not at all obvious that a parametrization scheme which is based on the variation of the ground state energy should be significant for excited states. The author and others have made ab-initio calculations in an extended Hartree-Fock formalism on excited Π_u- and Π_g-states of H_2 to simulate a situation where a π-electron in a π-electron system moves into a higher excited state (Jug *et al.* [97]). It turns out that although the σ-MO did not change much, the π-orbital exponents for the π_u- and π_g-orbitals differ considerably if the total energy of both states is minimized separately[16]. This yields as conclusion that not only in Hückel theory, but also in SCF theory one might not be able to describe properties of the ground state and excited states with the same set of parameters. Dewar has pointed this out earlier and uses a semiempirical technique to determine the resonance integral β from the heat of formation of molecules to get reliable ground state properties (*e.g.* Chung and Dewar [22]; Dewar and Gleicher [40]). The next steps should be taken towards an open-shell semiempirical theory. First attempts have already been made (Pople and Segal [178]; Kroto and Santry [114]).

In cases where ionization is involved, problems become even more critical because the elimination of one π-electron causes $\sigma - \pi$-deformation effects (Hoyland and Goodman [85, 86]), which are so large that the assumption of an unchanged core (Koopmans [110]) is no longer justified.

Some efforts have been made to include $3p\pi$- or $3d\pi$-orbitals into π-electron theory (Jacobs [93]; Hartmann [75, 76]; Sovers and Kauzmann [198]). Although some qualitative results have been given, which seemed to encourage proceedings along these lines, difficulties in the justification of the predictions of smaller order effects in connection with the involved approximations have led the development in other directions.

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[16] An indication for this result is given in a π-electron calculation by Huzinaga [91], however the σ-core has been subjected to certain approximations.

For a long time, it has been well-known that configuration interaction might be important in molecular calculations. Extensive calculations have been performed (Parr, Craig and Ross [167]; Pariser [160]; Koutecký *et al.* [113]), suggestions for excited states have been made (Pople [172]), but no systematic way has been developed yet how to choose the most important configurations and integrate them into a semiempirical scheme. Recently studies have been made on triplet and doublet states of polyenes and polyacenes to compare restricted open-shell treatment and limited configuration interaction (Wagnière [206]). Both methods may need different semiempirical parameters in π-electron systems and the quality of total energy values is found to be accidental sometimes. Another study which systematically treated the effect of more and more "excited" configurations revealed the fact that a large number of higher lying doubly excited configurations may cause a considerable change in the value of excitation energies (Allinger and Stuart [2]).

An encouraging step forward is the paper by Hansen [68] who has shown that in a two-configuration case for H_2 the formalism of the one-configuration case may be preserved by ascribing the $\beta_{\mu\nu}$ and $(\mu\mu|\mu\mu)$ parameters reduced and the $(\mu\mu|\nu\nu)$ parameters increased values. This leads to the conclusion that even in more complicated cases one may take care of correlation in semiempirical theories through a proper parameter choice.

Although there has been much work done on the explanation of correlation effects concerning the one-center repulsion integral $(\mu\mu|\mu\mu)$ (Kolos [108]; Julg [98, 99]; Arai and Lykos [4]; Hermann [79]; Orloff and Sinanoğlu [157]), few authors have concerned themselves to create a new scheme to include correlation. Perhaps the most extensive efforts have been made in the "méthode LCAO ameliorée" (Julg [100]; Julg and Bonnet [102]). There have been some difficulties in the fundamental argumentation. Later, the method was reduced to a semiempirical process where integrals are multiplied by reduction factors to account for correlation (*e.g.* Julg [101]). Unfortunately this process does not give insight into the underlying theoretical structure. For alternant hydrocarbons the *alternant molecular orbital* method (Löwdin [129]) seems to have special merits. It is equivalent to a limited configuration interaction treatment, but is superior because of its problem adapted character. A series of papers has proved its value for calculations on aromatic systems (de Heer [77, 78]; Pauncz *et al.* [169]; Pauncz [168]). Other methods which include correlation implicitly are the split-orbital method (Dewar and Sabelli [39]) and the non-paired spatial orbital method (Empedocles and Linnett [46]).

All these extensions cause a serious computational problem and prevent calculations for larger molecules. A solution out of this dilemma may be found in the idea of *building blocks* (Orloff and Fitts [156]; Newton, Boer, and Lipscomb [147]). The authors propose to build new matrices of the effective Hamiltonian for more complicated systems by using the results of previous SCF calculations on simpler similar systems. An equivalent idea is the method of grouping Gaussian type functions in ab-initio calculations (*e.g.* Preuss and Diercksen [180]).

Recently there has been drawn much attention on localized orbitals as the most appropriate for transfer to larger molecules (Edmiston and Ruedenberg

[45]; Trindle and Sinanoğlu [203]). Investigations on correlation in localized orbitals have also been started (Sinanoğlu and Skutnik [194]).

From a practical point of view, an idea for the calculation of multicenter integrals might prove useful: the expansion of two-center charge distributions as a truncated set of one-center distributions (Harris and Rein [71]; Cizek [23]).

Recently it has been attempted to get some more insight into π-electron theory by the method of second quantization (Linderberg and Öhrn [119, 120]; Öhrn and Linderberg [155]; R. Harris [73, 74]). So far it seems that the difficulties in calculations cannot be avoided by a simple recipe.

Acknowledgement. This research has been supported by a grant of the National Institutes of Health. The author is indebted to Professor P. G. Lykos and the members of the theoretical chemistry group for many valuable discussions. The author is most grateful to Professor R. G. Parr for drawing his attention to some recent papers and to Professor K. Ohno for suggesting references of all-valence electron methods. He also gratefully acknowledges comments and suggestions by Professors G. Berthier, I. Fischer-Hjalmars, F. Harris, R. Hoffmann, and J. A. Pople. Mr. A. Starshak was helpful in reading the manuscript.

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Dr. Karl Jug
Department of Chemistry
Saint Louis University
Saint Louis, Missouri, USA