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Commentationes

How Quantitative is the Concept of Maximum Overlap?*

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A criterion based on the concept of maximum overlap has been used as an optimizing principle to obtain approximate all valence electron wave functions for a variety of molecules. By means of this procedure, the wave functions are obtained without the use of parameters, semiempirical data, or integral approximations. Even though there are obvious errors in such an approach, the charge densities and dipole moments calculated from these wave functions have a surprising degree of validity. It does appear, though, that the results will be most reasonable for strongly covalent molecules, where large amounts of charge migration are not involved.

Ein Kriterium auf Grund der Konzeption der maximalen Überlappung wurde als Optimalisierungsprinzip verwendet, um Wellenfunktionen für alle Valenzelektronen einer ganzen Reihe von Molekülen zu finden. Auf diesem Weg werden keine Parameter, semiempirische Daten oder Integralnäherungen benötigt. Trotz der offensichtlichen Vernachlässigungen sind die erhaltenen Ladungsdichten und Dipolmomente erstaunlich gut. Allerdings scheint es, als ob die Ergebnisse bei ausgeprägt kovalenten Molekülen am besten wären, wo größere Ladungsverschiebungen nicht auftreten.

Utilisation d'un critère fondé sur le concept du recouvrement maximum comme principe pour obtenir des fonctions d'onde pour tous les électrons de valence de toute une variété de molécules. A l'aide de ce procédé les fonctions d'onde sont obtenues sans l'emploi de paramètres, de données semi-empiriques ou d'approximation d'intégrales. Quoique cette approche comporte des erreurs évidentes, les densités de charge et les moments dipolaires calculés à partir de ces fonctions d'onde ont un degré de validité surprenant. Il apparaît néanmoins que les résultats seront d'autant plus raisonnables que les molécules seront plus covalentes et ne comporteront pas de transferts de charges importants.

1. Introduction

The "criterion of maximum overlap" between the atomic orbitals of one atom and those of another leads to an appealing, though naive, picture of chemical bonding. Briefly, a bond in a molecule is thought to be most stable for a given bond length when the atomic orbitals on one center have the largest overlap with the orbitals on a second center. The connection between maximum overlap and the strength of a chemical bond originated in the studies of valence by Pauling and Slater as an aid in deciding which atomic orbitals, or combinations of them, could give the strongest bonds in molecules. Pauling defined an index of bond strength, solely on the basis of the angular dependence of the atomic orbitals, and concluded that "the energy of a bond is about proportional to the [strengths] of the bond orbitals of the two atoms" [1]. Mulliken generalized this idea suggesting that the overlap integral itself would logically be a better index of bond strength,

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since both the radial and the angular portions of the atomic orbital are taken into account [2].

Although the proportionality between bond energy and maximum overlap is only qualitative, it is the intention of this paper to investigate the degree of validity of a form of the "maximum overlap criterion" in a more quantitative sense than is customary, namely, as an optimizing principle to employ in generating simple wave functions for molecules.

This point of view seems to have been first used by Lykos and Schmeising [4], who employed a "maximum overlap criterion" in order to generate approximate wave functions for π-electron molecules. In addition, they applied the basic analysis to atoms which, though inconsistent with the "chemical" concept of maximum overlap, served to illustrate a defect of the method that is also apparent in molecular problems; and thirdly, generalizing an earlier analysis by Murrell [7], they employed the "overlap criterion" in its traditional valence-bond domain to predict hybrid orbitals. Our primary concern is with the first of these applications, since it is our objective to investigate the validity of wave functions obtained from the "maximum overlap criterion" but for more general systems where all valence electrons are considered.

It should be noted that the desired wave function is defined as the solution of the time independent Schrödinger equation corresponding to a particular eigenvalue which, for our purposes, will always be the ground state. Since this equation can only be solved exactly for a handful of special cases, it is conventional to assume a form for the wave function and obtain an approximation to it by utilizing the variational principle. Even this *ab initio* procedure is impractical for larger molecules, so one makes additional simplifications in the form of parameters, semi-empirical data, etc., in order to obtain an estimate of the actual eigenfunction. The maximum overlap approach is an attempt to generate very approximate wave functions from a different viewpoint, where no explicit consideration of a Hamiltonian and its associated variational principle is required, but where the use of a reasonable atomic basis assures some connection with atomic Hamiltonians.

If it were true that minimum energy and maximum overlap were equivalent, then it would be possible to obtain wave functions using the latter criterion, where only overlap integrals are needed, rather than the variational principle where one has the usual integral problems. Of course, this cannot actually be the case since a Hamiltonian contains much more information than can be gleaned from overlap considerations alone. However, if the maximum overlap criterion in conjunction with a reasonable atomic orbital basis has some correspondence with the minimum energy state for the molecule – as the qualitative analogy between the two would lead one to believe – then it should be possible to generate very approximate wave functions by imposing the criterion. Depending on the degree of validity of this approach, one will have certain advantages over the usual semi-empirical schemes.

This point of view may be somewhat unconventional, so it will be desirable to briefly illustrate some differences and similarities with the standard semi-empirical Hamiltonian approach. To begin with, the maximum overlap criterion can be imposed using only overlap integrals (in particular, the overlap matrix), and, as such, the wave functions are generated without any explicit use of a Hamiltonian. This has the necessary consequence that one normally does not obtain energies but only the approximate wave function. Many properties of experimental interest are determined as expectation values so there is a need for the wave functions themselves with total energies often of lesser interest to the problem. Although there is no explicit utilization of a Hamiltonian, by using an atomic orbital basis which is a set of approximate solutions to the atomic Hamiltonian, one is at least implicitly using a proper equation of motion.

In order to estimate the matrix elements, $F_{\mu\nu}$, of the "effective" Hamiltonian matrix F (Fock matrix), semi-empirical methods usually make use of parameterization and experimental data to some extent, as well as employing certain integral approximations such as the assumption of "zero differential overlap". Once this is done, the Hamiltonian is changed and the variational principle is no longer a strictly valid extremum condition for the original Hamiltonian (total energies below the experimental value are common), so that one is in a sense using an "approximate" optimizing principle. This fact may raise some questions about energies in semi-empirical theories, but since the approximate Fock matrix exhibits the molecular symmetry, one hopes that the corresponding wave functions still have some important features in common with their exact counterparts. Only in very special cases will symmetry alone determine the wave function, but it will often specify some of the one-electron functions as well as restricting the remainder, thereby helping to establish the form of the total wave function. This property is also true of the overlap matrix, and, as such, the "maximum overlap wave functions" also use symmetry to their advantage.

Another feature related to the maximum overlap idea that is peculiar to several semi-empirical methods, is the assumption that some sort of proportionality exists between the off-diagonal Fock matrix elements and the corresponding overlap. For example, it has been assumed that $F_{\mu\nu} = kS_{\mu\nu}$ where k is a parameter, as well as other even more exotic functions of the overlap. This kind of supposition could be considered a parameterized extension of the qualitative analogy between bond strength and overlap.

In the following using maximum overlap in the sense of Lykos and Schmeising [4], we shall generate simple approximate wave functions for a variety of molecules and investigate their validity by calculating dipole moments and charge densities. Comparisons with CNDO [10] wave functions will also be made.

2. Maximum Overlap Molecular Orbitals

Following Lykos and Schmeising [4], we shall impose the maximum overlap criterion by a consideration of the scalar products $\langle \chi_\mu | \psi_i \rangle$ where $\{\chi_\mu\}$ represent a set of atomic orbitals and

$$\psi_i = \boldsymbol{\chi} \boldsymbol{a}_i , \qquad \boldsymbol{\chi} = (\chi_1 \chi_2 \cdots \chi_m) \tag{1}$$

with the coefficients to be determined by the maximum overlap constraint. If the basis is orthogonal on one center, then this scalar product gives a constant depending on normalization and a sum of two center overlap integrals weighted by the linear coefficients, $\{a_{\nu_i}\}$. The overlap integrals are fixed by the choice of basis for a particular internuclear separation, so by properly choosing the molecular orbital coefficients, the sum of the two center overlaps can be made a maximum. Since it is possible that the scalar product $\langle \chi_\mu | \psi_i \rangle$ may be complex or negative, we will measure its magnitude in terms of the real and positive quantities,

$$\langle \chi_\mu | \psi_i \rangle^* \langle \chi_\mu | \psi_i \rangle = |\langle \chi_\mu | \psi_i \rangle|^2 \,. \tag{2}$$

By summing over all μ and i and requiring that sum to be a maximum subject to the usual orthonormality constraints, a set of "molecular orbitals" exhibiting maximum overlap in the defined sense can be obtained[1].

Introducing the Lagrangian multiplier, $-\lambda_{ji}$, it follows that the maximizing functional takes the form

$$q = \sum_i \sum_\mu \langle \psi_i | \chi_\mu \rangle \langle \chi_\mu | \psi_i \rangle - \sum_{i,j} \lambda_{ji} \langle \psi_i | \psi_j \rangle \,. \tag{3}$$

Defining the matrix $\boldsymbol{\Delta} = \langle \boldsymbol{\chi} | \boldsymbol{\chi} \rangle = \mathbf{1} + \boldsymbol{S}$ and using $\sum_\mu |\chi_\mu\rangle \langle \chi_\mu| = |\boldsymbol{\chi}\rangle \langle \boldsymbol{\chi}|$, we have

$$q = \sum_i \boldsymbol{a}_i^\dagger \boldsymbol{\Delta}^2 \boldsymbol{a}_i - \sum_{i,j} \lambda_{ji} \boldsymbol{a}_i^\dagger \boldsymbol{\Delta} \boldsymbol{a}_j \,. \tag{4}$$

Requiring that q be extreme gives

$$\boldsymbol{\Delta}^2 \boldsymbol{A} = \boldsymbol{\Delta} \boldsymbol{A} \boldsymbol{\lambda} \,, \qquad \boldsymbol{A} = (\boldsymbol{a}_1 \boldsymbol{a}_2 \ldots \boldsymbol{a}_m) \,. \tag{5}$$

We are at liberty to carry out a unitary transformation that will make $\boldsymbol{\lambda}$ diagonal, so

$$\boldsymbol{\Delta}^2 \boldsymbol{C} = \boldsymbol{\Delta} \boldsymbol{C} \boldsymbol{d} \,, \qquad \boldsymbol{C} = \boldsymbol{A} \boldsymbol{V}, \qquad \boldsymbol{d} = \boldsymbol{V}^\dagger \boldsymbol{\lambda} \boldsymbol{V}. \tag{6}$$

Assuming that $\boldsymbol{\Delta}$ is non-singular, which is necessary for a linearly independent basis set, we obtain the eigenvalue equation,

$$\boldsymbol{\Delta} \boldsymbol{C} = \boldsymbol{C} \boldsymbol{d} \,. \tag{7}$$

These are the usual equations that define the "canonical orthogonalization" procedure for an overlapping basis [5]. But in addition to this, the coefficients, $\boldsymbol{C}$, are the set of eigenvectors that manifest the maximum overlap criterion. If $\boldsymbol{U}$ is the unitary matrix that diagonalizes the Hermitian matrix, $\boldsymbol{\Delta}$, then $\boldsymbol{C} = \boldsymbol{U} \boldsymbol{d}^{-\frac{1}{2}}$ with $\boldsymbol{C}$ the properly normalized eigenvectors for an overlapping basis. The $\boldsymbol{U}$ vectors are the proper coefficients for a symmetrically orthogonalized basis [5, 6].

With these spatial one-electron functions determined, the N-particle wave function is assumed to be a single determinant composed of N-pure spin orbitals. The orbitals are consecutively occupied according to the magnitude of their associated overlap eigenvalues.

Maximum overlap in the sense used here, differs from the customary idea to some extent. Traditionally "maximum overlap" pertains to a particular "bond" in a molecule, where it is invoked to predict the hybrid that will give the largest overlap and, thusly, the strongest bond[2]. As used here, a set of "molecular orbitals" are found such that the weighted two center overlap in the entire molecule is maximized, regardless of whether any two particular centers coincide with

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[1] It is important to observe that it is always possible to obtain more overlap by expanding the basis set. Consequently, the concept of maximum overlap can only be meaningful for a specified basis.

[2] Variants of the previous formulation have been applied to this problem by Murrell [7], Gilbert and Lykos [8], and Golebiewski [28].

a "bond" in the chemical sense. Also, hybrids do not have their traditional significance, since in the present approach, as in most quantum chemical formulations, they are merely an arbitrary unitary transformation of the basis set that may be pictorially desirable, but has no effect on any observables.

Since the solution of (7) requires only an overlap matrix, the sole arbitrariness in formulating the problem is essentially the same as in an *ab initio* procedure, namely the choice of basis[3]. This being the case, by accepting the maximum overlap criterion one has immediately three advantages over many other semi-empirical or simplified methods: (1) there are absolutely no parameters of either the "fixed" or "adjustable" type needed; (2) there is no need for the use of any experimental data or approximately calculated quantities; and (3), the method is computationally about as simple an all valence electron treatment as is possible.

Besides the fact that parameters are usually considered to be unpalatable, a more pertinent reason for avoiding both the parameters and semi-empirical data is that the wave function predicted by the diagonalization of an approximate Fock matrix may be sensitive to the particular values used. Also, the set of parameters are usually only suitable for certain properties, requiring recalibration when others are desired. Due to this situation, the absence of parameters and other approximations necessarily results in a very desirable internal consistency. Thus, in the overlap procedure the question of the compatability of the various approximations and assumptions does not arise.

Another important consideration is that, contrary to some semi-empirical methods, the maximum overlap equations involve no approximations and, as such, will have the same invariance properties as the Roothaan SCF equations [9]. As a consequence, the expectation values calculated with the overlap wave function will be independent of a wide class of basis set transformations, such as local coordinate axis rotations, hybridization, and atomic orbital orthogonalization. The first two examples are unitary transformations, whereas the third is a more general type. Pople and coworkers [10] required that unitary invariance of their approximate Fock equations should be maintained as a consistency base for a great deal of the development in the CNDO, INDO, etc. schemes. Their methods, however, are not invariant to more general transformations that mix functions on different centers, such as atomic orbital orthogonalization.

3. Energy and Maximum Overlap

Before proceeding further, it should be emphasized that even though we shall obtain the maximum overlap molecular orbital (MO–MO) wave functions from (7), this equation should not be regarded as any kind of Hamiltonian eigenvalue problem where the approximate Fock matrix is assumed to be Δ (or its negative). The characteristic values of Δ will generally have no correspondence with any "one-electron" energies, but the wave functions may still have meaning. This is a hope derived from the fact that two commuting Hermitian matrices can be simultaneously diagonalized, but, of course, there is not necessarily any connection between the eigenvalues.

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[3] The choice of basis, however, will be more limited due to other considerations.

It is unlikely that an approximate $\boldsymbol{F}$ should actually commute with $\boldsymbol{\Delta}$, but the amount of similarity of the eigenvectors is dependent on a near commutability. If we assume that some Fock matrices that are used in semi-empirical theories at least roughly reflect the proper behavior of an accurate wave function, then it is possible to make a more detailed investigation of the degree of commutability between these $\boldsymbol{F}$'s and $\boldsymbol{\Delta}$. By so doing, some features of the MO–MO functions that limit their applicability shall be elucidated.

In the single determinant approximation, the general matrix equation to which solutions are sought is

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{\Delta}\boldsymbol{C}\boldsymbol{\varepsilon}\,. \tag{8}$$

Let us assume that $F_{\mu\mu} = \lambda_{\mu\mu}$ and $F_{\mu\nu} = kS_{\mu\nu}$, where k is a parameter independent of the particular basis functions involved. Then, with $\boldsymbol{\Delta} = \boldsymbol{1} + \boldsymbol{S}$,

$$\boldsymbol{F} = (\boldsymbol{\lambda} + k\boldsymbol{S}) = (\boldsymbol{\lambda} + k\boldsymbol{\Delta} - k\boldsymbol{1})\,. \tag{9}$$

With this substitution for $\boldsymbol{F}$, it follows that

$$\boldsymbol{\Delta}\boldsymbol{C} = (\boldsymbol{\lambda} - k\boldsymbol{1})\,\boldsymbol{C}(\boldsymbol{\varepsilon} - k\boldsymbol{1})^{-1} \tag{10}$$

where it is necessary that $\varepsilon_i \neq k$ for all i. By introducing the commutator,

$$[\boldsymbol{\lambda}, \boldsymbol{C}] = \boldsymbol{\lambda}\boldsymbol{C} - \boldsymbol{C}\boldsymbol{\lambda} \tag{11}$$

this can be put in the form,

$$\boldsymbol{\Delta}\boldsymbol{C} = \boldsymbol{C}(\boldsymbol{\lambda} - k\boldsymbol{1})\,(\boldsymbol{\varepsilon} - k\boldsymbol{1})^{-1} + [\boldsymbol{\lambda}, \boldsymbol{C}]\,(\boldsymbol{\varepsilon} - k\boldsymbol{1})^{-1}\,. \tag{12}$$

Thus if $[\boldsymbol{\lambda}, \boldsymbol{C}] = \boldsymbol{0}$, with this particular approximation for $\boldsymbol{F}$, it follows that the maximum overlap eigenvalues problem (7) with $\boldsymbol{d} = (\boldsymbol{\lambda} - k\boldsymbol{1})\,(\boldsymbol{\varepsilon} - k\boldsymbol{1})^{-1}$ is identical to that of the model Fock matrix.

For the case where $F_{\mu\mu} = \alpha_\mu$ for all μ, the commutation condition is satisfied. An example of this, of course, is the Hückel π-electron problem for a homonuclear system. Consequently, for these systems the maximum overlap wave functions and the Hückel wave functions are the same. This connection has been shown explicitly by Lykos and Schmeising [4], and previously observed in a different context by Chirgwin and Coulson [11][4] (see also Löwdin [6]). Although for more general molecules one does not generally assume that the diagonal elements of a Hückel "effective" Hamiltonian matrix are the same, if the assumption is made, the predicted wave function is the maximum overlap solution. Also, a set of "eigenvalues" could be associated with the overlap orbitals by choosing α and k. The calculations of the boron hydrides by Hoffmann and Lipscomb [3] fall into this category.

At this point, it should be mentioned that a detailed analysis of the interrelationship of the Hückel effective Hamiltonian matrix for π-electron systems and the corresponding overlap matrix, primarily within the "tight-binding" approximation, has been made by Ruedenberg [26] via the "topological" matrix.

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[4] Subject to the restriction of equal diagonal elements, a related proof that the Hückel minimum energy state of a molecule coincides with a maximum Mulliken overlap population has been given by R. Manne [27].

The second paper of this series considers the more general situation, which is closer to the present discussion, where all overlap integrals are included. In these papers, it is demonstrated that the commutation of Δ and $\boldsymbol{F}$ has additional consequences, of which one of the most important is that this feature is crucial to the validity of the "zero differential overlap" approximation within the π-electron domain.

Obviously, once the restriction of equal diagonal elements is removed, it is no longer apparent that λ and $\boldsymbol{C}$ will commute, but near commutability may apply if the diagonal elements are not too different. In the more general case of the extended Hückel theory of Hoffman [12], the parameter is replaced by the Wolfsberg-Helmholz [13] type of approximation where $k = \frac{K}{2}(\lambda_{\mu\mu} + \lambda_{\nu\nu})$. This approximation removes the restriction that k be independent of the particular orbitals involved. By partitioning $\boldsymbol{F}$ and Δ into segments corresponding to the different centers, it can be shown that the one center and two center commutation terms are

$$\begin{aligned}(\boldsymbol{F}\Delta - \Delta\boldsymbol{F})_{\alpha\beta} &= \sum_{m\notin A} (F_{\alpha m}S_{m\beta} - S_{\alpha m}F_{m\beta})\\ (\boldsymbol{F}\Delta - \Delta\boldsymbol{F})_{\alpha\gamma} &= \sum_{k\in A} F_{\alpha k}S_{k\gamma} - \sum_{l\in B} S_{\alpha l}F_{l\gamma} + \sum_{m\notin A \text{ or } B} (F_{\alpha m}\Delta_{m\gamma} - S_{\alpha m}F_{m\gamma})\end{aligned} \tag{13}$$

with α and β two functions on a single center and γ situated on another center. Using the Wolfsberg-Helmholz approximation in conjunction with the one center orthogonality of the basis set, these equations give

$$\begin{aligned}(\boldsymbol{F}\Delta - \Delta\boldsymbol{F})_{\alpha\beta} &= (\lambda_{\alpha\alpha} - \lambda_{\beta\beta})\,\frac{K}{2} \sum_{m\notin A} S_{\alpha m}S_{m\beta}\\ (\boldsymbol{F}\Delta - \Delta\boldsymbol{F})_{\alpha\gamma} &= (\lambda_{\alpha\alpha} - \lambda_{\gamma\gamma})\left(S_{\alpha\gamma} + \frac{K}{2} \sum_{m\notin A \text{ or } B} S_{\alpha m}S_{m\gamma}\right).\end{aligned} \tag{14}$$

Therefore, the lack of commutability for both terms is especially dependent on the difference in the diagonal elements corresponding to the various basis functions. If the particular basis functions happen to be two members of a degenerate atomic orbital set, then these terms would vanish giving a higher degree of commutability.

In these semi-empirical theories, the diagonal elements are primarily responsible for the energy difference between the basis functions. In the overlap approach, there is no comparable facility for an energy distinction among the members of the basis, so one must depend solely on the form of the chosen basis set to reflect to some extent the energy disparities that are encountered. This factor will require some restrictions on the basis as well as having an effect on the predicted wave function.

Though it may seem intuitive that as overlap increases, bonding increases, this analogy can be pushed too far. It is true that since overlap is something of a measure of the charge concentration between two positive centers, as overlap is increased, binding also increases up to a point; but, overlap continues to increase beyond the point where the magnitude of the binding energy begins to decrease, due to the enhanced kinetic energy and interelectronic repulsion that is associated with the charge buildup.

To give an example, a distinctive feature that sacrifices energy for increased overlap can be illustrated by considering a p_σ- and an s-orbital of the same principal quantum number located on a center in a molecule. The s and p orbitals are at different energies, but due to the angular dependence and more diffuse nature of the p_σ-function, it is possible to obtain more overlap with it than with the s-function. This will have the obvious consequence that although a $2s$ state is at a lower energy than the $2p$, the maximum overlap criterion will populate the $2p$ orbital proportionately more than the $2s$ with the accompanying sacrifice in energy. An illuminating example of this is given by Slater [14]. This problem would be considerably more pronounced if a function of a higher unoccupied valence state were added to the molecular basis.

Due to these factors that sacrifice energy for overlap, it is necessary to establish three guidelines for these calculations to partially avert obvious errors:

1. As is customary in simplified theories, inner shell $1s$ electrons will be treated as an unpolarizable core;
2. No functions of a higher n, l value than is necessary to describe the component atoms in their Hartree-Fock ground states will be included in the basis;
3. To reduce the error incurred in the relative populations of the valence orbitals, we will limit our calculations to molecules formed from the first row atoms where the disparity in energy between the $2s$ and $2p$ states is relatively small.

4. Charge Densities and Dipole Moments

In order to test the accuracy of the charge distributions of the maximum overlap wave functions, we have made calculations of the dipole moments and population matrices for a variety of molecules.

The dipole moment in atomic units[5] is defined as the expectation value of the operator

$$\vec{\mu}_{\text{op}} = \sum_{i=1}^{n} \vec{r}_i - \sum_{\alpha=1}^{N} Z_\alpha \vec{R}_\alpha \tag{15}$$

where $n = \#$ of electrons, $N = \#$ of nuclei, Z_α is the nuclear charge of the α^{th} nucleus, with $\vec{r}_i$ and $\vec{R}_\alpha$ as the position vectors of the electrons and nuclei respectively. The dipole moment is invariant to the origin of the coordinate system for neutral molecules. We shall define the dipole in the sense that the negative charge in the positive direction results in a positive dipole moment. In particular, for a normalized single determinant of orthonormal spatial orbitals, $\{\psi_i\}$, and their associated populations, n_i,

$$\vec{\mu} = \sum_{i=1}^{\text{occ}} n_i \langle \psi_i(1) | \vec{r}_1 | \psi_i(1) \rangle - \sum_{\alpha} Z_\alpha \vec{R}_\alpha . \tag{16}$$

Using the matrix notation, with $\psi_i = \boldsymbol{\chi} \boldsymbol{a}_i$

$$\vec{\mu}_{\text{el}} = \sum_{i=1}^{\text{occ}} n_i \boldsymbol{a}_i^\dagger \, \vec{\boldsymbol{r}} \boldsymbol{a}_i , \qquad \vec{\boldsymbol{r}} = \langle \boldsymbol{\chi} | \vec{r}_1 | \boldsymbol{\chi} \rangle \tag{17}$$

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[5] a.u. = 2.5416 Debye.

or,

$$\vec{\mu}_{\text{el}} = \sum_{i=1}^{\text{occ}} \sum_{\mu,\nu} n_i a^*_{\mu_i} a_{\nu_i} \vec{r}_{\mu\nu} \,. \tag{18}$$

Defining the single particle density matrix,

$$P_{\mu\nu} = \sum_{i=1}^{\text{occ}} n_i a^*_{\mu_i} a_{\nu_i} \,, \tag{19}$$

$\vec{\mu}_{\text{el}}$ can be written as

$$\vec{\mu}_{\text{el}} = \sum_{\mu,\nu} P_{\mu\nu} \vec{r}_{\mu\nu} \,. \tag{20}$$

The dipole could be separated into three contributions: (1) a net atomic charge term, (2) a polarization term, and (3) a two center contribution. In this manner,

$$\vec{\mu} = \vec{\mu}_A + \vec{\mu}_{PLZ} + \vec{\mu}_{TC} \,. \tag{21}$$

Indicating the various centers in the molecule by α and β, we define the components as

$$\begin{aligned} \vec{\mu}_A &= \sum_{\mu} P_{\mu\mu} \vec{r}_{\mu\mu} - \sum_{\alpha} Z_\alpha \vec{R}_\alpha = \sum_{\alpha} (P_\alpha - Z_\alpha)\, \vec{R}_\alpha \\ \vec{\mu}_{PLZ} &= \sum_{\alpha} \sum_{\mu,\nu}{}' P_{\mu\nu} \vec{r}^{\,\alpha\alpha}_{\mu\nu} \\ \vec{\mu}_{TC} &= \sum_{\alpha,\beta}{}' \sum_{\mu\in\alpha} \sum_{\nu\in\beta} P_{\mu\nu} \vec{r}^{\,\alpha\beta}_{\mu\nu} \end{aligned} \tag{22}$$

where $\vec{r}^{\,\alpha\beta}_{\mu\nu} = \langle \chi_\mu(\vec{r}_\alpha) | \vec{r}_1 | \chi_\nu(\vec{r}_\beta) \rangle$, with $\chi_\mu(\vec{r}_\alpha)$ meaning a basis function located on center α, and $P_\alpha = \sum_{\mu\in\alpha} P_{\mu\mu}$[6].

The total dipole moment will always be invariant to any transformation of the basis set, but the various contributions will not be. When the dipole is approximated, the class of transformations to which it is invariant is reduced. In the CNDO and INDO approximations, the calculated dipole moments are generally good, but they have the undesirable feature that they are approximated by

$$\vec{\mu}_{\text{approx.}} = \vec{\mu}_{\text{A}} + \vec{\mu}_{PLZ} \tag{23}$$

with the two-center term neglected. This leads to an ambiguity. It seems more valid to calculate the dipole moment including the two-center term but to assume the CNDO wave function to be built up from a symmetrically orthogonalized atomic orbital basis. This naturally, will give a different value for the dipole moment. This ambiguity is absent from the maximum overlap method because

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[6] These definitions assume that the basis functions are of the atomic type, i.e., functions of the coordinates of one-center only. For a non-atomic basis, such as an orthogonalized atomic orbital basis, the $\{\bar{\chi}_\mu\}$ are functions of the coordinates of more than one center and, consequently, the definitions must be interpreted with $\chi_\mu(\vec{r}_\alpha) = \bar{\chi}_\mu(\vec{r}_\alpha, \vec{r}_\beta, \ldots)$ meaning the basis function predominately corresponding to the atomic orbital $\chi_\mu(\vec{r}_\alpha)$. Since the symmetrically orthogonalized orbitals minimize $|(\chi_\mu - \bar{\chi}_\mu)^2|$ [15], there is generally little ambiguity in making "atomic" interpretations relative to this basis. However, although $\vec{\mu}_{\text{A}} = \sum_{\mu} P_{\mu\mu} \vec{r}_{\mu\mu} - \sum_{\alpha} Z_\alpha \vec{R}_\alpha$, $\vec{\mu}_A \neq \sum_{\alpha} (P_\alpha - Z_\alpha)\, \vec{R}_\alpha$, since the latter equation depends on the one-center property. In this instance the terminology "net charge" component loses much of its physical validity.

the entire dipole is used and there are no approximations in the method to destroy its invariance properties. In particular, the two-center contribution will be important in our predicted dipole moments. Coulson and Rogers have discussed the importance of this term [16].

The single particle density matrix previously defined (19) takes on two general forms depending on whether the basis set is orthogonal or not [17]. The general matrix can be written

$$\boldsymbol{P} = \boldsymbol{A}\boldsymbol{A}^{\dagger} \tag{24}$$

where the matrix $\boldsymbol{A} = (\sqrt{n_1}\,\boldsymbol{a}_1 \sqrt{n_2}\,\boldsymbol{a}_2 \dots \sqrt{n_k}\,\boldsymbol{a}_k)$ for the occupied spatial eigenvectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \dots, \boldsymbol{a}_k$ and their respective populations n_i. If the basis is non-orthogonal, then following Löwdin [17], we shall define $\boldsymbol{P} = \boldsymbol{R}$ which is often called the "charge and bond order matrix". For this case $\mathrm{Tr}(\boldsymbol{R}) \neq n$ but $\mathrm{Tr}(\Delta\boldsymbol{R}) = n$. Alternatively, if the basis is orthogonalized, then $\boldsymbol{P} = \boldsymbol{Q}$, where the eigenvectors $\{\boldsymbol{a}_i\}$ are understood to be relative to this basis. We now have the convenient property that $\mathrm{Tr}(\boldsymbol{Q}) = n$.

The $\boldsymbol{R}$ matrix is often considered to be the more chemically meaningful density (see Löwdin [6, 17]), but for the purpose of an approximate comparison with the fairly extensive CNDO calculations that have been made, it is more convenient to use the $\boldsymbol{Q}$ matrices, where the basis is symmetrically orthogonalized. The orthogonalization transformation is

$$\bar{\chi} = \chi \Delta^{-\frac{1}{2}} \tag{25}$$

which leads to $\boldsymbol{Q}$ and $\boldsymbol{R}$ being related by

$$\boldsymbol{Q} = \Delta^{\frac{1}{2}} \boldsymbol{R} \Delta^{\frac{1}{2}} . \tag{26}$$

With this particular orthogonalization, a qualitative "atomic" interpretation of $\boldsymbol{Q}$ is reasonable[6] and it gives the closest possible correspondence with the CNDO densities. Similarly, the components of the dipole moment will be referred to this basis.

5. Results and Discussion

Two different atomic orbital basis sets were used in these calculations, the "best atom" STO basis of Clementi and Raimondi [18] and the "double zeta" basis of Clementi [19]. In both bases, Hydrogen was assumed to be adequately described by a single 1*s*-function with an orbital exponent of 1.20. Both the best atom and the double zeta basis use no functions of a higher *n*, *l*-value than is needed to accomodate all of the atom's electrons. This property, as has been described in 3, is an important one from the point of view of applying the maximum overlap criterion. (For Li and Be the best atom STO basis was augmented by 2*p* STO's with the same orbital exponent as the 2*s*.)

All of the calculations were carried out on the IBM-360/65 at the University of Florida Computing Center with a maximum execution time of about a minute for pyridine using a 29 STO basis.

Table 1. *Molecular dipole moments*

Molecule (A^+B^- $\mu > 0$)	Equilibrium geometry	CNDO[a] (μ approx.)	Small basis *ab initio*	Maximum (STO)	Overlap (DZAO)	Exp.[f]
HF	$r_e = 0.9170$ Å	1.86	1.12[b]	1.714	1.578	1.91
H_2O	$r_{OH} = 0.9584$ Å $\widehat{HOH} = 104.45°$	2.14	1.58[c]	2.151	1.997	1.82
H_3N	$r_{NH} = 1.015$ Å $\widehat{HNH} = 106.6°$	2.05	1.97[d]	1.861	1.772	1.47
HCN	$r_{CH} = 1.062$ Å $r_{CN} = 1.157$ Å $\widehat{HCN} = 180.0°$	2.46	3.37[e]	2.142	1.859	2.80
H_3CF	$r_{CH} = 1.095$ Å $r_{CF} = 1.386$ Å $\widehat{HCH} = 108.60°$ $\widehat{HCF} = 110.33°$	1.73	—	1.489	0.965	1.79
C_5H_5N	(Ref. [25])	—	—	1.815	—	2.15

[a] These CNDO/II values were made available to the authors by Dr. Roy Bruns of the Department of Chemistry, University of Florida.

[b] Ransil, B. J.: Rev. mod. Physics **32**, 245 (1960). (Best atom calculation.)

[c] Ohno, K.: Proc. Roy. Soc. (London) A **255**, 367 (1960).

[d] Higushi, J.: J. chem. Physics **24**, 535 (1956).

[e] Pan, D. C., Allen, L. C.: J. chem. Physics **46**, 1797 (1967).

[f] McClellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman 1963.

In Table 1 the dipole moments calculated by the maximum overlap method are listed along with the experimental values and those from a limited *ab initio* computation. The approximate dipoles calculated from the CNDO method are also included. There may be slight differences in the assumed equilibrium geometry in the three cases, but for our purposes this is of negligible importance.

HCN

A discussion of the HCN molecule will illustrate some of the undesirable features of the maximum overlap wave functions. In Table 2 the Q matrices for the MO-MO wave function and a minimal basis LCAOSCF calculation by McLean [20] can be compared. It should be noticed that the *ab initio* calculation indicates that the $\bar{p}_\pi$ (the bar means an orthogonal atomic orbital, OAO) populations on carbon and nitrogen are slightly different, yet the MO–MO calculation gives exactly equal populations. This result is a consequence of the symmetry of the molecule and the fact that the overlap matrix has identical diagonal elements. For diatomic molecules, and in particular the triple bond in HCN, there is no distinction between π orbitals on different centers. This results in the MO–MO's being of the form

$$\psi_\pi = \frac{1}{\sqrt{2}}(\bar{p}_{\pi_A} \pm \bar{p}_{\pi_B}) \qquad (27)$$

Table 2. *Charge and bond order matrices for* HCN *(linear; z taken as σ axis)*

	C($2s$)	C($2p_z$)	C($2p_y$)	C($2p_x$)	N($2s$)	N($2p_z$)	N($2p_y$)	N($2p_x$)	H($1s$)
MO–MO best atom basis									
C($2s$)	0.9299	0.0017	0.0	0.0	0.5470	−0.4523	0.0	0.0	0.7009
C($2p_z$)		1.0714	0.0	0.0	0.5996	−0.3695	0.0	0.0	−0.7063
C($2p_y$)			1.000	0.0	0.0	0.0	1.00	0.0	0.0
C($2p_x$)				1.000	0.0	0.0	0.0	1.00	0.0
N($2s$)					1.3321	0.4706	0.0	0.0	0.0977
N($2p_z$)						1.6613	0.0	0.0	0.0151
N($2p_y$)							1.000	0.0	0.0
N($2p_x$)								1.000	0.0
H($1s$)									1.0053
Reference calculation[a]									
C($2s$)	1.0228	−0.1159	0.0	0.0	0.3890	−0.5773	0.0	0.0	0.7031
C($2p_z$)		1.0765	0.0	0.0	0.5156	−0.4975	0.0	0.0	−0.6815
C($2p_y$)			1.0287	0.0	0.0	0.0	1.00	0.0	0.0
C($2p_x$)				1.0287	0.0	0.0	0.0	1.00	0.0
N($2s$)					1.5987	0.4587	0.0	0.0	0.0113
N($2p_z$)						1.4470	0.0	0.0	0.771
N($2p_y$)							0.9713	0.0	0.0
N($2p_x$)								0.9713	0.0
H($1s$)									0.8466

[a] This Density matrix was computed in second paper of Ref. [10].

which leads to an equal population in the $\bar{p}_{\pi_A}$ and $\bar{p}_{\pi_B}$ orbitals. Judging from the *ab initio* result, this constraint is not too bad for the case of HCN, but in general it is a serious restriction. For example, the charge distributions derived from an MO–MO wave function cannot be meaningful for most diatomic molecules. Although it might be thought that this problem would also be present in the CF bond of a molecule such as methyl fluoride, this is not the case, since the three hydrogen atoms lift the symmetry; restrictions that would apply if CF were treated as a diatomic molecule, allowing unequal populations in the $2p$-orbitals perpendicular to the threefold axis of symmetry.

The other feature that is apparent from the population matrices is the slight under-emphasis of $2\bar{s}$ populations and over-emphasis of the Nitrogen $2\bar{p}_\pi$. As previously discussed in 3, this is inherent in the maximum overlap criterion since with conventional orbital exponents, more overlap can be obtained from a $2p$ orbital than a $2s$. Therefore, the $2p$ will usually be proportionately more populated. This factor will be apparent in all of our calculations.

Diatomic Hydrides

Another special case that deserves mention is the first row hydrides. Due to the lack of p_π orbitals on hydrogen, one does not have the previously discussed π-electron problem which would be present for other diatomics. However, there is still a complication caused by the diatomic symmetry and the identical diagonal elements of the overlap matrix. The typical first row hydride basis, $\{H(1s), B(2s),$

$B(2p_0)$, $B(2p_{\pm 1})\}$, leads to a blocking of the secular equation into a 3×3 σ block and a diagonal π-orbital part with overlap eigenvalues of 1.00. The σ block leads then to the equation

$$\begin{array}{c} B(2s) \\ B(2p_0) \\ H(1s) \end{array} \begin{vmatrix} (1-\lambda) & 0.0 & a \\ 0.0 & (1-\lambda) & b \\ a & b & (1-\lambda) \end{vmatrix} = 0 = (1-\lambda)\left[(1-\lambda)^2 - (b^2 + a^2)\right] \qquad (28)$$

where a σ eigenvalue is seen to be 1.00 also. The single σ coupled with the two π orbitals gives a triply degenerate set which can lead to ambiguities in occupying the orbitals. Also, the σ MO–MO corresponding to overlap characteristic value 1.00 will be constrained so that the H(1*s*) orbital will have a zero coefficient. This will tend to make it difficult for charge to relocate as one moves across the first row from LiH to FH.

For LiH and HF there will be no ambiguity in the occupance of the MO–MO's, but for BeH, BH, CH, NH, and OH, one is faced with this problem. Since a Hamiltonian formulation would place the σ orbital at a lower energy, we chose to occupy the σ orbital twice before beginning to occupy the π-orbitals in calculating the dipole moments in Table 3. It should be noticed that at the two end points LiH and HF, the dipoles are fairly accurate. Both of these cases involve no ambiguity since for LiH none of the degenerate MO–MO's are occupied and in the case of HF, all are doubly occupied. The hydrides adjacent to the end points have the next most accurate dipoles, with those in the middle, BH, CH, and NH, being the least accurate.

If the diagonal elements had been different, as in any Hamiltonian formulation, the somewhat accidental degeneracy of σ and π-MO's could not have occured. However, this is a relatively minor restriction since it happens only for the special case of the first row hydrides and the water molecule. Of these, LiH, HF, and H_2O have no occupancy ambiguity. Just as happened previously, additional atoms in the molecule will lift the restrictive diatomic symmetry leading to no problem of this type for the larger molecules.

Table 3. *Dipole moments of diatomic hydrides*

Molecule (A^+B^- $\mu > 0$)	Equilibrium geometry	CNDO[a]	Small basis *ab initio*	Maximum overlap	Exp.
HLi	$r_e = 1.595$ A	−6.02	−6.48[b]	−5.951	−5.90[d]
HBe	$r_e = 1.343$ A	—	—	−0.334	(−0.248)[f]
HB	$r_e = 1.232$ A	1.94	1.03[b]	2.709	(1.733)[f]
HC	$r_e = 1.1197$ A	1.55	0.93[c]	2.299	(1.570)[f]
HN	$r_e = 1.0377$ A	1.33	1.68[b]	2.046	(1.627)[f]
HO	$r_e = 0.9705$ A	1.25	0.92[c]	1.861	1.65[e]
HF	$r_e = 0.9170$ A	1.27	1.12[b]	1.714	1.91[d]

[a] All of the CNDO values are from second paper of Ref. [10] (Version I).

[b] Ref. (b), Table 1.

[c] Krauss, M.: J. chem. Physics **28**, 1021 (1958).

[d] Ref. (f), Table 1.

[e] Meyer, R. T., Myers, R. J.: J. chem. Physics **34**, 1074 (1961).

[f] Cade, P. E., Huo, W. H.: J. chem. Physics **45**, 1063 (1966). (SCF Calculation.)

HF, H_2O, NH_3, CH_4

The isoelectronic sequence HF, H_2O, NH_3 and CH_4 gives an interesting test of the overlap procedure. The MO–MO dipole moments of the first three members of the series are seen to be surprisingly accurate despite the naivete of the method. In fact, they are comparable, or even better, than the small basis *ab initio* calculations. This is no doubt partially fortuitous, but it also indicates that the wave function has a degree of realism.

In order to directly compare the MO–MO dipole components with those from CNDO calculations, the CNDO basis was symmetrically orthogonalized and, then, the entire dipole computed. As discussed in 4, the resultant dipole will differ from the usual dipole approximation used in the CNDO method. The actual differences in the cases studied vary from 0.2 to 0.5 debye units, moving both toward, and away from, the experimental values. As suggested by Pople *et al.*, this method of calculating dipole moments with CNDO wave functions is probably to be preferred [10]. One can see from Table 4 that the CNDO "net charge" component is generally more positive than its MO–MO counterpart, whereas the two center terms are considerably more prevalent in the latter. This is primarily a result of the overlap criterion overpopulating the $2p_\sigma$-orbitals relative to the $2s$, which leads to a greater concentration of charge between the atomic centers. In both cases the principal dipole contribution is the polarization term.

The purpose of using the double zeta basis (DZAO) was to investigate the effect the more diffuse atomic orbitals would have in connection with the maximum

Table 4. *Composition of the dipole moments*

Molecule	Method	μ_A	μ_{PLZ}	μ_{TC}	μ
HF	MO–MO				
	Sym. 0 – STO	−0.3554	1.2901	0.7796	1.714
	Sym. 0 – DZAO	0.0248	1.2871	0.2659	1.578
	CNDO[a]	0.6989	0.7787	0.1969	1.6745
		(1.049)	(0.8059)	—	(1.855)
H_2O	MO–MO				
	Sym. 0 – STO	0.0834	1.385	0.683	2.151
	Sym. 0 – DZAO	0.5263	1.4045	0.0665	1.997
	CNDO	0.4520	1.2180	0.0917	1.7617
		(0.8027)	(1.3379)	—	(2.141)
H_3N	MO–MO				
	Sym. 0 – STO	0.2942	1.235	0.3317	1.861
	Sym. 0 – DZAO	0.7037	1.274	−0.2057	1.772
	CNDO	0.2262	1.5048	−0.1465	1.5845
		(0.4149)	(1.636)	—	(2.051)
H_3CF	MO–MO				
	Sym. 0 – STO	−0.477	1.401	0.565	1.489
	Sym. 0 – DZAO	−0.2169	1.359	−0.178	0.965
	CNDO	0.9097	0.4376	0.0880	1.4353
		(1.315)	(0.417)	—	(1.732)

[a] The numbers in parentheses are the values for the usual CNDO dipole approximation.

overlap criterion. It has been observed that the "maximum overlap" state actually involves a greater degree of overlap than would be present for the molecule's minimum energy state. Consequently, using a more diffuse set could cause additional errors. To the contrary, though, it appears that the overlap criterion is rather insensitive to the basis change. As judged by the sum of the eigenvalues of the occupied eigenvectors, the DZAO basis gives only a very slightly increased overlap (<0.1), whose effect is essentially to increase the population of the Hydrogen $1s$ orbitals. Actually, the inherent error in the $2s$, $2p_\sigma$ populations is reduced for this basis as is indicated by the diminished effect of the two center dipole contribution. The polarization terms are almost unaffected.

Although underestimating the $2s$ population is inherent in an MO–MO wave function, it is coupled with an overestimation of the occupancies of the $2p$ orbitals which tends to give a partial cancellation. This is evident from a comparison of the net charges per atom[7] of the MO–MO wave functions for this group of molecules with the values obtained by the CNDO approximation. For convenience these are listed in Table 5. It is seen that the MO–MO net charges[8] with both basis sets are similar to the CNDO values.

Since the determinantal wave function is invariant to basis hybridization, one can utilize this freedom to obtain a particularly illustrative description of this sequence by using a set of equivalent tetrahedral hybrids for the heavy atom [21]. In Table 6 are listed the charge and bond order matrices relative to the sp^3 hybrids formed from the symmetrically orthogonalized best atom STO basis. The population matrices for the orthogonalized DZAO basis are essentially the same.

The four orthonormal tetrahedral hybrids are of the form

$$t_i = \sum_{\mu}^{4} \bar{\chi}_\mu \alpha_{\mu_i}, \qquad i = 1, 2, 3, 4 \tag{29}$$

with the bar indicating the OAO functions. The specific values for the coefficients $\{\alpha_{\mu_i}\}$ depend on the orientation of the coordinate system. By means of the

Table 5. *Atomic valence charges*

Molecule	MO–MO Best atom STO		MO–MO Double zeta		CNDO/I[a]		CNDO/II[b]	
HF	F : 7.00	H : 1.00	F : 7.00	H : 1.00	F : 7.080	H : 0.920	F : 7.282	H : 0.768
H_2O	O : 6.120	H : 0.940	O : 6.094	H : 0.953	O : 6.116	H : 0.942	O : 6.282	H : 0.859
NH_3	N : 5.201	H : 0.933	N : 5.173	H : 0.9423	N : 5.141	H : 0.953	N : 5.234	H : 0.922
CH_4	C : 4.214	H : 0.947	C : 4.196	H : 0.951	C : 4.142	H : 0.965	C : 4.049	H : 0.988
CH_3F	C : 4.124 F : 6.954	H : 0.974	C : 4.104 F : 6.923	H : 0.991	—	—	C : 3.821 F : 7.194	H : 0.995
CH_3CH_3	C : 4.1137	H : 0.9621	—	—	C : 4.100	H : 0.9666	—	—

[a] Second paper of Ref. [10].
[b] Ref. (a), Table 1.

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[7] See Footnote 6.

[8] HF must have the values 7.00 and 1.00 due to the symmetry restrictions discussed above.

Table 6. *Charge and bond order matrices for* HF, H_2O, NH_3, *and* CH_4 *(tetrahedral hybrids)*

	HF				
	$F(t_1)$	$F(t_2)$	$F(t_3)$	$F(t_4)$	$H(1s)$
$F(t_1)$	1.1527	−0.2077	−0.2077	−0.2077	0.9205
$F(t_2)$		1.9491	−0.0509	−0.0509	0.2256
$F(t_3)$			1.9491	−0.0509	0.2256
$F(t_4)$				1.9491	0.2256
$H(1s)$					1.000

	H_2O					
	$O(t_1)$	$O(t_2)$	$O(t_3)$	$O(t_4)$	$H_1(1s)$	$H_2(1s)$
$O(t_1)$	1.1196	−0.1738	−0.1738	−0.1738	0.9447	−0.0113
$O(t_2)$		1.1196	−0.1774	−0.1774	−0.0113	0.9447
$O(t_3)$			1.9403	−0.0597	0.1570	0.1570
$O(t_4)$				1.9403	0.1570	0.1570
$H_1(1s)$					0.9401	0.2335
$H_2(1s)$						0.9401

	NH_3						
	$N(t_1)$	$N(t_2)$	$N(t_3)$	$N(t_4)$	$H_1(1s)$	$H_2(1s)$	$H_3(1s)$
$N(t_1)$	1.9438	−0.1489	−0.1489	−0.1489	0.1194	0.1194	0.1194
$N(t_2)$		1.0858	−0.1345	−0.1345	0.9665	−0.0089	−0.0089
$N(t_3)$			1.0858	−0.1345	−0.0089	0.9665	−0.0089
$N(t_4)$				1.0858	−0.0089	−0.0089	0.9665
$H_1(1s)$					0.9329	0.1532	0.1532
$H_2(1s)$						0.9329	0.1532
$H_3(1s)$							0.9329

	CH_4							
	$C(t_1)$	$C(t_2)$	$C(t_3)$	$C(t_4)$	$H_1(1s)$	$H_2(1s)$	$H_3(1s)$	$H_4(1s)$
$C(t_1)$	1.0534	−0.1030	−0.1030	−0.1030	0.9825	−0.0052	−0.0052	−0.0052
$C(t_2)$		1.0534	−0.1030	−0.1030	−0.0052	0.9825	−0.0052	−0.0052
$C(t_3)$			1.0534	−0.1030	−0.0052	−0.0052	0.9825	−0.0052
$C(t_4)$				1.0534	−0.0052	−0.0052	−0.0052	0.9825
$H_1(1s)$					−0.9466	0.1030	0.1030	0.1030
$H_2(1s)$						0.9466	0.1030	0.1030
$H_3(1s)$							0.9466	0.1030
$H_4(1s)$								0.9466

localizing effect gained by the tetrahedral hybrid transformation, the terms in the density matrix can be easily categorized into bonds, lone pairs, and repulsive terms. It can be seen from Table 6 that the charge and bond order matrices of HF, H_2O, and NH_3 prominently exhibit the non-bonding electron "lone pairs" with a population apparently independent of the specific molecule involved. If we indicate the various repulsive terms in the density matrices as B–LP (bond – lone pair), B–B (bond–bond), LP–LP (lone pair – lone pair), and B–H (bond–Hydrogen atom), then it is seen that in all cases the B–LP term has the largest magnitude, followed by the B–B, LP–LP, and B–H terms respectively. In HF the B–LP value is about four times greater than the LP–LP term which tends to imply a distorted tetrahedron with an angle between the bond and the lone pair directions considerably greater than the tetrahedral value. This observation is consistent with the studies of the polymeric structure of HF in crystalline form by Atoji and Lipscomb [22]. They found infinite zig-zag coplanar chains with a bond angle of 120.1.°

The usual oversimplified explanation of the fact that the angles between the bonds of H_2O and NH_3 are less than the tetrahedral value is that the B–LP repulsion is greater than the B–B repulsion. This is reflected by the MO–MO population matrices, though it is also indicated that in water the LP–LP repulsive term is an important factor as would be expected. For CH_4 the bonds assume the maximum spatial separation with the consequent reduction in the B–B and B–H terms of the population matrix.

C_2H_6, CH_3F

In going from methane to ethane there is very little change in the features of the density matrices, the principal effect being a slight increase in the charge on the hydrogens with an accompanying decrease on carbon. The agreement between the MO–MO net charges and the CNDO values is very close. For comparison, the net charges from the Q matrix constructed from the extended Hückel wave function of Hoffman [12] are 4.242 and 0.9193.

The transition to methyl fluoride involves a larger increase in the charge on the hydrogens coupled with the somewhat surprising (and probably erroneous) result that the fluorine atom has a very slight net positive charge while the carbon atom is negative. This fact leads to a negative "net charge" contribution to the dipole moment, although the polarization and the two center terms counter balance it to give a resultant dipole of 1.49 D with its negative end at the fluorine atom.

The reason for this discrepancy is again the relative populations of the fluorine $2s$ and $2p$ orbitals. Due to the large energy disparity between the $F(2s)$ and the carbon orbitals, an energy criterion will tend to occupy the $F(2s)$ to a large extent. The actual value for a CNDO calculation is 1.844 as compared to an MO–MO value of 1.348. As has been discussed, we expect the MO–MO wave function to underestimate this value, but the consequent effect is expected to be partially neutralized by the increased $2p$ population. For this particular case, the $F(2s)$ CNDO population is greater than the MO–MO value by about 0.5 electrons. The $F(2p_z)$ value, though, is greater than the CNDO by only about half of this which accounts for the difference in the net charges. Contrary to HF, H_2O, and NH_3, the error is more pronounced for the DZAO basis resulting in a poorer dipole moment.

Pyridine

To investigate the suitability of a maximum overlap wave function for an aromatic molecule, pyridine was treated. For this case, one will obtain a π wave function as well as one for the σ "core". The former would simply be the Hückel

Table 7. *Atomic net charges for pyridine*

	PPP(π)[a]	*ab initio*(π)[b]	MO–MO(π)	*ab initio*(σ and π)[b]	MO–MO(σ and π)
N	−0.1827	−0.0102	−0.0152	−0.2262	−0.0374
C (*ortho*)	0.0454	−0.0048	0.0028	−0.1097	0.0411
C (*meta*)	−0.0173	−0.0024	−0.0094	−0.2252	−0.0346
C (*para*)	0.0855	0.0245	0.0304	−0.2024	0.0353
H (*ortho*)				0.2217	0.0116
H (*meta*)				0.2172	0.0060
H (*para*)				0.2203	0.0002

[a] Ref. [24].

[b] Ref. [25]: These net charges are calculated with the Mulliken Population Analysis.

solution if the molecule were homonuclear, but in the heteronuclear case, it is a similar type of approximation. It is advantageous, however, that one can also calculate the σ structure with a treatment somewhat comparable to the simple theories developed for the π electrons.

The π solution indicates only a slight distinction in the net charges on each atom. The actual values are listed in Table 7. A Pariser-Parr-Pople [23] type of calculation implies that there is much more migration of charge than the MO–MO method would suggest [24]. To the contrary, a comparison with a Mulliken net charge analysis of Clementi's *ab initio* calculation [25] seems to denote that very little migration actually takes place. One should not necessarily interpret this as support for the MO–MO π calculation, however, since by the nature of the method (as illustrated in CH_3F) it cannot effectively transfer large amounts of charge. Also, there is no precise correspondence between our charge and bond-order matrices and the Mulliken analysis, but the qualitative features should be the same.

If the σ electrons are included, one sees that the net negative and positive MO–MO charges are slightly incremented, whereas the *ab initio* result suggests greater σ migration. This is indicated by the larger net positive charge on the hydrogens.

It may be noticed that both the PPP and MO–MO π net charges are consistent with the well known nucleophilic *(ortho-para)* and electrophilic *(meta)* directional properties of pyridine, but the *ab initio* values are not. Although the directional properties of aromatic systems are often considered to be primarily a function of the π electrons, the importance of the σ "core" is emphasized by the *ab initio* result, since it is necessary to include the σ net charges to obtain an agreeable electrostatic picture. Even though the net charge magnitudes in the maximum overlap method may be too small, they also give a proper electrostatic description.

6. Conclusion

By imposing a criterion derived from the traditional chemical concept of maximum overlap, it is possible to obtain very approximate molecular wave functions solely from a diagonalization of the overlap matrix. These "maximum overlap" functions are consequently determined without recourse to semi-empirical data, parameterization, or other approximations. From a different perspective, the "overlap" wave functions can be identified as those that would be obtained from a Hückel theory subject to the restriction that the diagonal elements of the "effective" Hamiltonian matrix are assumed equal. Or, equivalently, with this restriction, the state of maximum overlap for a molecule coincides with its minimum Hückel energy.

Despite the fact that there are obvious errors in any such procedure, with a realistic atomic orbital basis the charge densities and dipole moments calculated from the "overlap" wave functions are surprisingly accurate for a variety of molecules. Much of this accuracy is indebted to partial cancellations of errors, however.

For predominately covalent systems, there is, at least, some reality to the MO–MO functions. Thus, it seems likely that they would be a convenient internally generated starting set for more sophisticated calculations. Also, in π-electron theory a simple wave function for the σ "core" is an asset both as a rough extention of the calculation to include all valence electrons and, possibly, to construct a better effective potential for the π-electrons.

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References

1. Pauling, L.: The nature of the chemical bond, 3rd Ed., p. 110. New York: Cornell University Press 1960.
2. Mulliken, R. S.: J. Amer. chem. Soc. **72**, 4493 (1950).
3. Hoffman, R., Lipscomb, W. N.: J. chem. Physics **36**, 2179 (1962).
4. Lykos, P. G., Schmeising, H. N.: J. chem. Physics **35**, 288 (1961).
5. Löwdin, P. O.: Philos. Mag. Supplement **5**, 1 (1956).
6. — J. chem. Physics **18**, 365 (1950).
7. Murrell, J. N.: J. chem. Physics **32**, 767 (1960).
8. Gilbert, T. L., Lykos, P. G.: J. chem. Physics **34**, 2199 (1961).
9. Roothaan, C. C.: Rev. mod. Physics **23**, 69 (1951).
10. Pople, J. A., Santry, D. P., Segal, G. A.: J. chem. Physics **43**S, 129 (1965); Pople, J. A., Segal, G. A.: J. chem. Physics **43**S, 136 (1965); **44**, 3289 (1966).
11. Chirgwin, B. H., Coulson, C. A.: Proc. Roy. Soc. (London) A **201**, 196 (1950).
12. Hoffman, R.: J. chem. Physics **39**, 1397 (1963).
13. Wolfsberg, M., Helmholz, L.: J. chem. Physics **20**, 837 (1952).
14. Slater, J. C.: Quantum theory of molecules and solids. Vol. I, pp. 146–147. New York: Mc Graw-Hill 1963.
15. Carlson, B. C., Keller, J. M.: Physics. Rev. **105**, 102 (1957).
16. Coulson, C. A., Rogers, M. T.: J. chem. Physics **35**, 593 (1961).
17. Löwdin, P. O.: Physics Rev. **97**, 1490 (1955).
18. Clementi, E., Raimondi, D. L.: J. chem. Physics **38**, 2686 (1963).
19. — Tables of atomic functions. IBM J. Res. Develop., Supplement, **9**, 2 (1965).
20. McLean, A. D.: J. chem. Physics **37**, 627 (1962). (The density matrix is taken from Ref. [10], second paper.)
21. Pople, J. A.: Quart. Reviews **11**, 273 (1957).
22. Atoji, M., Lipscomb, W. N.: Acta crystallogr. **7**, 173 (1954).
23. Parr, R. G.: The quantum theory of molecular electronic structure. New York: W. A. Benjamin 1963.

24. Mataga, N., Nishimoto, K.: Z. physik. Chem., N.F., **13**, 140 (1957).
25. Clementi, E.: J. chem. Physics **46**, 4731 (1967).
26. Ruedenberg, K.: J. chem. Physics **34**, I. 1861, II. 1878, III. 1884, IV. 1892, V. and E. M. Layton, 1897, VI. 1907, (1961).
27. Manne, R.: Int. J. quant. Chemistry **2**, 69 (1968).
28. Golebiewski, A.: Trans. Faraday Soc. **57**, 1849 (1961); – Acta Phys. Polon. **23**, 243 (1963), and A **37**, 319 (1970).

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