On the Hartree–Fock Theory of Local Regions in Molecules

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Abstract: This paper offers an ab initio perspective on local electronic structure in molecules. The energy of a single determinant wave function is minimized, but each orbital is expanded using only those basis functions local to a particular region. This procedure permits rigorous quantum mechanical evaluation of the properties of isolated bonds or functional groups. Each local orbital satisfies a Hartree–Fock-like secular equation within its own basis space. The orbital eigenvalue satisfies Koopmans' theorem and affords an ab initio definition of the orbital energy used in PMO models of functional group interaction. The regional orbital model offers definite computational advantages over traditional molecular orbital theory. Because each local orbital is determined by a reduced dimension secular equation, unwieldy Fock matrix diagonalizations are avoided for large molecules. Further, the formalism shows that an accurate wave function for a region of a molecule can *in principle* be determined without calculation of a wave function for the entire molecule. Ab initio calculations for prototype molecules show that the local orbital constraint entails little loss of accuracy. Energies obtained from local orbital determinants and molecular orbital determinants agree within a tolerance of several kilocalories per mole. The eigenvalue for each type of bond or lone pair is highly transferable from molecule to molecule.

I. Introduction

A significant issue in contemporary chemistry is the theoretical description of local regions within molecules—both in isolation and in interaction with other parts of the molecule. Present interest in this topic stands in reaction to a fundamental paradox within quantum chemistry. On the one hand, chemistry is primarily a property of local regions within molecules. The principal features of conformation and reactivity are identified with chemical bonds or functional groups, in isolation or interaction. Nevertheless, traditional quantum mechanical methods require a wave function for the entire molecule, even if much of that information is irrelevant. This paper offers one step toward the resolution of the paradox. It is shown that Hartree–Fock wave functions for local regions of molecules can be obtained without sacrifice of quantum mechanical rigor.

These same tensions are apparent in selection of quantum mechanical models for chemical problems. Ab initio molecular orbital theory predicts many chemical properties with quantitative accuracy, but does not lend itself to simple chemical models for these properties. In contrast to ab initio theory, the perturbative molecular orbital (PMO) method and its variants[1] have qualitatively explained trends in conformation and reactivity for a wide variety of organic molecules. Despite their lack of rigor, PMO models are significant because they match chemical intuition: the behavior of molecular orbitals is ascribed to interactions between pairs of chemical bonds. Fukui,[2] Woodward and Hoffmann,[3] and Salem[4] have pioneered with their analysis of chemical reactivity in terms of interactions between regional orbitals. More recently, Epiotis,[5] Hehre, Pople, and Schleyer,[6] Salem,[7] and Hoffmann et al.[8] have used PMO models to rationalize the conformational preferences of numerous organic molecules. Heilbronner[9] has used photoelectron spectra to parameterize a PMO Hamiltonian and has thereby accounted for substituent effects on photoelectron spectra. Finally, the burgeoning literature of transition metal chemistry has predominantly adopted a PMO approach to electronic structure. Bonding in transition metal complexes is understood via correlation diagrams which describe the intermixing of metal and ligand orbitals.[10]

The intuitive appeal of PMO models has been established, but their credibility is still controversial. Conclusions derived from a PMO approach are critically sensitive to numerical values of bond energies and matrix elements for orbital interaction, but there is little agreement on which numbers should be used. This paper indicates how these ambiguities can be resolved in an ab initio context. A single determinant wave function is energy optimized, subject to the constraint that each orbital is local to a particular bond. This procedure permits rigorous specification of bond energies and matrix elements needed by PMO theory.

The present work presumes that it is legitimate to discuss the quantum mechanics of an isolated region in a molecule. This question has been affirmatively resolved in a paper by Mazziotti, Parr, and Simons,[11] and in a series of papers by Bader and Srebrenick.[12] If a molecule is partitioned into regions defined by saddle points in the electron density

$$\nabla\rho(\mathrm{r}) \cdot \mathrm{n}(\mathrm{r}) = 0 \tag{1.1}$$

each such region satisfies the virial theorem and is quantum mechanically separable from its environment. The density gradient criterion affords a strict spatial separation of molecular fragments, but is difficult to implement. This paper, in contrast, shows that meaningful molecular subunits can be defined by simple partitioning of the LCAO basis space.

A general theory of regional Hartree–Fock orbitals was formulated by Adams and Gilbert.[13] The key step in Adams-Gilbert theory is projection of the molecular Hartree–Fock equations onto the Hilbert space spanned by regional orbitals. As modified by Matsuoka,[14] the Adams-Gilbert equations are

$$(1 - PFP + P_iW_iP_i)X_i = \epsilon X_i \tag{1.2}$$

F is the Fock matrix, P is a projection operator for the space of occupied orbitals, and W_i is a one-electron operator which is diagonal in the subspace which contains orbital X_i. The Adams-Gilbert equations have been extensively applied,[15] but suffer from ambiguity in the definition of the regional operators W_i. The regional orbital equations derived in this paper are compatible with the Adams-Gilbert equations, but the present method is preferable for two reasons. First, the energy minimization condition leads to a unique prescription for the regional operators W_i:

$$W_i = P_iFP_i \tag{1.3}$$

In eq 1.3, P_i is the projection operator for occupied orbitals in the ith region. A second advantage of the present approach is

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reduced dimensionality. The one-electron orbitals local to a particular region are expanded using a subset of the complete LCAO basis, and the final variational equations only involve these basis functions.

There have been several other studies of regional electronic structure, but they are distinct from the present approach. Peters,[16] for instance, has shown how localized orbitals may be directly determined from noncanonical Hartree–Fock equations. In that formulation, each localized orbital is an eigenstate of a distinct *non-Hermitian* secular equation, and the secular equations have the same dimensions as the full basis set. More recently, simulated ab initio procedures[17] have employed the direct transfer of Fock matrix elements from one molecule to another. The idea of a transferrable regional Hamiltonian is implicit in such procedures as these. Finally, Whangbo et al.,[18] Morokuma et al.,[19] and Payne[20] have independently suggested that orbitals local to a particular region could be chosen by diagonalizing an appropriate block within the Fock matrix. These methods are all unsatisfactory, since variational stability requires that the Fock operator must be projected onto the basis space of the particular region. Extraction of a block from within the Fock matrix is only accurate if the basis set is orthogonal.

Localized orbitals[21] provide yet another context for reconciliation of quantum mechanical rigor with traditional chemical concepts. There is no energetic penalty for the localized orbital description since the localized orbitals are defined by a unitary transformation of occupied molecular orbitals. Nonetheless, localized orbital analysis of bonds and bond interactions is beset by some critical weaknesses. First, the expense of a localized orbital calculation greatly exceeds the cost of an ordinary molecular orbital calculation. Second, even though this problem can be surmounted through transfer of localized orbitals from small molecules to larger molecules,[22] such transfers are still quite controversial. The transferred orbitals are not self-consistent and must be reorthogonalized. Only minimal knowledge is available concerning the sensitivity of bond properties to transfer vs. in situ calculation of localized orbitals. Finally, localized orbitals do not define a strictly regional quantum chemistry and their interpretation is ambiguous. This ambiguity arises because localized orbital tails extend throughout the molecule, and these tails have a major influence on properties of chemical interest.[22]

The local orbital approach taken in this paper specifically avoids each of the stated weaknesses of localized molecular orbital theory. The interpretative ambiguities caused by orbital tails are avoided because each one-electron orbital is expanded on a regional basis subset. The local orbitals are not required to be orthogonal, and so should be more transferable than localized molecular orbitals. The local orbitals are directly calculated in lieu of a canonical molecular orbital wave function, and are obtained far more easily than localized molecular orbitals. But computational simplicity does not have an adverse effect on molecular energy. Test calculations on small organic molecules (see Section III) demonstrate that a determinant of local orbitals is energetically competitive with traditional molecular orbital theory. This observation is in accord with the work of Levy et al.,[23] who recently found that truncation of localized molecular orbital tails has negligible effect on electronic energy. The local orbital wave function employed herein is the variationally best set of truncated one-electron orbitals, and so must be lower in energy than wave functions derived from truncation of localized molecular orbitals.

The key concept in this paper is variational optimization of a single determinant wave function, subject to the constraint that each one-electron orbital is expanded using a subset of the basis functions. This idea of different basis sets for different orbitals has been proposed in two other contexts. Silverstone et al.[24] have investigated the use of nested basis sets in atomic Hartree–Fock theory, and have obtained variational equations equivalent to those which are derived here. However, Silverstone et al. restricted their theory to orthogonal one-electron orbitals, whereas no orthogonality constraints are imposed in the present approach. Von Niessen's molecules-in-molecules method[25] describes certain bonds by transfer of localized orbitals and variationally optimizes remaining bond orbitals using a restricted basis set. Our analysis is different because all local orbitals are variationally optimized; none is transferred from a different molecule. Further, due to Von Niessen's inexact treatment of orbital orthogonality, the projected Fock operator of molecules-in-molecules theory is an approximate version of the effective Fock operator which we employ.

The present work is distinct from all previous uses of bond orbital wave functions. Consider, for example, the work of Sovers, Kern, Pitzer, and Karplus.[26] Their calculations on ethane and methanol employ bond orbitals which are linear combinations of idealized valence hyids. The minimum energy attained with such a wave function is a few *tenths* hartree above the MO-SCF energy obtained from the same basis set. The present work is distinct because each bond orbital is variationally optimized within the full basis space of the two bonded atoms. No assumptions are made about idealized hybrid orbitals. The present approach leads directly to that bond orbital determinant which has lowest energy, and it is shown in Section III that the energy gap between bond orbital and MO-SCF wave functions is reduced to a few *hundredths* hartree. This is an order of magnitude improvement over the work of Sovers et al.

Formal aspects of the theory are developed in Section II, and illustrative results for small organic molecules are presented in Section III. It is found that the energy of a local orbital determinant lies only a few kilocarories/mole above the energy obtained from a conventional molecular orbital wave function.

II. Theoretical Development

A. Outline of Method. Conventional molecular orbital theory is derived by minimizing the energy of a single determinant of one-electron orbitals. If each molecular orbital is written as a linear combination of atomic basis functions, optimization of the wave function generates the Hartree–Fock–Roothan equations.

Our concern in this paper is with variational optimization of bond orbitals. We shall assume, as in molecular orbital theory, that the wave function is a single determinant of one-electron orbitals. But unlike what is done in molecular orbital theory, we impose the constraint that only a few functions of the basis set contribute to a particular one-electron orbital. Thus, a bond orbital is a one-electron orbital which is expanded using only those basis functions associated with a particular pair of atoms. In certain electron-deficient or unsaturated species we may wish to relax this constraint so that some bond orbitals extend over three centers. The bond orbital theory presented in this paper is a variant of molecular orbital theory, with the constraint that most of the basis expansion coefficients are zero.

Conventional molecular orbital theory constrains the molecular orbital to be orthonormal, but we shall not make such an assumption. It would clearly be computationally advantageous to choose the orbitals to be orthogonal, since variational equations derived from a determinant of orthogonal orbitals are much simpler than variational equations for nonorthogonal orbitals. But there are nonetheless compelling reasons for use of nonorthogonal orbitals. First, for any basis set of moderate size, we might not be able to choose bond orbitals to be orthogonal without violating our prior constraints on the LCAO coefficient matrix. This will surely be the case if the number of basis functions which contribute to a bond orbital is less than the number of other orbitals. Our second objection is that orthogonality constraints stand in opposition to the variation principle, since LCAO coefficients are kept from assuming those values which would minimize molecular energy. Finally, a determinantal wave function constructed from nonorthogonal orbitals is equivalent to a determinant in which these orbitals have been orthogonalized within their own linear space. Orbital orthogonality has little to do with physical necessity, but rather is a dispensable computational convenience.

We shall find that each bond orbital satisfies an eigenvalue equation of reduced dimension. It is well known that Hartree-Fock molecular orbital theory leads to an eigenvalue equation

$$F\phi = S\phi\epsilon \qquad (1)$$

in which the Fock matrix F corresponds to an effective one-electron Hamiltonian and S is the overlap matrix of basis functions. Each column of ϕ contains basis expansion coefficients for a particular molecular orbital and ϵ is a diagonal matrix of orbital eigenvalues. We let γ_k be the vector of those coefficients which are not constrained to be zero in bond orbital χ_k. It will be shown that γ_k satisfies an eigenvalue equation of form

$$\tilde{F}\gamma_k = \tilde{S}\gamma_k\tilde{\epsilon} \qquad (2)$$

where $\tilde{F}$ and $\tilde{S}$ are obtained in the following manner. We let Q_k denote the projection operator for that part of the *occupied* bond orbital space which is orthogonal to bond orbital X_k, and form the matrix $= (1 - Q_k)F(1 - Q_k{}^t)$. The reduced dimension matrices $\tilde{F}$ and $\tilde{S}$ are defined by eliminating from F and S all rows and columns which correspond to basis functions that do not participate in bond orbital X_k.

B. Variation of Energy for Nonorthogonal Orbitals. We wish to choose bond orbitals $X_1, X_2, \ldots X_n$ so as to minimize the energy expectation value of the single determinantal wave function

$$\Psi = \frac{1}{\sqrt{(2N)!}} \det|X_1\alpha X_1\beta \ldots X_n\alpha X_n\beta| \qquad (3)$$

Although we shall consider only closed shell systems, our results can be directly generalized to the open shell case. The bond orbitals X_i are not assumed to be orthonormal, but in fact have overlap matrix

$$\sigma_{ij} = \int d^3r X_i{}^*(r)X_j(r) \qquad (4)$$

We are free to scale each bond orbital to unit norm, but such a choice has the consequence that Ψ is no longer normalized to 1. Instead, following Slater[27] and Lowdin,[28] we find

$$\int d\tau, \ldots, d\tau_{2n}\Psi^*\Psi = (\det \sigma)^2 \qquad (5)$$

In carrying out the variation it is not necessary to place any constraints on the norm of Ψ. The energy expectation value

$$\langle E \rangle = \langle \Psi|H|\Psi\rangle / \langle \Psi|\Psi\rangle \qquad (6)$$

does not depend on the norm of Ψ, so those bond orbitals which optimize $\langle E \rangle$ do not have to reproduce a preselected norm for Ψ.

The electronic energy for nonorthogonal orbitals may be straightforwardly derived from matrix elements discussed by Slater,[26] Lowdin,[27] and McWeeny and Sutcliffe.[28] For the reader's convenience we include the derivation as an Appendix to this paper. The final energy expression is

$$\begin{aligned}\langle E \rangle = {} & 2\sum_{i,j}^{n} h_{ij}\sigma_{ji}{}^{-1} \\ & + \sum_{ijkl}^{n} \sigma_{ji}{}^{-1}\sigma_{lk}{}^{-1}\left[2\left(ij\left|\frac{1}{r_{12}}\right|kl\right) - \left(il\left|\frac{1}{r_{12}}\right|kj\right)\right] \qquad (7)\end{aligned}$$

where h_{ij} is a matrix element of the one-electron Hamiltonian and $(ij|1/r_{12}|kl)$ is the usual electron repulsion integral.

$$h_{ij} = \langle \chi_i|h|\chi_j\rangle$$

$$\left(ij\left|\frac{1}{r_{12}}\right|kl\right) = \int d\tau_1 d\tau_2 \chi_i{}^*(1)\chi_j(1)\frac{1}{r_{12}}\chi_k{}^*(2)\chi_l(2)$$

We now rewrite this energy expression in terms of the bond orbital coefficient matrix. Expand each bond orbital X_i in terms of the atomic basis functions $\phi_1 \ldots \phi_m$

$$X_i(r) = \sum_{s}^{m} C_{si}\phi_s(r) \qquad (8)$$

The matrix C is rectangular, $m \times n$, and only has as many columns as there are occupied bond orbitals. Many elements in each column of C will be zero, corresponding to our assumption that only a few basis functions contribute to each bond orbital. The bond orbital overlap matrix σ can be expressed in terms of the basis function overlap matrix S

$$\sigma = C^tSC \qquad (9)$$

where

$$S_{st} = \int d^3r \phi_s{}^*(r)\phi_t(r) \qquad (10)$$

Substitution of eq 8 and eq 9 into eq 7 affords the desired energy expression

$$\begin{aligned}\langle E \rangle = {} & 2\sum_{s,t}^{m} [C(C^tSC)^{-1}C^t]_{ts}h_{st} \\ & + \sum_{stuv}^{m} [C(C^tSC)^{-1}C^t]_{ts}[C(C^tSC)^{-1}C^t]_{vu} \\ & \times \left\{2\left(st\left|\frac{1}{r_{12}}\right|uv\right) - \left(sv\left|\frac{1}{r_{12}}\right|ut\right)\right\} \qquad (11)\end{aligned}$$

Variation of the bond orbital coefficient matrix generates a corresponding variation in the energy expectation value.

$$\delta\langle E \rangle = 2\sum_{st} \delta[C(C^tSC)^{-1}C^t]_{ts}F_{st} \qquad (12)$$

The usual definition of the Fock matrix has been employed in eq 12, specifically,

$$F_{st} = h_{st} + \sum_{uv} [C(C^tSC)^{-1}C^t]_{vu}\{2(st|uv) - (sv|ut)\} \qquad (13)$$

The constraint that certain elements of C remain zero is introduced via Lagrange multipliers. If coefficient C_{sk} is constrained to be zero throughout the variation, $\delta C_{sk} = 0$ and

$$2\sum_{sk} [\beta_{ks}{}^t(\delta C_{sk}) + (\delta C)_{ks}{}^t\beta_{sk}] = 0 \qquad (14)$$

If a coefficient C_{sk} is to be free to vary, the corresponding Lagrange multipliers must be identically zero. But nonzero multipliers β_{sk} correspond to cases $C_{sk} = 0$.

C. Solution of the Variational Equations. The optimum bond orbitals are those which minimize the energy expectation value, subject to the constraint indicated in eq 14. We take $\delta\langle E \rangle$ from eq 12 and obtain

$$\begin{aligned}0 = {} & \sum_{st} \delta[C(C^tSC)^{-1}C^t]_{ts}F_{st} \\ & - \sum_{sk} (\beta_{ks}{}^t\delta C_{sk} + (\delta C)_{ks}{}^t\beta_{sk}) \qquad (15)\end{aligned}$$

To carry out the variation $\delta[C(C^tSC)^{-1}C^t]$ we need to know how to take the variation of $(C^tSC)^{-1}$. For any invertible matrix M, $\delta M^{-1} = -M^{-1}(\delta M)M^{-1}$. Hence,

$$\begin{aligned}& \delta[C(C^tSC)^{-1}C^t]_{ts} \\ & \quad = [(1 - C(C^tSC)^{-1}C^tS)(\delta C)(C^tSC)^{-1}C^t]_{ts} \\ & \quad + [C(C^tSC)^{-1}(\delta C^t)(1 - SC(C^tSC)^{-1}C^t)]_{ts} \qquad (16)\end{aligned}$$

The second term of eq 16 is exactly the transpose of the first term. We may therefore separate eq 15 into two equivalent parts, each of which is the transpose of the other. We obtain, after some rearrangement,

$$0 = \sum_{uk} (\delta C^t)_{ku} \left\{ \sum_{st} [1 - SC(C^tSC)^{-1}C^t]_{us}F_{st} \right. \\ \left. \times [C(C^tSC)^{-1}]_{tk} - \beta_{uk} \right\} \quad (17)$$

The variations $(\delta C^t)_{uk}$ which appear in eq 17 may now be considered to be arbitrary, and we may equate the terms which appear in brackets.

$$(1 - SC(C^tSC)^{-1}C^t)FC(C^tSC)^{-1} = \beta \quad (18)$$

There are two formal steps which permit simplification of eq 18. The leftmost factor in eq 18 is related to the closed shell density matrix

$$D = C(C^tSC)^{-1}C^t \quad (19)$$

The rightmost factor may be removed by a suitable orthogonalization of the local orbitals $\{X_i\}$. There is a transformation W_k which orthogonalizes the occupied local orbitals by mixing them with one another, yet leaves the orbital X_k invariant. The coefficient matrix for orthogonalized orbitals is

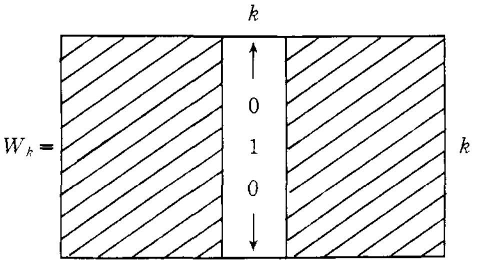
$$\overline{C}_k \equiv CW_k \quad (20)$$

Substitution of eq 19 and 20 into 18 yields

$$(1 - SD)F\overline{C}_k = \beta(W_k{}^t)^{-1} \quad (21)$$

since, by hypothesis, $\overline{C}_k{}^tS\overline{C}_k = 1$.

Further simplification occurs if we isolate a particular orbital X_k, which has coefficient vector Γ^k. This vector corresponds to column k of the general coefficient matrices C or $\overline{C}_k$. Because W_k leaves the kth column of C unchanged, it must have the structure



(22)

and $(W_k{}^t)^{-1}$ has the same structure. Hence, $(W_k{}^t)^{-1}$ leaves the kth column of β unchanged. Isolation of this column on both sides of eq 21 gives

$$\sum_s [(1 - SD)F]_{ts}C_{sk} = \beta_{tk} \quad (23)$$

The dimensionality of eq 24 can be reduced. Because X_k is a local orbital most of the expansion coefficients C_{sk} are zero, and corresponding columns s of $(1 - SD)F$ can be eliminated. Similarly, the Lagrange multipler $\beta_{tk} = 0$ if coefficient $C_{tk} \neq 0$ (see eq 14). Define the reduced coefficient vector γ_k by eliminating all elements of Γ^k which are constrained to be zero, and eliminate corresponding rows and columns from $(1 - SD)F$. Then,

$$[(1 - SD)F]_{\mathrm{red}}\gamma_k = 0 \quad (24)$$

There are still two problems which preclude immediate use of eq 24. First, it is not an eigenvalue equation since the operator $(1 - SD)F$ depends on γ_k through D. Second, the matrix $(1 - SD)F$ is not Hermitian. Each of these difficulties is easily resolved. The implicit dependence of D on γ_k is compensated by adding $S\Gamma^k(\Gamma^k)^tF\Gamma^k$ to each side of eq 24. The quantity $(\Gamma^k)^tF\Gamma^k$ is some scalar ϵ_k, and an eigenvalue equation results:

$$[(1 - SD + S\Gamma^k(\Gamma^k)^t)F]_{\mathrm{red}}\gamma_k = S_{\mathrm{red}}\gamma_k\epsilon_k \quad (25)$$

The factor which multiplies F from the left may also be inserted on the right. This is possible because SD, acting to the left, is a projection operator for the space of occupied orbitals. In particular, $\gamma_k{}^t(SD)_{\mathrm{red}} = \gamma_k{}^t$ and, in consequence,

$$[1 - SD + S\Gamma^k(\Gamma^k)^t]_{\mathrm{red}}{}^t\gamma_k = \gamma_k \quad (26)$$

Define the projection operator

$$Q_k = 1 - DS + \Gamma^k(\Gamma^k)^tS \quad (27)$$

It follows from eq 25 and 26 that

$$(Q_k{}^tFQ_k)_{\mathrm{red}}\gamma_k = S_{\mathrm{red}}\gamma_k\epsilon_k \quad (28)$$

This is the final working equation. The local orbital coefficients must be determined by a double iteration procedure. For a given Fock matrix, the projector Q_k depends on coefficients of orbitals other than γ_k, and must be iterated to self-consistency. The Fock operator also has an implicit dependence on the orbital coefficients and so must be made self-consistent.

D. Relationship to Adams–Gilbert Formalism. The Adams–Gilbert equations for regional Hartree–Fock orbitals bear a close resemblance to the formalism developed in this paper, and this relationship is now examined more closely. It is especially convenient to begin with Matsuoka's[14] modification of the Adams–Gilbert equation:

$$(F - P^{\ddagger}FP + P_k{}^{\ddagger}WP_k)|X_k\rangle = \epsilon_k|X_k\rangle \quad (29)$$

Here, P is a projection operator for the space of occupied orbitals $X_1 \ldots X_n$, and P_k is a projector for the subspace associated with orbitals $X_{k1} \ldots X_{km}$. The matrix W is undefined, except for the constraint that it must be diagonal in each subspace. This ambiguity in W has been one of the major drawbacks to practical implementation of the Adams–Gilbert equations, but we now show how this ambiguity can be resolved.

The projection operators employed by Matsuoka are defined by

$$P_k = \sum_{l=1}^{M}\sum_{j=1}^{M} |\chi_{kl}\rangle(\sigma_{\mathrm{red}}{}^{-1})_{kl,kj}\langle X_j| \quad \text{for subgroup } k \quad (30)$$

$$P = \sum_{l,j} |X_k\rangle\sigma_{kl}{}^{-1}\langle X_l| \quad (31)$$

where σ is the orbital overlap matrix, $\sigma_{kl} = \langle X_l|X_k\rangle$.

It is straightforward to reconcile our approach with the modified Adams–Gilbert equation (29). Equation 28 may be written in the projection notation as

$$(1 - P^{\ddagger} + P_k{}^{\ddagger})F(1 - P + P_k)|X_k\rangle = \epsilon_k|X_k\rangle \quad (32)$$

In view of the identities $|X_k\rangle = P_k|X_k\rangle = P|X_k\rangle$, this equation may be rearranged as

$$(F - P^{\ddagger}FP + P_k{}^{\ddagger}FP_k)|X_k\rangle = \epsilon_k|S_k\rangle \quad (33)$$

This is identical with eq 29. But our procedure demonstrates that the choice $W = F$ corresponds to variational optimization of total energy.

E. Evaluation of Ionization Potentials. Koopman's theorem does hold for the local orbital determinant. This is so because all other orbitals may be orthogonalized to any particular local orbital without changing either that orbital or its eigenvalue. The density matrix is then separable into contributions from that orbital and from all other orbitals. The Koopmans' theorem proof then carries through as for canonical Hartree–Fock theory. The energy required to ionize an electron from a local orbital is equal to its eigenvalue!

Table I. Total Energies from Molecular Orbital and Local Orbital Wave Functions

Molecule	Molecular orbital[a] energy, au	Local orbital energy, au	Difference, kcal
CH_4	−40.1369	−40.1298	4.5
NH_3	−56.0983	−56.0869	7.1
H_2O	−75.9032	−75.8879	9.6
C_2H_6 (staggered)	−79.1158	−79.0942	13.5
C_2H_6 (eclipsed)	−79.1114	−79.0913	12.6
CH_3NH_2 (staggered)	−95.0650	−95.0337	19.6
CH_3NH_2 (eclipsed)	−95.0619	−95.0347	17.0
CH_3OH (staggered)	−114.8672	−114.8311	22.6
CH_3OH (eclipsed)	−114.8653	−114.8291	22.7

[a] From ref 32.

III. Illustrative Application

In order to establish the practical value of this local orbital model several issues must be resolved. First, there is the question of accuracy. How closely does a determinant of local orbitals reproduce the energy of a molecular orbital wave function? Owing to the severe restraints on LCAO coefficients, the minimum energy cannot be as low as the energy attained in conventional molecular orbital theory. Nonetheless, the accuracy is competitive. The second issue is transferability. If local orbitals are identified with particular bonds or lone pairs, how much variation is there from molecule to molecule? Third, conformational energies provide a very sensitive test of the local orbital model. It is well established that rotational barriers can be calculated within the Hartree–Fock molecular orbital approximation.[30] Are local orbital determinants equally reliable?

Local orbital wave functions have been determined for a representative sample of molecules: methane, ammonia, water, and staggered and eclipsed conformers of ethane, methylamine, and methanol. The 4-31 G basis set was chosen,[31] and integral evaluation was done with Gaussian 70 routines. In order to facilitate comparison with 4-31 G molecular orbital wave functions, the molecular geometries obtained by Pople et al.[32] were adopted for the present calculations. The local orbital model does not offer fresh insights into the electronic structure of these particular molecules, which have already been studied to exhaustion. Rather, these molecules, as representative prototypes, provide a context for evaluation of the local orbital theory.

The regional orbitals have been chosen so as to correspond to bond pairs, lone pairs, or inner shell electrons. The orbital for a bond pair is expanded using valence basis functions associated with the two bonded atoms; no other basis functions contribute. Inner shell and lone pair orbitals are restricted to the basis space of a particular atom. In eq 28, the lowest energy eigenvector is the inner shell orbital, and the eigenvectors with next lowest energy are identified with lone pairs if they are present.

Table I compares total energies from local orbital and molecular orbital wave functions. It is clear that the local orbital model works exceedingly well. The energy expectation values obtained from local orbital and molecular orbital wave functions differ by only a few kilocalories/mole. This small difference is largely due to omission of inner shell basis functions from the bond orbital basis set. The variation in energy between local orbital and molecular orbital wave functions is no greater than the basis set dependence of molecular orbital energies, so the two approaches are in fact comparable in accuracy.

Table II. Comparison of Rotational Barrier Heights (kcal/mol)

Molecule	Molecular orbital wave function	Local orbital wave function
Ethane	2.77	1.82
Methylamine	1.94	−0.63
Methanol	1.19	1.26

Nonetheless, it appears that the accuracy of our local orbital wave functions may not be sufficient for reliable prediction of rotational barrier heights. Table II contrasts the rotational barrier heights obtained from local orbital and molecular orbital wave functions. The local orbital barrier height for methanol is in exact agreement with the molecular orbital result, and the rotational barrier of ethane is qualitatively reproduced. But the methylamine barrier has the wrong sign! Sovers, et al.[26] also employed a bond orbital wave function, and their rotational barrier heights for ethane and methanol are in reasonable agreement with our own. They did not report a calculation for methylamine.

To understand why rotational barriers derived from local orbitals could be ill behaved we turn to several contemporary models. CNDO and INDO studies[34] have shown that interference terms between vicinal charge distributions dominate the barrier. The same idea has been confirmed at the ab initio level, where it was shown that the leading terms in the barrier are proportional to vicinial overlap integrals.[35] From yet another perspective, Christiansen and Palke[36] and Levy, Nee, and Parr[37] have demonstrated that vicinial orthogonality is important for an accurate description of rotational barriers. Most recently, Weinhold and Brunck[38] have presented evidence that mixing of local bond orbitals with vicinal antibond orbitals is critical to the rotational barrier mechanism. Each of these contemporary models leads to the same conclusion: vicinal delocalization of electrons is essential to rotational barriers. The local orbital theory, as developed in this paper, explicitly excludes vicinal delocalization, so it is not surprising that rotational barriers can be ill behaved.

Local orbital transferability can be assessed through comparison of local orbital eigenvalues for different molecules. This information is summarized in Table III and Figure 1. The local orbital eigenvalue is the expectation value of the Fock operator for an electron in that orbital, and thus provides a sensitive measure of orbital shape and the external field. It is seen that each orbital type spans a distinct range of energies. Eigenvalues which correspond to CH, NH, and OH bonds vary no more than a few hundredths of an atomic unit. Because the lone pairs do not participate in bonding, their eigenvalues are sharply defined, and have maximum range of one-hundredth atomic unit. We emphasize that this study is only a prototype, but our results show that each type of bond or lone pair is characterized by a unique and transferable range of eigenvalues.

Several features of the orbital eigenvalues deserve special attention. First, it is significant that the two lone pairs of oxygen are inequivalent. In both methanol and water, one long pair lies in a pure p orbital and has π symmetry. The other lone pair is a directed sp hybrid which lies in the plane of the other bonds to oxygen. This is an ab initio result, and is not the consequence of a priori constraints. The lone pairs, by definition, correspond to eigenfunctions of the Fock operator after it is projected onto the basis space of the oxygen atom.

The orbital eigenvalues do reflect changes in nuclear charge and bond environment. As the nuclear charge on atom X increases, the eigenvalue of an XH bond pair drops steeply—from −0.88 au (av) for CH bonds to −1.92 au (av) for OH

Table III. Energy Eigenvalues for Local Orbitals (au)

Molecule	CH	NH	OH	N:	σO:	πO:
CH_4	−0.843					
C_2H_6 (s)	−0.853					
C_2H_6 (e)	−0.853					
NH_3		−1.249		−0.550		
CH_3NH_2 (s)	−0.892[a] 2(−0.868)	−1.232		−0.544		
CH_3NH_2 (e)	−0.870[a] 2(−0.884)	−1.315		−0.540		
H_2O			−1.935		−0.994	−0.476
CH_3OH (s)	−0.876[a] 2(−0.906)		−1.918		−1.003	−0.479
CH_3OH (e)	−0.911[a] 2(−0.893)		−1.923		−0.997	−0.479

[a] Only two of the CH bonds are equivalent by symmetry.

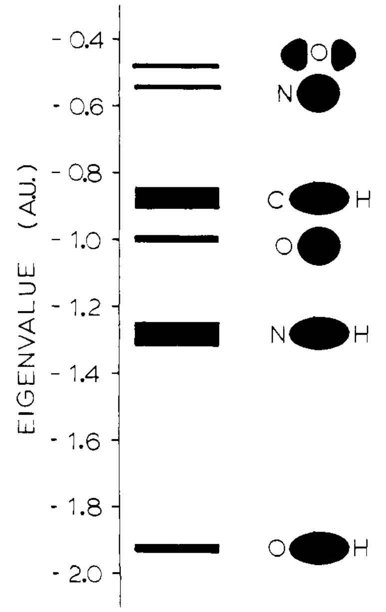


Figure 1. Range of eigenvalues for each type of local orbital.

bonds. The CH bonds in methylamine and methanol rotate in an anisotropic field. The CH bond eigenvalue is more positive if the dihedral angle with a vicinal lone pair is small. This confirms our intuition that lone pairs are more repulsive than bond pairs. The CH bond eigenvalues for methylamine and methanol are about 1 eV more negative than CH bond eigenvalues in methane or ethane since the more positive nuclei are less easily shielded by their electrons.

IV. Significance of the Regional Orbital Model

This paper has presented a Hartree-Fock theory appropriate for local regions of molecules. In contrast to conventional molecular orbital theory, each one-electron orbital is expanded using only those basis functions associated with a particular region. This constraint has several consequences, all of which are advantageous for interpretation or computation.

A significant challenge is posed for photoelectron spectroscopy since the local orbital eigenvalues satisfy Koopmans' theorem. The local orbital eigenvalue is equal in magnitude to the energy required for vertical ionization from that orbital. This fact raises a very important physical question: How local is the ionization process? The local orbital eigenvalue spectrum differs from the molecular orbital eigenvalue spectrum, so which set of eigenvalues is in better agreement with experimental ionization potentials? The local orbital ionization potentials also offer a useful index of nucleophilic reactivity. The most nucleophilic electron pairs are those which are most weakly bound.

The orbital eigenvalue is the energy expectation value for an electron confined to the local orbital. Calculations on prototype molecules indicate that these eigenvalues are highly transferable, in corroboration of chemical intuition. Our present results provide motivation for additional investigation of local orbital transferability. It is important to examine kinetic energy expectation values, as they provide a very sensitive measure of orbital shape. It will also be important to test direct transfer of local orbitals from small molecule wave functions to determinants for large molecules.

The orbital eigenvalues discussed in this paper should not be confused with thermodynamic bond enthalpies. The latter quantity is a bond dissociation energy, and cannot be understood apart from inclusion of electron correlation. Nonetheless, the local orbital determinant discussed here does provide an excellent framework for a theory of correlated pairs.

The regional orbital model provides a rigorous foundation for PMO theories of functional group interaction. The regional orbital eigenvalue is an ab initio equivalent to the reference energies used in orbital correlation diagrams. We have seen that these eigenvalues are highly transferable, and that the eigenvalues for each type of bond or lone pair span a distinct range. Transformation of the Fock matrix onto a basis space of bonds and antibonds permits ab initio evaluation of the matrix elements for interaction of bonds and antibonds with one another.

The regional model has distinct computational advantages for large molecules. Electronic structure of a particular region is completely determined by projection of the full Fock operator onto the basis set associated with the region. This means that accurate information about the electron structure of a particular region or functional group can in principle be obtained *without* calculation of an equally accurate wave function for the whole molecule. A crude wave function outside the region will determine the projection operator needed in eq 28, and multipole expansions may be used to estimate long-range contributions to the local Fock operator. Characterization of such approximations is critical to future work.

The only grounds for pessimism is the unreliability of rotational barriers calculated from a bond orbital determinant. This difficulty probably arises from absence of vicinal mixing of the local bonding and antibonding manifolds. But here too there is hope and a challenge to subsequent research. In molecules larger than those studied here, the description of internal rotation should improve significantly if regional orbitals extend over atoms vicinal to the particular bond. It is important to establish how much localization can in fact be attained without sacrifice of conformational energy.

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Appendix

Derivation of Energy Expression for Nonorthogonal Orbitals. We consider a determinantal wave function

$$\Psi = ((2n)!)^{-1/2} \det (\chi_1\chi_2 \cdots \chi_{2n}) \qquad \text{(A1)}$$

The orbitals χ_i are nonorthogonal spin orbitals with overlap matrix

$$S_{ij} = \int \mathrm{d}\tau_1 X_i^*(1) X_j(1) \qquad \text{(A2)}$$

The wave function Ψ is normalized so that $\langle\Psi|\Psi\rangle = \det S$, and the energy expectation value is

$$\langle E\rangle = (\det S)^{-1} \left\langle \Psi \left| \sum_i^{2n} h(i) + \sum_{i<j}^{2n} \frac{1}{r_{ij}} \right| \Psi \right\rangle \qquad \text{(A3)}$$

In eq A3, $h(i)$ is the one-electron Hamiltonian for electron i, and $1/r_{ij}$ is the electron repulsion of electrons i and j.

To get the matrix elements of one and two electron operators we follow Slater[27] and Lowdin[28] and define the matrices $W^{(1)}$ and $W^{(2)}$, as follows: $W^{(1)}(i|j)$ is the matrix formed from S when the ith row and jth column are deleted; $W^{(2)}(i,k|j,l)$ is the matrix formed from S when the ith and kth rows and jth and lth columns are deleted.

We obtain

$$\langle E\rangle = (\det S)^{-1} \left\{ \sum_{i,j}^{2n} h_{ij}(-1)^{i+j} \det W^{(1)}(i|j) \right. \\ \left. + \frac{1}{2} \sum_{i\neq k}^{2n} \sum_{j\neq l}^{2n} \left(ij\left|\frac{1}{r_{12}}\right|kl\right) (-1)^{i+j+k+l} \det W^{(2)}(i,k|j,l) \right\} \qquad \text{(A4)}$$

In eq A4, h_{ij} is the matrix element of the one electron Hamiltonian and $(ij|\,1/r_{12}|kl)$ is the usual electron repulsion integral:

$$\left(ij\left|\frac{1}{r_{12}}\right|kl\right) = \int \mathrm{d}\tau_1 \mathrm{d}\tau_2 X_i^*(1) X_j(1) \frac{1}{r_{12}} X_k^*(2) X_l(2) \qquad \text{(A5)}$$

The expression in eq A4 may be considerably simplified via Jacobi's ratio theorem, as has been discussed by McWeeny and Sutcliffe.[29] According to that theorem,

$$\det W^{(1)}(i|j) = (-1)^{i+j}(\det S)(S^{-1})_{ji} \qquad \text{(A6)}$$

$$\det W^{(2)}(i,k|j,l) = (-1)^{i+j+k+l}(\det S) \\ \times [(S^{-1})_{ji}(S^{-1})_{lk} - (S^{-1})_{jk}(S^{-1})_{li}] \qquad \text{(A7)}$$

Substitution of eq A7 and eq A6 into eq A4 affords

$$\langle E\rangle = \sum_{i,j}^{2n} h_{ij}S_{ji}{}^{-1} + \frac{1}{2} \sum_{i\neq k}^{2n} \sum_{j\neq l}^{2n} [(S^{-1})_{ji}(S^{-1})_{lk} \\ - (S^{-1})_{jk}(S^{-1})_{li}] \left(ij\left|\frac{1}{r_{12}}\right|kl\right) \qquad \text{(A8)}$$

The equation above is completely general, but we now specialize to closed shells. We assume that the first N orbitals have α spin, and are paired with the succeeding N orbitals, which have β spin. The overlap matrix S becomes block diagonal

$$S = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}$$

The matrix σ is the overlap matrix between spin orbitals with like spin. Because S is block diagonal, eq A8 simplifies as

$$\langle E\rangle = 2 \sum_{i,j}^{n} h_{ij}\sigma_{ji}{}^{-1} + \sum_{ijkl} \sigma_{ji}{}^{-1}\sigma_{lk}{}^{-1} \\ \times \left[2\left(ij\left|\frac{1}{r_{12}}\right|kl\right) - \left(il\left|\frac{1}{r_{12}}\right|kj\right) \right] \qquad \text{(A9)}$$

If the orbitals X_i happen to be orthonormal we immediately recover the usual Hartree–Fock energy expression:

$$\langle E\rangle_{\mathrm{ort}} = 2 \sum_{i}^{n} h_{ii} \\ + \sum_{i,k}^{n} \left(2\left(ii\left|\frac{1}{r_{12}}\right|kk\right) - \left(ik\left|\frac{1}{r_{12}}\right|ki\right) \right) \qquad \text{(A10)}$$

References and Notes

(1) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74,** 3341, 3345, 3350, 3353, 3357 (1952); C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **191,** 39 (1947); **192,** 16 (1947); **193,** 447, 456 (1948); **195,** 188 (1948); H. C. Longuet-Higgins, *J. Chem. Phys.*, **18,** 265, 275, 283 (1950); G. Klopman, *J. Am. Chem. Soc.*, **90,** 223 (1968); L. Salem, *Chem. Br.*, **5,** 449 (1969); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New york, N.Y., 1969; K. Fukui, *Top. Curr. Chem.*, **15,** 1 (1970); R. Hoffmann, *Acc. Chem. Res.*, **4,** 1 (1971); E. Heilbronner, *Pure Appl. Chem., Suppl., 23rd Int. Congr.*, 7, 9 (1971); W. L. Jorgensen and L. Salem, "The Organic Chemists' Book of Orbitals", Academic Press, New York, N.Y., 1973.

(2) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20,** 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *ibid.*, **22,** 1433 (1954); K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jpn.*, **27,** 423 (1954); *J. Chem. Phys.*, **26,** 831 (1957); **27,** 1247 (1957); K. Fukui, C. Nagata, T. Yonezawa, H. Kato, and K. Morokuma, *ibid.*, **21,** 287 (1959); K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **40,** 2018 (1967).

(3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87,** 395, 2046, 2511 (1965); "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1971.

(4) L. Salem, *Proc. R. Soc. London, Ser. A*, **264,** 379 (1961); *J. Am. Chem. Soc.*, **90,** 543 (1968).

(5) N. D. Epiotis, *J. Am. Chem. Soc.*, **95,** 1191, 1200, 1206, 1214, 3087 (1973); N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *ibid.*, **95**, 7558 (1973); N. D. Epiotis, R. L. Yates, and F. Bernardi, *ibid.*, **97,** 4198, 5961 (1975); R. L. Yates, N. D. Epiotis, and F. Bernardi, *ibid.*, **97,** 6615 (1975).

(6) For some recent work see P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **11**, 330 (1972); R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94,** 6221 (1972); W. A. Lathan, L. Radom, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Fortschr. Chem. Forsch.*, **40,** 1 (1973); W. J. Hehre, *J. Am. Chem. Soc.*, **95,** 5807 (1973); W. J. Hehre and L. Salem, *J. Chem. Soc., Chem. Commun.*, 754 (1973); L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95,** 6531 (1973); W. J. Hehre and P. C. Hiberty, *ibid.*, **96,** 302, 2665 (1974); L. Radom, J. Paviot, J. A. Pople, and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 58 (1974); J. F. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **97,** 2902 (1975).

(7) For some recent work see J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94,** 8917 (1972); L. Salem, R. Hoffmann, and P. Otto, *Proc. Natl. Acad. Sci. U.S.A.*, **70,** 531 (1973); S. David, O. Eisenstein, W. Hehre, L. Salem, and R. Hoffmann, *J. Am. Chem. Soc.*, **95,** 3806 (1973); O. Eisenstein, N. T. Anh, Y. Jean, A. Devaquet, J. Cantacuzene, and L. Salem, *Tetrahedron*, **30,** 1717 (1974); L. Salem, *Jerusalem Symp. Quantum Chem. Biochem.*, **6,** 329 (1974).

(8) For some recent work see R. Gleiter, W. D. Stohrer, and R. Hoffmann, *Helv. Chim. Acta.*, **55,** 893 (1972); R. Hoffmann, C. Levin, and R. Moss, *J. Am. Chem. Soc.*, **95,** 629 (1973); C. Levin, R. Hoffmann, and W. J. Hehre, *J. Chem. Soc., Perkin Trans 2*, 210 (1973); R. Hoffmann, P. Mollere, and E. Heilbronner, *J. Am. Chem. Soc.*, **95,** 4860 (1973); R. Hoffmann, C. Wan, and V. Neagu, *U.S. N. T. I. S., AD Rep.*, No. 761425 (1970); C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Am. Chem. Soc.*, **95,** 8192 (1973); L. Libit and R. Hoffmann, *ibid.*, **96,** 1370 (1974); H. Fujimoto and R. Hoffmann, *J. Phys. Chem.*, **78,** 1167, 1874 (1974); P. D. Mollere and R. Hoffmann, *J. Am. Chem. Soc.*, **97,** 3680 (1975).

(9) For some recent work see F. Brogli, E. Heilbronner, and J. Ipaktschi, *Helv. Chim. Acta*, **55,** 2447 (1972); M. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *ibid.*, **56,** 294 (1973); E. Heilbronner, R. Gleiter, T. Hoshi, and A. DeMeijere, *ibid.*, **56,** 1594 (1973); E. Heilbronner and H. D. Martin, *Chem. Ber.*, **106,** 3376 (1973); E. Heilbronner and J. Maier, *Helv. Chim. Acta.*, **57,** 151 (1974); G. Bieri, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, and J. Wirz, *ibid.*, **57,** 1265 (1974); E. Heilbronner, "Aspects of UPS", *World Quantum Chem., Proc. Int. Congr. Quantum Chem., 1st, 1973;* E. Heilbronner, *Pure Appl. Chem.*, **40,** 549 (1974); E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, **58,** 936 (1975).

(10) See, for instance, R. Hoffman, M. Chen, M. Elian, A. Rossi, and D. M. Mingos, *Inorg. Chem.*, **13,** 2666 (1974); M. Elian and R. Hoffmann, *ibid.*, **14,** 1058 (1975); P. J. Hay, J. C. Thibeault, and R. Hoffman, *J. Am. Chem. Soc.*, **97,** 4884 (1975); C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962.

(11) A. Mazziotti, R. G. Parr, and G. Simons, *J. Chem. Phys.*, **59,** 939 (1973).

(12) R. F. W. Bader, P. M. Beddall, and P. E. Cade, *J. Am. Chem. Soc.*, **93,** 3095

(1971); R. F. W. Bader and P. M. Beddall, *Chem. Phys. Lett.*, **8**, 29 (1971); *J. Chem. Phys.*, **56**, 3320 (1972); R. F. W. Bader, P. M. Beddall, and J. Pesiak; Jr., *ibid.*, **58**, 557 (1973); R. F. W. Bader and P. M. Beddall, *J. Am. Chem. Soc.*, **95**, 305 (1973); S. Srebrenick and R. F. W. Bader, *J. Chem. Phys.*, **61**, 2536 (1974).

(13) W. H. Adams, *J. Chem. Phys.*, **34**, 89 (1961); **37**, 2009 (1962); **42**, 4030 (1965); T. L. Gilbert in "Molecular Orbitals in Chemistry, Physics and Biology", P. O. Lowdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, p 409; T. L. Gilbert, *Phys. Rev. Sect. A*, **6**, 580 (1972); *J. Chem. Phys.*, **60**, 3835 (1974).

(14) O. Matsuoka, *J. Chem. Phys.*, **66**, 1245 (1977).

(15) A. B. Kunz, *Phys. Rev. Sect. B* **2**, 2224, 5015 (1970); **4**, 609 (1971); **7**, 4021, 5369 (1973); **8**, 1690 (1973); *J. Phys. C*, **3**, 1542 (1970); N. O. Lipari and A. B. Kunz, *Phys. Rev. B*, **3**, 491 (1971); **4**, 1374 (1971); *J. Phys. Chem. Solids*, **32**, 1141 (1971).

(16) D. Peters, *J. Chem. Phys.,* **46**, 4427 (1967); **51**, 1559, 1566 (1969).

(17) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966); P. G. Burton and R. D. Brown, *Chem. Phys.*, **4**, 220, 226 (1974); P. G. Burton, *Chem. Phys.*, **6**, 419 (1974); For a comprehensive review of Fock matrix transferability see B. O'Leary, B. J. Duke, and J. E. Eilers, *Adv. Quantum Chem.*, **9**, 1 (1975).

(18) M.-H. Whangbo, H. B. Schlegel, and S. Wolfe, *J. Am. Chem. Soc.*, **99**, 1296 (1977).

(19) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1975).

(20) P. W. Payne, Ph.D. Dissertation, Princeton University, 1975.

(21) For some recent reviews see W. England, L. S. Salmon and K. Ruedenberg, *Fortschr. Chem. Forsch.*, **23**, 31 (1971); H. Weinstein, R. Pauncz and M. Cohen, *Advan. At. Mol. Phys.*, **7**, 97 (1971); O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu, Ed., "Localization and Delocatization in Quantum Chemistry", D. Reidel, Boston, Mass., 1975; B. O'Leary, B. J. Duke, and J. E. Eilers, *Adv. Quantum Chem.*, **9**, 1 (1975).

(22) W. England and M. S. Gordon, *J. Am. Chem. Soc.*, **93**, 4649 (1971); **94**, 4818, 5168 (1972); **95**, 1753 (1973); M. S. Gordon and L. Neubauer, *ibid.*, **96**, 5690 (1974); W. England and M. S. Gordon, *Chem. Phys. Lett.*, **15**, 59 (1972); V. Magnasco and G. F. Musso, *J. Chem. Phys.*, **60**, 3744 (1974); G. F. Musso and V. Magnasco, *ibid.*, **60**, 3754 (1974); M. S. Gordon, *J. Mol. Struct.*, **23**, 399 (1974).

(23) S. Rothenberg, *J. Chem. Phys.*, **51**, 3389 (1969); M. Levy, W. J. Stevens, H. Shull, and S. Hagstrom, *ibid.*, **61**, 1844 (1974); D. Leahy and M. Levy, to be published.

(24) T. A. Weber, N. C. Handy, and R. G. Parr, *J. Chem. Phys.*, **52**, 1501 (1970); M. T. Marron, N. C. Handy, R. G. Parr, and H. J. Silverstone, *Int. J. Quantum Chem.*, **4**, 25 (1970).

(25) W. von Niessen, *J. Chem. Phys.*, **55**, 1948 (1971); *Theor. Chim. Acta*, **31**, 111, 297 (1973); **33**, 113 (1974).

(26) R. McWeeny and G. DelRe, *Theor. Chim. Acta,* **10**, 13 (1968); J. H. Letcher and T. H. Dunning, *J. Chem. Phys.*, **48**, 4538 (1968); M. L. Unland, T. H. Dunning, and J. R. Van Wazer, *ibid.*, **50**, 3208 (1969); O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *ibid.*, **49**, 2592 (1968); J. D. Petke and J. L. Whitten, *ibid.*, **51**, 3166 (1969); J. R. Hoyland, *J. Am. Chem. Soc.*, **90**, 2227 (1968); *J. Chem. Phys.*, **50**, 473 (1969); J. H. Letcher, *ibid.*, **54**, 3215 (1971); C. W. Kern, R. M. Pitzer, and O. J. Sovers, *ibid.*, **60**, 4683 (1974); P. A. Christiansen and W. E. Palke, *Chem. Phys. Lett.*, **31**, 462 (1975); M. Levy, T. S. Nee, and R. G. Parr, *J. Chem. Phys.*, **63**, 316 (1975).

(27) J. C. Slater, "Quantum Theory of Molecules and Solids", Vol. 1, McGraw-Hill, New York, N.Y., 1963, pp 285–289.

(28) P. O. Lowdin, *Phys. Rev.*, **97**, 1474, 1490 (1955).

(29) R. McWeeny and B. Sutcliffe, "Methods of Molecular Quantum Mechanics", Academic Press, New York, N.Y., 1968, pp 50–52.

(30) J. A. Pople, *Tetrahedron*, **30**, 1605 (1974); A. Golebiewski and A. Parczewski, *Chem. Rev.,* **74**, 519 (1974).

(31) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(32) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).

(33) P. W. Payne and L. C. Allen, "*Ab Initio* Calculation of Barriers to Rotation and Inversion", in "Modern Theoretical Chemistry", Vol. 4, H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1977.

(34) W. England and M. S. Gordon, *J. Am. Chem. Soc.*, **93**, 4649 (1971); M. S. Gordon and W. England, *ibid.*, **95**, 1753 (1973).

(35) G. F. Musso and V. Magnasco, *J. Chem. Phys.*, **60**, 3754 (1974).

(36) P. A. Christiansen and W. E. Palke, *Chem. Phys. Lett.*, **31**, 462 (1975).

(37) M. Levy, T. S. Nee, and R. G. Parr, *J. Chem. Phys.*, **63**, 316–318 (1975).

(38) F. Weinhold and T. K. Brunck, to be published.

Bifunctional Proton Transfer and Acid–Base Properties of 1,4,7,10-Tetraazacyclododecane (Cyclen)[1]

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Abstract: Stepwise acid dissociation constants of $(H_2NCH_2CH_2)_4{}^{4+}$ (cyclen·4HCl) in water at 25 °C are $pK_1 < 1$; $pK_2 = 1.15$ ($I = 0.6$); $pK_3 = 9.60$ ($I = 0$); $pK_4 = 10.53$ ($I = 0$). For the diprotonated species, the equilibrium ratio [1,7-diprotiocyclen]/[1,4-diprotiocyclen] is estimated as 1/400. Bifunctional proton transfer with water participation is fast. For 1,7-diprotiocyclen → 1,4-diprotiocyclen, $k_1 = 3.3 \times 10^4\ s^{-1}$; for 1-protiocyclen → 4-protiocyclen, $k_{cyclic} = 1.1 \times 10^8\ s^{-1}$. Reactions of 1,7-diprotiocyclen with H_3O^+ or OH^- are diffusion controlled.

The acid-base chemistry of the cation-complexing agent 1,4,7,10-tetraazacyclododecane, $(HNCH_2CH_2)_4$ (cyclen),[2,3] is of interest because of the possibility of fast intramolecular proton transfer. We wish to report the results of a kinetic study by dynamic NMR,[4] which confirms this possibility, as well as acid dissociation constants.

pK_a Measurements. Pure crystalline cyclen tetrahydrochloride[3] served as starting material. The acid dissociation scheme for this substrate in aqueous solution is shown in Figure 1. Values of pK_3 and pK_4, listed in that figure, were obtained by potentiometric titration at 0.017 M substrate concentration and have been corrected to zero ionic strength, using the Debye–Hückel formula: $\log \gamma_i = -0.509 z_i{}^2 I^{1/2}/(1 + I^{1/2})$ (γ_i = molar activity coefficient and z_i = charge number of ith solute species; I = ionic strength).

pK_2 was determined with a precision of better than 0.1 unit by measurement of the CH_2 vs. H_2O NMR chemical shift as a function of pH in the range 1–3, using the CH_3 proton resonance of either acetone (0.1 M) or t-$BuNH_3{}^+$ (0.1 M) as internal standard.[5] These measurements were made at 0.12 M substrate concentration. Because of the high ionic strength (~0.6 M), it was not deemed practical to correct pK_2 to zero ionic strength.

Electrostatic Repulsions. Our notation for molecular species and sites of protonation is indicated in Figure 1. pK_3 and pK_4 for the acid dissociation steps $A_2 \rightleftarrows A_1 \rightleftarrows B$ are similar in magnitude to the stepwise pK_a values[6a] for $^+H_3N(CH_2)_5NH_3{}^+$, where the nitrogen atoms are likewise separated by a five-atom chain. Electrostatic repulsion between the $NH_3{}^+$ groups lowers pK_{a1} of this compound by about 0.4 pK unit; we would expect a similar electrostatic interaction between positive charges on N_1 and N_7. The much greater electrostatic interaction between positive charges on N_1 and N_4 may be estimated from stepwise pK_a values[6b] for the cyclic diamines piperazine (1,4-diazacyclohexane), where it amounts to 3.6 pK units, or 1,4-diazacycloheptane, where it amounts to 3.0 pK units. Adopting an average value of ~3.3 units, we expect a total electrostatic contribution to pK_2 of 6.6 units (7.0 units in A_3, less 0.4 unit in A_2), compared to an electrostatic contribution to pK_3 of 0.4 unit. Thus $pK_2 - pK_3$ should be −6.2